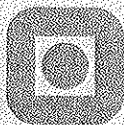


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Oxygen-assisted conversion of
propane over metal and
metal oxide catalysts

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Oxygen-assisted conversion of propane over
metal and metal oxide catalysts

by

Leiv Låte

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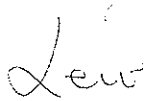
My colleagues at the Department of Chemical Engineering and SINTEF are highly appreciated for their support and friendship.

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Trondheim 2002

A handwritten signature in cursive script, appearing to read 'Leiv'.

Leiv

'Some people believe football is a matter of life and death.
I'm very disappointed with that attitude.
I can assure you it is much, much more important than that.'

Bill Shankly

Abstract

An experimental set-up has been build and applied in activity/selectivity studies of the oxygen- assisted conversion of propane over metals and metal oxide catalysts. The apparatus has been used in order to achieve an improved understanding of the reactions between alkanes/alkenes and oxygen.

Processes that have been studied are the oxidative dehydrogenation of propane over a VMgO catalyst and the selective combustion of hydrogen in the presence of hydrocarbons over Pt-based catalysts and metal oxide catalysts.

From the experiments, the following conclusions are drawn:

A study of the oxidative dehydrogenation of propane over a vanadium-magnesium-oxide catalyst confirmed that the main problem with this system is the lack of selectivity due to complete combustion. Selectivity to propene up to about 60% was obtained at 10% conversion at 500°C, but the selectivity decreased with increasing conversion. No oxygenates were detected, the only by- products were CO and CO₂. The selectivity to propene is a strong function of the conversion of propane. The reaction rate of propane was found to be 1.0 ± 0.1 order in propane and 0.07 ± 0.02 order in oxygen. The kinetic results are in agreement with a Mars van Krevelen mechanism with the activation of the hydrocarbons as the slow step. The rate of propene oxidation to CO₂ was studied and found to be significantly higher than that of propane.

Another possible process involves the simultaneous equilibrium dehydrogenation of alkanes to alkenes and combustion of the hydrogen formed to shift the equilibrium dehydrogenation reaction further to the product alkenes. A study of the selective combustion of hydrogen in the presence of propane/propene was found to be possible under certain reaction conditions over some metal oxide catalysts. In₂O₃/SiO₂, unsupported Bi₂O₃

and ZSM-5 show the ability to combust hydrogen in a gas mixture with propane and oxygen with good selectivity. $\text{Bi}_2\text{O}_3/\text{SiO}_2$ and $\text{PbO}_x/\text{SiO}_2$ show moderate properties as selective hydrogen combustion catalysts, and $\text{Cr}_2\text{O}_3/\text{SiO}_2$ and VMgO are ineffective as SHC catalysts. If propene is added to the gas mixture, $\text{Bi}_2\text{O}_3/\text{SiO}_2$ and $\text{PbO}_x/\text{SiO}_2$ are no longer able to selectively combust hydrogen. $\text{In}_2\text{O}_3/\text{SiO}_2$, on the other hand, combusts hydrogen with 90% selectivity at low oxygen flows, and with 80% selectivity at stoichiometric amounts (to water) of oxygen. Bi_2O_3 (unsupported) combusts hydrogen with 60% selectivity independent of the oxygen flow. $\text{In}_2\text{O}_3/\text{SiO}_2$ and $\text{Bi}_2\text{O}_3/\text{SiO}_2$ are found to be the most active catalysts for the conversion of oxygen.

The selective combustion of hydrogen in the presence of propane/propene over Pt-based catalysts was also found to be possible at some reaction conditions. It seems like tin has a stabilising effect on the catalyst activity, PtSn being more stable than Pt. Both Sn and PtSn seem to be able to selectively combust hydrogen in a gas mixture with propane and oxygen. Pt does not show this quality. If propene is added to the gas mixture, Sn is no longer able to selectively combust hydrogen. PtSn on the other hand combusts hydrogen with about 80% selectivity at 550°C and 90% selectivity at 500°C as long as the oxygen flow is less than half the amount of hydrogen. As soon as the oxygen flow exceeds half the amount of hydrogen, the selectivity to CO_x increases at the expense of water.

A Langmuir-Hinshelwood type of reaction mechanism is proposed over the Pt, Sn and PtSn catalysts. It is also proposed that oxygen is strongly adsorbed on both Pt and Sn, but the adsorption on Pt is preferred to Sn as long as there is Pt available in the system. Alkanes are strongly adsorbed on Pt, but do not adsorb on Sn, in contrast to alkenes that adsorb on all the catalysts. Sn reduces the Pt ensembles and the adsorption strength of the Pt, and as a consequence reduces the formation of the undesired products.

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List of publications

Articles

This thesis is based on the following articles:

L. Låte, J.-I. Rundereim and E. A. Blekkan, "Catalytic dehydrogenation of propane over a PtSn/SiO₂ catalyst with oxygen addition: Selective oxidation of H₂ in the presence of hydrocarbons", *Studies in Surface Science and catalysis* (2001)289.

L. Låte and E. A. Blekkan, "Oxidative dehydrogenation of propane over a VMgO catalyst" *Manuscript submitted*.

L. Låte, J.-I. Rundereim and E. A. Blekkan "Selective combustion of hydrogen in the presence of hydrocarbons over Pt based catalysts", *Manuscript submitted*.

L. Låte, W. Thelin and E. A. Blekkan "Selective combustion of hydrogen in the presence of hydrocarbons over metal oxide based catalysts", *Manuscript submitted*.

Oral presentations

The following presentations have been given at international meetings based in results produced during this work:

L. Låte and E. A. Blekkan, "Oxidative dehydrogenation of propane over Mg-V-O catalyst." Lecture, 9th Nordic Symposium on Catalysis, Stockholm June 4-6, 2000.

L. Låte, J.-I. Rundereim and E. A. Blekkan, "Selective combustion of hydrogen in the presence of hydrocarbons over Pt-based catalysts", Recent Report Session, 12th ICC, Granada, Spain 9-14 July 2000.

L. Låte and E. A. Blekkan, "Oxidative dehydrogenation of propane over VMgO catalysts." Lecture, 220th ACS National Meeting of the ACS, Washington DC, 20-24 August 2000.

L. Låte, J.-I. Rundereim and E. A. Blekkan, "Catalytic dehydrogenation of propane over a PtSn/SiO₂ catalyst with oxygen addition: Selective oxidation of H₂ in the presence of hydrocarbons.", Lecture, 6th NGCS, Alaska 17-22 June, 2001.

L. Låte, W. Thelin and E. A. Blekkan, " Selective combustion of hydrogen in the presence of hydrocarbons: Comparison of different catalysts", Lecture, EuropaCat V, Limeric 2001.

List of symbols and abbreviations

Symbol	Denomination	Explanation
A_i	-	Response area component i
C!	-	Coke
F	ml/min	Flow rate
FID		Flame ionisation detector
f_i	-	Molar response factor for component i
f_{iR2}	-	Relative response factor of component i
GC		Gas Chromatograph
GHSV	l/g·h	Gas hourly space velocity
HC		Hydrocarbons
i.d.	mm	Inner diameter
k_i	-	Rate constant component i
MFC		Mass flow control
m_i	g	Mass of component i
n_{Ci}	-	Number of C-atoms in propane relative to number of C-atoms in component i
n_{Oi}	-	Number of O-atoms in oxygen relative to number of O-atoms in component i
n_i	mol	Number of mole of component i
ODH		Oxidative dehydrogenation
P	atm	Total pressure

x		
P_i	atm	Partial pressure component i
PM		Pressure meter
r	mol/g·min	Reaction rate
R	J/mol·K	Gas constant
R	ml·atm/K·mol	Gas constant
S	%	Carbon selectivity
S_{BET}	m^2/g_{cat}	Surface area
S_O	%	Oxygen selectivity
SV	min^{-1}	Space velocity
T	°C and K	Temperature
TC		Temperature control
TM		Temperature meter
TPR		Temperature programmed reduction
W_{cat}	g	Weight catalyst
WHSV	$g_{reactant}/g_{cat} \cdot h$	Weight hourly space velocity
XRD		X-ray Diffraction
θ		Fraction of active points in reduced condition
η	%	Conversion
ΔH	kJ/mol	Standard enthalpy of formation
ΔG	kJ/mol	Gibbs free energy of formation

1 Introduction

1.1 A short introduction to catalysis

Although nowadays we know that catalytic processes have already been applied for a long period of time, it was not until 1836 that Berzelius introduced the term "catalysis" [Bond (1987)]. Later, in 1895, William Ostwald was the first to formulate a definition of a catalyst: "A catalyst is a substance that changes the rate of a chemical reaction without itself appearing in the products". It is important to note that a catalyst does not influence the thermodynamic equilibrium of reactants and products. Therefore, the current definition is slightly better, though close to Ostwald's description: "A catalyst is a substance that increases the rate of approach to thermodynamic equilibrium of a chemical reaction without being substantially consumed" [Gates (1992)]. Today, almost 70% of all chemicals that are produced have been in contact with a catalyst somewhere in their synthesis process. This number stresses the importance of the role of catalysis in the chemical industry. Without a catalyst, processes are less clean and sometimes impossible to perform.

1.2. Natural gas conversion

The following paragraph is based on information from The Norwegian Ministry of Petroleum and Energy [The Norwegian Ministry of Petroleum and Energy (2000)] together with world wide statistical data from British Petroleum- Amoco [BP Amoco (2000)]

By the end of 1999 the Norwegian proven gas resources were $3,3 \cdot 10^9 \text{ Sm}^3$, which represents about 2% of the proven world resources ($147 \cdot 10^9 \text{ Sm}^3$). The natural gas production from the Norwegian continental shelf is approximately $45 \cdot 10^9 \text{ Sm}^3 / \text{year}$ (1999), which is about 2% of the total world production of

gas in 1999 ($2200 \cdot 10^9 \text{ Sm}^3 / \text{year}$). Less than $0.7 \cdot 10^9 \text{ Sm}^3 / \text{year}$ (<2%, 1998) is used locally for methanol production at Tjeldbergodden. The rest is piped from Kårstø and Kollsnes to Emden (Germany), Zeebrugge (Belgium) and Dunkerque (France). The sales of natural gas to western Europe is expected to level out at about $70\text{-}75 \cdot 10^9 \text{ Sm}^3/\text{year}$ in the coming decade, which will represent about 17% of the total consumption. By the end of 1999 a total of 90000 people were employed in the petroleum sector and direct spin-offs including exploration, drilling, production, construction and maintenance of platforms. Norway is among the ten largest gas exporting countries, and the export to Western Europe is large. Around 10% of the gas consumption in Western Europe is provided by Norwegian gas.

At the present rates of production, it is estimated that Norway's remaining discovered oil resources will last for about 18 years and the equivalent time for natural gas is roughly 85 years. The limited amount of oil together with environmental considerations has led to an increased interest in utilisation of natural gas. The natural gas on the Norwegian continental shelf consists mostly of methane (80-90%). The most important large-volume liquid products from methane are methanol and ammonia. Synthetic fuels can also be produced from methane by Fischer-Tropsch (F-T) synthesis, but this technology needs long term petroleum prices above about 20 USD/barrel in order to be competitive. Polymers made by using natural gas as raw material is also a big market, and Borealis, which is partly owned by Statoil, produces polyethene (PE) and polypropene (PP), and Norsk Hydro has a production facility for polyvinylchloride (PVC). Extensive research in Norway has been carried out on heterogeneous catalysis since this is a key factor for developing processes for natural gas conversion. The major industrial contributors have been Norsk Hydro who among other processes studied methanol to olefins (MTO) [Vora (1997)] and Statoil with their work on gas to middle distillates (GMD) and autothermal propane dehydrogenation (ADH). Work on MTO is still being performed and the process was ready for commercialisation in

November 95 [Vora (1997)]. Statoil has recently build a large-scale plant for methanol production (830 000 tonnes methanol/year [Statoil, 1997]) at Tjeldbergodden utilising natural gas supplied from the Heidrun field.

1.3. Processes for dehydrogenation of hydrocarbons

The catalytic dehydrogenation of light alkanes like propane and butane is growing in importance, in the case of propane due to an imbalance between the growth in demand for propene and etene [Eur. Chem. News.,67 (1997)28] Propene is an important petrochemical raw material, especially in the manufacture of polypropene. Other uses of propene are in the manufacture of acrylonitrile, propene oxide, isopropanol, cumene and acrolein.

The dehydrogenation of alkanes to alkenes is a potentially important route to convert low-value paraffinic feedstock's (C_3 - C_4) into more useful chemicals. Although steam cracking is the most important route to light alkenes, this process has limitations, especially in the production of propene and higher alkenes. The current commercial catalytic process use promoted Pt(Sn)/support or Cr_2O_3/Al_2O_3 [Resasco (1994)] for the direct dehydrogenation in which alkanes are converted to unsaturated hydrocarbons and hydrogen. The disadvantage of the direct dehydrogenation route is that it is a strongly endothermic and equilibrium limited reaction, and the severe conditions required (high temperatures and low pressures) lead to coke formation on the catalyst. These features dominate the reactor design, which has to allow for the transfer of the heat as well as allow for frequent decoking and regeneration of the catalyst.

The oxidative dehydrogenation (ODH) of lower alkanes is an interesting alternative to the conventional dehydrogenation of LPG, owing to the possibility of working at lower reaction temperatures. This reaction is not limited by the thermodynamic equilibrium, and catalyst deactivation is usually

not a problem since coke and its precursors can be efficiently removed by oxygen. This reaction has been much studied over recent years, the main drawback being the lack of selectivity at high conversions, with total oxidation to CO_2 and H_2O being the main side reactions. Much research has concentrated on vanadium-oxide based catalysts for oxidative dehydrogenation. In particular vanadium-magnesium-oxide (VMgO) catalysts have demonstrated a promising yield for alkenes and have been studied by several groups [Pantazidis (1996), Char (1988), Kung (1997), Patel (1988)] among others.

Mobil [Agaskar (1995)] has patented a process which involves simultaneous equilibrium dehydrogenation of alkanes to alkenes and combustion of the hydrogen formed to shift the equilibrium dehydrogenation reaction further to the product alkenes. In the reaction, the alkane feed is dehydrogenated over a dehydrogenation catalyst in a first reactor, and the effluent from the first reactor is then passed into a second reactor containing a reducible metal oxide which serves to selectively combust hydrogen in an oxidation/reduction reaction.

The dehydrogenation process, where a hydrocarbon feed is dehydrogenated in a dehydrogenation zone and then oxidatively reheated by the combustion of hydrogen in an oxidation zone containing an oxidation catalyst is improved and patented by UOP [Tagamolila (1991)]. In the UOP patent the process is improved by using a stream of dilution steam as an educing fluid to draw oxygen into contact with the effluent from the dehydrogenation zone ahead of the oxidation zone. The stream of dilution steam is often combined with the dehydrogenation zone effluent in order to control the oxygen concentration ahead of the oxidation zone and to lower the hydrogen partial pressure.

It is also possible to use noble metal systems as catalysts for the oxidative conversion of hydrocarbons. In the Autothermic DeHydrogenation (ADH) process from Statoil, the amount of oxygen in the system is limited to the level where the total reaction becomes heat balanced. In this reaction it is possible to oxidise hydrogen selectively from a mixture with hydrocarbons without a total combustion of the hydrocarbons [Læg Reid (1993)].

1.4. Scope of the work

The project is aimed at the study of reactions between mixtures of hydrogen and light alkanes with oxygen over heterogeneous catalysts, both oxidic and metallic systems. The goal of the work is to obtain an improved understanding of the reaction between alkanes/alkenes (C_2-C_4) and oxygen, with the development of new processes for the production of valuable products like alkenes and oxygenates in mind. Traditional activity-/selectivity measurements have been used in order to investigate the product stability and the formation of carbon oxides (CO_x).

2 Theory and relevant literature

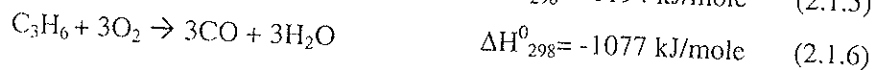
2.1 Propane and oxygen: Reactions and thermodynamics

All main reactions concerning the conversion of propane are in this chapter listed with their corresponding reaction enthalpies. It can be noted that all oxidation reactions, both partial oxidation and total oxidation reactions are exothermic, and that all dehydrogenation reactions are endothermic.

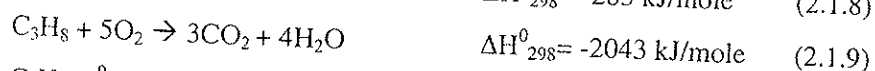
Dehydrogenation:

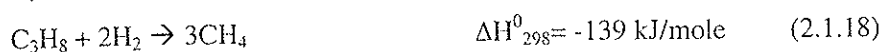
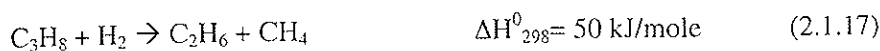


Partial oxidation:



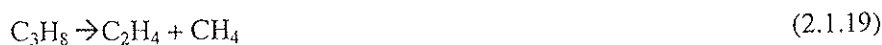
Combustion:



Water-gas Shift:**Carbon formation and gasification:****Catalytic cracking and hydrogenolysis:**

Cracking of propane to ethene and methane (2.1.16) is an undesirable reaction that can be thermal or catalytic. Catalytic cracking occurs on acidic catalysts. Thermal cracking is usually not important at temperatures below 650-700°C [Beretta (1998)]

Another side-reaction that can be of importance is coking. The reaction pathway can be via a parallel or a sequential reaction mechanism [Holmen (1996)].

Parallel:

a and b are dependent of the content of C and H in the coke.

Sequential:

The production of coke leads to catalyst deactivation and reduced catalytic activity. Under oxidative dehydrogenation, it is usually assumed that the amount of coking will be reduced since the coke can be continuously burned off by oxygen [Alkhazov (1980)].

Polymerisation and cyclisation of alkenes to give higher-molecular weight compounds is also possible with propene.

A further possibility is the conversion of hydrocarbons to oxygenated products. In Fig. 2.1.1 the possible routes to oxygenated products are shown.

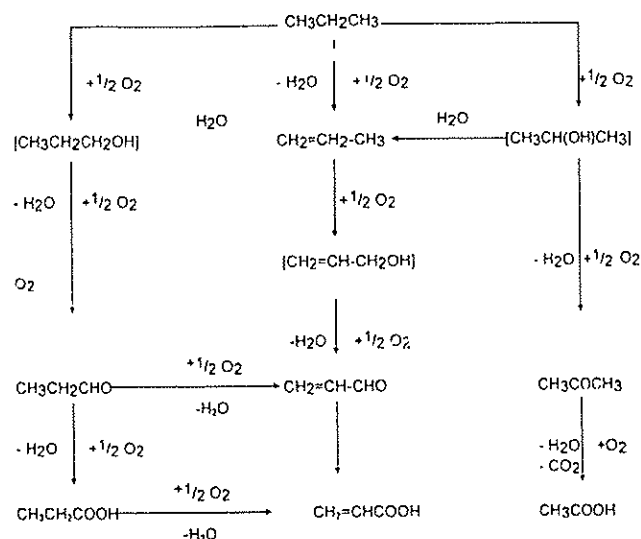


Figure 2.1.1 The main oxygenate products of the partial oxidation of propane and propene [Bettahar (1996)].

2.2 Catalytic dehydrogenation of hydrocarbons

Commercial production of light alkenes (C_2 - C_4) is mainly done by steam cracking of various hydrocarbon feedstock, ethene is the major product from steam cracking. Propene and heavier olefins are the most important by-products and their yields cannot substantially be increased by a change of operating conditions. Fluidised bed catalytic cracking (FCC) gives rise to a low yield of light olefins. Additional C_3 and C_4 alkenes can be recovered from refinery streams or produced by catalytic dehydrogenation of the corresponding alkane. Another way of transforming an alkane into its corresponding alkene is to add oxygen to the system of hydrocarbons in catalytic dehydrogenation. The added oxygen can react in two ways; oxidative dehydrogenation (ODH) and the selective hydrogen combustion (SHC). The theory of catalytic dehydrogenation, ODH and SHC is described in detail in the next chapters.

2.2.1 Catalytic dehydrogenation without oxygen supply

Since the demand for propene is increasing, catalytic dehydrogenation of propane is a feasible alternative to selectively producing propene. This is an interesting process in Norway due to the large quantities of natural gas including LPG (C_3 - C_4 alkanes) at the Norwegian Continental Shelf [The Norwegian Ministry of Petroleum and Energy (2000)].

The current commercial catalytic process use $Pt(Sn)/Al_2O_3$ or Cr_2O_3/Al_2O_3 [Resasco (1994)] catalysts for direct dehydrogenation from the alkane, which in the case of propane is:



$$\Delta H_r^0 = +124 \text{ kJ/mole and } \Delta G_r^0 = +86 \text{ kJ/mole at } 25^\circ\text{C and}$$

$$\Delta H_r^0 = +130 \text{ kJ/mole and } \Delta G_r^0 = -6.5 \text{ kJ/mole at } 700^\circ\text{C}$$

This reaction is endothermic and its conversion is limited by thermodynamic equilibrium. High conversion of propane and high selectivity to propene are important parameters in the industrial processes based on catalytic dehydrogenation. The main reasons are the large cost requirements due to the separation of propane/propene and gas recirculation [Centi (2001), Cavani (1994), Pujado (1983), Berg (1980)]. At 500°C the maximum theoretical attainable yield of propene from propane permitted by thermodynamics is 20%, and reaction temperatures above 600°C are necessary to achieve 50% equilibrium conversion of propane (at 1atm pressure of propane and without H₂ present in the inlet gas). [Stephenson (1966)]. At these high temperatures, cracking of the hydrocarbon can occur, reducing the selectivity to the desired products. But more importantly, coke depositions cause a decrease in catalyst activity and frequent regeneration of the catalyst is needed. Hydrogenolysis can also become significant at higher temperatures. Another drawback of conventional dehydrogenation processes is that they are endothermic, requiring the addition of heat via an external heat supply that is expensive. H₂ present in the inlet gas reaction mixture decreases the equilibrium conversion of propane markedly. However since deactivation due to coke formation occurs, recirculation of H₂ or a high partial pressure of steam is unavoidable in the industrial processes [Centi (2001), Cavani (1994)]. In the Houdry process steam and oxygen are used for catalyst regeneration. Irreversible deactivation due to sintering, volatilisation of the catalyst components and morphological or phase transformations of the support is another problem [Centi (2001), Cavani (1994)].

The industrial important processes for classical dehydrogenation of propane comprises the "Oleflex" process (UOP Inc.), the "Catofin" or "Houdry" process (developed by Air Products and Chemicals), the "STAR" process (Steam Active Reforming, Phillips) and the Snamprogetti-Yarsintez process [Vatcha (1993)]. Also, a process from Linde/BASF exists, but is not yet in

commercial operation. Although the efficiencies of these processes and their respective catalysts are highly optimized, they nonetheless all suffer from the common disadvantages that their olefin yields per pass are thermodynamically limited and that they all require heat supply.

The STAR, Houdry and Linde/BASF processes use fixed bed reactors, the Oleflex process uses moving bed reactor, and the Snamprogetti process uses fluidized bed reactors.

The Oleflex and STAR processes are based on supported platinum catalyst systems, whereas the Houdry, Snamprogetti and Linde/BASF processes are based on supported chromium oxide catalyst systems. The main differences between the two catalyst systems are that the loading of chromia is much higher than that of platinum due to higher specific activity on Pt. The deactivation rates due to coke formation are higher on chromia and more frequent regeneration of the catalyst is needed. The advantage of this regeneration is that the gasification of coke with oxygen is very exothermic and provides heat to the endothermic dehydrogenation reaction.

2.2.2 Oxidative dehydrogenation (ODH)

The oxidative dehydrogenation (ODH) of lower alkanes is an interesting alternative to the conventional dehydrogenation of LPG, owing to the possibility of working at lower reaction temperatures. The reaction is able to proceed at temperatures at which the formation of carbon and cracking products is insignificant, but temperatures above 500°C is necessary for the activation of propane [Mamedov (1995)]. The main problem with ODH is the lack of selectivity due to complete combustion, especially of the more reactive alkene. In the presence of O₂, other oxidation reactions, such as partial oxidation to aldehydes or acids and combustion to CO_x can occur. The total oxidation is the most undesirable reaction.

ODH according to Eq. 2.2.2 is not limited by the thermodynamic equilibrium, and catalyst deactivation is usually not a problem since coke and its precursors can be efficiently removed by oxygen. In this reaction, oxygen reacts directly with the hydrocarbon molecule on the catalyst surface yielding the products of ODH.



Since hydrogen desorption to the gas phase does not take place here, the reaction can occur on catalysts which are not active in H_2 oxidation [Alkhozov (1980)].

2.2.2.1 Catalytic systems for ODH

Catalysts for combustion must provide a high rate of oxygen activation. To do so they must have a large number of sites for coordinating oxygen molecules, and have the ability to easily donate and accept electrons. Oxides of 3d elements with an unfilled d shell exemplify materials suitable for combustion [Oyama (1996)]. The catalysts should be able to activate the C-H bond at sufficiently low temperatures. Among the most promising catalysts for ODH of propane are oxides of Mg, Sb, Nb, La, Bi. A great variety of catalytic systems have been studied for this reaction (Dahl (1991), Centi (1997), Cavani (1997), Mamedov (1995), Fox (1973), Ushkov (1988), Cherrak (1992), Smits (1992), Chaar (1988), Nguyen (1991), Kung (1992), Siew Hew Sam (1990), Corma (1992)) such as alkali molten salts (Dahl (1991), Buiten (1968)), metal molybdates (Cherrak (1992), Miller (1999)) or vanadates (Mamedov (1995), Chaar (1988), Nguyen (1991), Kung (1992), Siew Hew Sam (1990), Corma (1992)), niobium pentoxide (Mazzoccia (1991)). Ushkov et al. [Ushkov (1988)] studied the system of metal sulphates, Takita et al. [Takita (1989)] investigated metal phosphates, Romero et al. [Shenoy (1986), Sing (1990)] nickel and iron oxides and Fujimoto et al. [Fujimoto (1989)] ZSM-5 based catalysts. The system consisting of vanadium-

magnesium oxide is one of the most tested and promising catalysts for ODH, but a break-through allowing commercial utilization is still lacking (Chaar (1988), Nguyen (1991), Kung (1992), Siew Hew Sam (1990), Corma (1992), Burch (1993), Corma (1993), Pantazidis (1996)). The selectivities to the desired products are so far too low. Pantazidis and Mirodatos [Pantazidis (1996)] found propene selectivities of about 70% at propane conversion of 10% for the VMgO system at 500°C and 60% at 15% conversion for the same temperature. The vanadium content of the catalyst is an important factor for the activity of the catalyst. Several different research groups (Chaar (1988), Gao (1994), Siew Hew Sam (1990), Corma (1994)) have studied the effect of the vanadium content and the best catalytic performance was achieved at about 24 wt% V_2O_5 . In general, for all the catalysts, it is most often found that the selectivity to the alkene is inversely related to the conversion, while the selectivity to total combustion is proportional to the conversion.

2.2.2.2 *Active phases and active sites of the VMgO catalyst*

Kung et al. [Chaar (1987)] found in their initial XRD studies of the VMgO catalyst in the ODH of n-butane that the catalyst consisted of MgO and magnesium orthovanadate ($Mg_3V_2O_8$) phases. The authors' catalysts prepared containing between 3 and 54 wt% V_2O_5 . They proposed that the most active and selective phase of the catalyst was the magnesium orthovanadate phase. This hypothesis was based on the fact that structurally the orthovanadate phase contains only V-O-Mg linkages and no V-O-V or V=O bonds as with magnesium pyrovanadate ($Mg_2V_2O_7$), magnesium metavanadate (MgV_2O_6) and V_2O_5 . Since Mg is less easily reduced than V, the presence of Mg-O-V bonds causes oxygen to be less reactive than the case is for V-O-V and V=O bonds which allows oxygen to attack indiscriminately either C-H or C-C bonds thus promoting the total combustion.

Siew Hew Sam et al. [Siew Hew Sam (1990)] believe that only the pyrovanadate phase is taking part in the dehydrogenation, and that the orthovanadate is responsible for the total oxidation. The VMgO system consists of a vanadium phase, which provides the oxidising properties needed and a magnesia phase, which provides the base properties decreasing the consecutive oxidation of propene. It is proposed that high propene selectivity needs both V=O and V-O-V isolated sites.

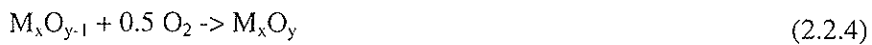
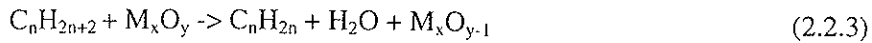
Kung and co-workers [Kung (1992)] found in a later study that the preparation method is an important factor, and that Siew Hew Sam et al. [Siew Hew Sam (1990)] used a preparation method that resulted in traces of potassium in the final catalyst. The effect of traces of potassium in the V-Mg-O catalyst was studied. Mg orthovanadate and Mg pyrovanadate were prepared by the method of Siew Hew Sam et al. [Siew Hew Sam (1990)] and their activities and selectivities were compared with those of potassium free catalyst. The orthovanadate with potassium was less selective than the corresponding potassium free catalyst. Both Kung's group and Siew Hew Sam et al. needed to use calcination temperatures above 650°C to produce sufficiently pure phases.

Gao et al. [Gao (1994)] found that the size and morphology of the pure phase Mg-V-O catalyst was a function of the calcination temperature.

Creaser et al. [Creaser (1999)] supports the widely held view that ODH proceeds through a mechanism involving just orthovanadate. The only phases identified in their catalysts were magnesium oxide and magnesium orthovanadate.

2.2.2.3 Reaction kinetics for the ODH

When metal oxides are used as ODH catalyst the catalyst is first contacted with hydrocarbon, resulting in oxidative dehydrogenation of hydrocarbon and partial reduction of the metal oxide. The reduced metal oxide is continuously reoxidised by gas phase oxygen according to a Mars Wan Krevelen reaction mechanism [Bielanski (1991)]:



No gas phase oxygen is taking part in the reaction with the hydrocarbon. On the basis of this reaction mechanism Mars and van Krevelen developed a kinetic model for description of partial oxidation reactions [Bielanski (1991)]: The assumption is that the oxidation rate (r_1) is proportional to the fraction of active points in oxidized condition and to the partial pressure of reactant (R):

$$r_1 = k_1 \cdot P_R \cdot (1-\theta) \quad (2.2.5)$$

where θ is the fraction of active points in reduced condition. The rate for reoxidation of the catalyst (r_2) is assumed to be proportional to the number of active points in reduced form and to the partial pressure of O_2 ($P_{O_2}^n$):

$$r_2 = k_2 \cdot P_{O_2}^n \cdot \theta \quad (2.2.6)$$

At equilibrium the rate of r_1 equals the rate of r_2 :

$$r = \frac{k_1 \cdot k_2 \cdot P_R \cdot P_{O_2}^n}{k_1 \cdot P_R + k_2 \cdot P_{O_2}^n} \quad (2.2.7)$$

(2.2.7) is the Mars-van Krevelen reaction rate expression.

Chaar et al. [Chaar (1988)] found a propane reaction rate effect of 0.6 order in propane partial pressure and zeroth order in oxygen partial pressure for the ODH of propane over VMgO catalyst at 500°C. They observed a propene selectivity of 65% at a propane conversion of 10%.

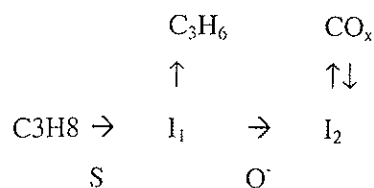
Pantazidis and Mirodatos [Pantazidis (1996)] found a first order dependence in propane and close to zero (0.13) order in oxygen partial pressure for the reaction rate of propane on VMgO catalyst at 500°C. They observed a selectivity of about 70% at a propane conversion of 10%.

Several groups propose a first order dependence in propane [Anderson (1994), Smits (1994), de Morais (1995)] and zero order dependence in oxygen [Smits (1994), de Morais (1995),] on the reaction rate of propane.

2.2.2.4 Reaction pathway for the ODH

There is a general agreement in literature that the rate-determining step of the reaction is the breaking of the first C-H bond, leading to a propyl species [Centi (1988), Sulikowski (1994), Patel (1988)]. But what happens after the activation is much debated.

Pantazidis and Mirodatos [Pantazidis (1996)] have proposed a reaction pathway for the ODH of propane over VMgO catalyst. They proposed that the initial step of propane occurred on a single type of site (S) as described in Scheme 2.3.1. I_1 and I_2 are intermediates in the reaction pathway described in Scheme 2.3.1.



Scheme 2.3.1 ODH of propane simplified reaction scheme.

They discuss a reaction pathway in which no CO_x is formed from propene oxidation (see Scheme 2.3.1), and that there is no adsorption/desorption equilibrium of propene under reaction conditions. They suggest that all ODH products are primary products. They further suggest that the first activated propane, intermediate I_1 , can desorb as propene or react with another species and transform into another intermediate (I_2) leading to CO_x formation. Since only a weak dependency of the partial pressure of oxygen on the CO_x formation is observed, they proposed that the transformation of I_1 to I_2 did not involve gaseous oxygen, but oxygen adspecies arising from gaseous oxygen activation.

In a TAP reactor investigation of ODH of propane over VMgO Pantazidis et al. [Pantazidis (1998)] found that both propene and carbon oxides are primary products and that CO_x is also produced by secondary oxidation of propene. They proposed that partial and deep oxidation of propane occur at the same surface site, but involve different forms of reactive oxygen, associated to different site arrangements. Nucleophilic oxygen takes part in the partial oxidation whereas electrophilic oxygen takes part in the total oxidation. The secondary oxidation of propene could involve both types of oxygen.

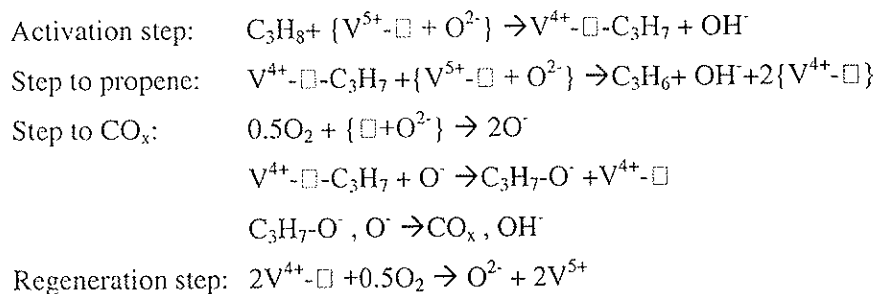
Chen et al. [Chen (1999)] studied the propane dehydrogenation on VO_x/ZrO_2 and found that the reaction pathway goes via parallel and sequential reactions.

Propene is the most abundant primary product. CO and CO₂ form via a secondary combustion of propene, and CO₂ is also formed directly from the combustion of propane.

Creaser and Anderson [Creaser (1996)] propose a reaction pathway in which one has a slow initial propane activation, and the adsorbed C₃H₇-specie reacts fast with an oxygen specie to form an adsorbed C₃H₆ specie which again can desorb to form propene or it can react with another oxygen specie to form CO_x. This is in contrast to Pantazidis and Mirodatos [Pantazidis (1996)] a consecutive reaction pathway where the CO₂ formation goes via adsorbed propene as an intermediate.

2.2.2.5 Reaction mechanism for the ODH of propane over VMgO

The following reaction mechanism is proposed by Pantazidis and Mirodatos [Pantazidis (1996)], and involves reducible V⁵⁺ surface ions and lattice vacancies as the active surface:



From the figure one can see that the intermediate propyl radical (V⁴⁺-□-C₃H₇) can either desorb as propene after a second H-abstraction by a lattice oxygen ion, or it can react further to form CO_x.

2.2.3 Autothermal dehydrogenation and selective hydrogen combustion

The principal idea of autothermal dehydrogenation (ADH) of propane is to supply the heat by combustion of about half of the hydrogen formed in the dehydrogenation reaction in the reactor itself [Lægheid (1993)]. In this way the system is heat balanced and no external heat has to be supplied. This selective hydrogen combustion selective hydrogen combustion (SHC) is an alternative to the thermodynamically limited dehydrogenation and the thermodynamically not limited oxidative dehydrogenation processes. This process consists of two reactions occurring in sequence either on different sites of one catalyst or on different catalysts (Eq 2.2.8 and Eq 2.2.9).



In the ADH/SHC, oxygen is facilitating the pure dehydrogenation reaction by converting molecular hydrogen to water and in this way providing in situ heating as well as shifting the equilibrium towards the formation of the dehydrogenated products. In the concept of ADH, [Lægheid (1993)], alternating zones of oxidation and dehydrogenation are used. They showed that for propane dehydrogenation at 600° and with a gas feed rate of 2100 ml/g-h and with steam as a diluant, high conversions and selectivities to propene are obtained for certain catalysts. They used a catalyst consisting of Sn-Pt-Cs/ZnAl₂O₄, and achieved selectivities of 95% propene at 38% propane conversion. They also developed a new catalyst system with high surface area and with Pt as the active metal and produced a stable (for at least 50h on stream) catalyst that achieved 96% selectivity to propene at 59% propane conversion. They found a yield pr. pass to be 56% for the catalyst (after 25 h on stream) compared to 30% for the catalyst according to a patent by UOP (Sn-Pt-Cs/Al₂O₃ [Tagamolila (1991)]).

In a patent from 1991 UOP made use of a steam eductor to supply oxygen for oxidative reheating in dehydrogenation of C_3+ hydrocarbons [Tagamolila (1991)]. A dehydrogenation process, where a hydrocarbon feed is dehydrogenated in a dehydrogenation zone and then oxidatively reheated by the combustion of hydrogen in an oxidation zone containing an oxidation catalyst, is improved by using a stream of dilution steam as an educing fluid to draw oxygen into contact with the effluent from the dehydrogenation zone ahead of the oxidation zone. A stream of dilution steam is often combined with the dehydrogenation zone effluent in order to control the oxygen concentration ahead of the oxidation zone and to lower the hydrogen partial pressure. The use of dilution steam eliminates the need for compression of the oxygen containing gas.

Grasselli and coworkers [Tsikoyiannis (1999)] studied systems of different metal-oxide catalysts for the dehydrogenation (DH) - selective hydrogen combustion (SHC). The main advantage of this system compared to the ODH is claimed to be that one does not have to handle gaseous hydrogen and oxygen in the same system and thus preventing the possibility of explosions. The hydrogen can be oxidised by lattice oxygen from the SHC- catalyst. The metal oxide (SHC-catalyst) periodically has to be reoxidised by oxygen. Oxygen can also be used to burn off coke deposited on the catalyst surface preventing a loss of catalytic activity. It is possible to run the DH-SHC system in two different ways: Alternating zones, like the ADH process where a sequential DH-SHC is taking place, or in a mixed zone with physically mixed DH and SHC catalysts. It is important that the catalyst for the SHC attack and oxidise the hydrogen with great preference to alkane/alkene, since any loss of hydrocarbons to CO_x lowers the selectivities and yield to the desired products. It is also very important for the DH-SHC catalyst to be steam resistant and CO_x compatible [Tsikoyiannis (1999)]. Grasselli and coworkers have in several papers investigated catalysts for SHC [Tsikoyiannis (1999, Grasselli (1999)]. Several catalyst candidates (metal oxides and mixed metal oxides)

were compared using a gravimetric investigation of reduction rates in hydrogen and hydrocarbon gases respectively. From these experiments it was proposed that materials that were more reactive towards hydrogen compared to propane or propene were suitable SHC catalysts, and they identified materials like Bi_2O_3 , $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, In_2O_3 , $\text{In}_2\text{Mo}_3\text{O}_{12}$, Sb_2O_4 and WO_3 (all supported on SiO_2) as candidates. In a catalytic experiment $\text{Bi}_2\text{O}_3/\text{SiO}_2$ was exposed to alternate pulses of hydrogen/propane followed by oxygen. In this red-ox mode a high conversion of hydrogen and virtually no conversion of propane was observed, the hydrogen reacting with lattice oxygen to form water. This catalyst was also tested successfully in co-feed experiments, both with propane and propene as the hydrocarbon compound in the gas phase. In separate papers this and other catalysts were tested in co-feed mode in a reactor set-up in series (DH-SHC-DH) and in the red-ox mode a mixed catalyst phase, both with very promising results [Grasselli (1999)].

The $\text{DH} \rightarrow \text{SHC} \rightarrow \text{DH}$ system was pioneered by Imai et al. [Imai (1984), O'Hara (1986), Bricker (1988), Imai (1989)] in the process for conversion of ethylbenzene to styrene, but has also been applied in the conversion of propane to propene [Imai (1988)]. Either alkali promoted Fe-Cr oxides or Group VIII noble metals were used as DH catalysts and alkali-promoted Group VIII noble metals, in particular Cs-Pt-(Sn)-based alumina supported systems as SHC catalysts. Problems with instability of Cs-Pt-based catalyst due to volatile Cs under reaction conditions is one possible explanation why this process has not been commercialised. Safety hazards from simultaneously using hydrogen and oxygen in the same system are another problem connected to the process.

3 Experimental

The experimental techniques used for activity /selectivity measurements and for catalyst characterisation are described in this chapter. The experimental set-up for activity/selectivity experiments is used for both the oxidative system and for selective hydrogen combustion systems, the only difference being the conditions.

3.1 Apparatus for the activity-/selectivity measurements

The reactions were studied in a U-shaped, fixed bed quartz microreactor with an inner diameter of 3.5 mm. The catalyst was located in one arm of the U-tube. The catalyst loadings were in the range 0.10 to 0.45 g. The reactions were carried out at atmospheric pressure using air as the oxidant. The reactor was placed in an electrical furnace, and controlled using external and internal thermocouples. The temperature was varied from ambient to 775 °C. The total flow rate was 100 ml/min with varying compositions of propane, air, propene, hydrogen, the balance being helium. The rig is shown in figure 3.1. There was one by-pass line in parallel with the reactor. Gases were premixed and fed to the reactor using electronic mass flow controllers (Bronkhurst). The product gas was analysed for hydrocarbons ($C_1 - C_4$) and for permanent gases (O_2 , N_2 , CO , CO_2) by GC. The chromatograph used was a Perkin Elmer autosystem XL equipped with a TCD (Carbosieve SII, 10ft, mesh 80) and a FID (PoraPLOT Q, 27.5 m, i.d. 0.53mm).

In some of the experiments the catalyst was prereduced with hydrogen (15 ml/min) with a heating rate of 10°C/min from ambient to 500°C. The catalyst was kept at this temperature for two hours. Water and hydrogen produced are not analysed by the GC, but were calculated through mass balances. The calculation procedures are given in Appendix 1.

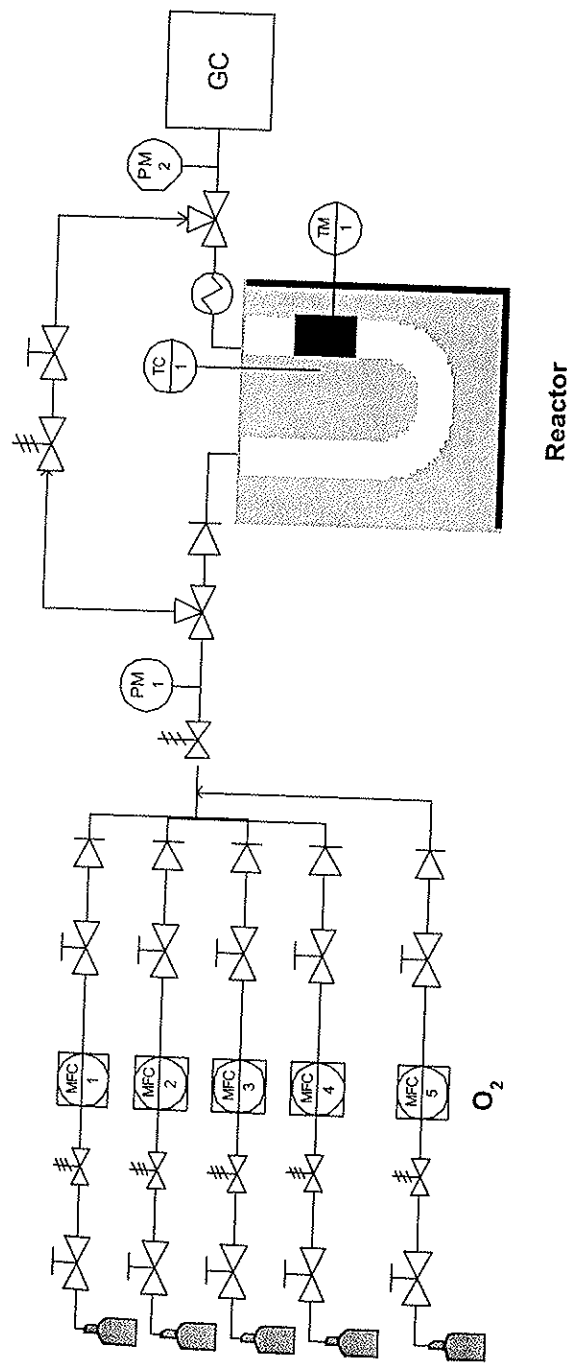
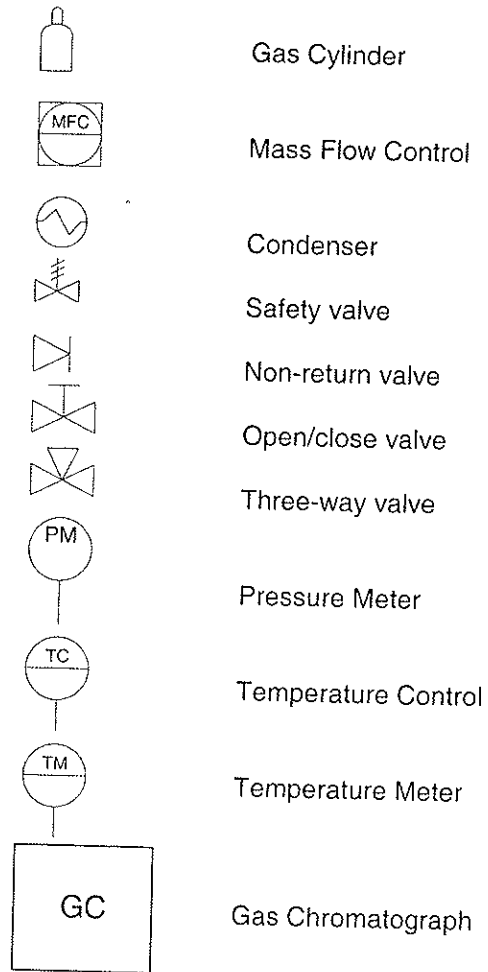


Figure 3.1.1 Apparatus for activity/selectivity measurements



3.2 Other techniques used

TPR is an experimentally simple technique for characterization of heterogeneous catalysts. TPR profiles provide indications of reducibility and of optimum temperatures for reduction of the catalyst. The TPR apparatus is described elsewhere [Blekkan (1993)]. The experiments were performed at a heating rate of 10°C/min from 25°C to 900°C with 7% hydrogen in argon. The hydrogen consumption was measured by analysing the effluent gas with a gas chromatograph equipped with a thermal conductivity detector (TCD).

The x-ray diffraction (XRD) experiments were performed in order to identify the different crystalline phases in the catalyst. XRD were conducted at the Dep. of Chemistry, NTNU using a Phillips 1710 spectrometer equipped with a Cu K α radiation and a graphite crystal monochromator.

BET surface area measurements were performed by Gunnar Carlsen at SINTEF Applied Chemistry in a Carbo Erba Multisampler 1900 apparatus using liquid nitrogen at its boiling point. The samples were evacuated and dried at 150°C prior to the surface area measurements.

3.3 Catalyst preparation

Several different catalytic systems were prepared and tested. All the catalyst preparation methods are described in this chapter.

The VMgO catalyst was prepared by impregnating $\text{Mg}(\text{OH})_2$ with an aqueous solution of NH_4VO_3 . The vanadium: magnesium atomic ratio was adjusted to 0.32. The catalyst was dried for 12 hours at 120°C before it was calcined at 550°C for 9 hours with a ramp rate of $5^\circ\text{C}/\text{min}$ from room temperature using an airflow of 50 ml/min (GHSV = 0.35). The surface area (BET) was found to be $48 \text{ m}^2/\text{g}$. The preparation is in accordance to the procedure given by Pantazidis and Mirodatos [Pantazidis (1996)]

The Sn/SiO₂ (1.0 wt% Sn), Pt/SiO₂ (1.0 wt% Pt) and PtSn/SiO₂ (0.35 - 1.0 wt%) catalysts were prepared by aqueous incipient wetness impregnation of silica (Merck Kieselgel 60, $S_{\text{BET}} = 483 \text{ m}^2/\text{g}$, particle size 0.063 - 0.2 mm), using $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. The dissolution of the tin salt was aided by addition of HNO_3 . The catalysts will be termed Sn, Pt and PtSn, respectively. The catalysts were calcined at 600°C for 12 hours with a ramp rate of $5^\circ\text{C}/\text{min}$ from room temperature using an airflow of 50 ml/min (GHSV = 0.35 l/g h). The surface areas (BET) of the catalysts were found to be: Sn/SiO₂ = $457 \text{ m}^2/\text{g}$, Pt/SiO₂ = $415 \text{ m}^2/\text{g}$ and PtSn/SiO₂ = $428 \text{ m}^2/\text{g}$.

Bi₂O₃/SiO₂, In₂O₃/SiO₂, Cr₂O₃/SiO₂ and PbO/SiO₂ were prepared by refluxing aqueous solutions of the appropriate metal nitrates in the presence of silica (Merck Kieselgel 60, $S_{\text{BET}} = 483 \text{ m}^2/\text{g}$, particle size 0.063 - 0.2 mm). 50 wt% of the salts and 50 wt% of silica were used for both cases. In the preparation of Bi₂O₃/SiO₂ HNO_3 was added to the solution in order to aid the solubility of bismuth-nitrate. The resulting slurries were refluxed for 16 hours at 70°C , dried at 120°C for 12 hours. The catalysts were then calcined at 600°C for 12 hours with a ramp rate of $5^\circ\text{C}/\text{min}$ from room temperature using an airflow of

50 ml/min (GHSV=0.35). The surface areas (BET) were found to be: $\text{Bi}_2\text{O}_3/\text{SiO}_2=242 \text{ m}^2/\text{g}$ and $\text{In}_2\text{O}_3/\text{SiO}_2=278 \text{ m}^2/\text{g}$.

The zeolite (ZSM-5) catalyst was kindly donated by Prof. Stein Kolboe, UiO. The catalyst was ion exchanged with aqueous NH_4OH (1 mol/l) and calcined at 550°C for 12 hours with a ramp rate of $5^\circ\text{C}/\text{min}$ from room temperature using an airflow of 50 ml/min (GHSV=0.35 l/g-h).

4 Results and discussions

This chapter is divided into three parts:

Chapter 4.1 presents the experimental data for the empty reactor at various temperatures and gas compositions. Chapter 4.2 deals with the process of oxidative dehydrogenation of propane over a VMgO catalyst. Chapter 4.3 focuses on catalysts for the process of selective hydrogen combustion in gas mixtures of propane, propene, hydrogen and oxygen.

All the activity/selectivity tests have been performed using the apparatus described in chapter 3.1.

4.1 Empty reactor

Without hydrogen in the feed

There was no significant conversion of propane at temperatures below 575°C for the empty reactor. The results indicate that the contribution from the gas phase reactions initiated in the gas phase is low within the temperature interval used in the experiments. There is still a possibility for reactions to be initiated at the catalyst surface and continued in the gas phase.

With hydrogen in the feed

The results for the empty reactor are shown in Fig 4.1.1. From the figure it can be seen that there was no significant conversion of propane at temperatures below 600°C. For oxygen conversion there was a gradual increase as the temperatures increased from ambient, and at temperatures of about 550°C the conversion was about 10%. Above 600°C the conversions of both oxygen and propane increased and at temperatures about 700°C there was more or less a complete conversion of oxygen (96%) and a 40% conversion of propane. By looking at the product distribution one can see that propene and ethene were the main products at low propane conversions, and that the selectivities of methane, ethene and CO increased at the expense of propene as the conversion increases. The selectivity to CO₂ was constant and low for all temperatures. The results are in good agreement with what Beretta et al. [Beretta (1998) and Beretta (1999)] have observed, but somewhat different from the results of Burch and Crabb [Burch and Crabb (1993)], who observed significant propane conversion in the empty reactor already at 550°C. The main difference in gas composition of our experiments compared to the results of the other groups, is that we had a co-injection of hydrogen in the feed. By looking at the oxygen selectivity in Fig. 4.1.1 it is evident that below 600°C all the oxygen reacting was forming water. Above 600°C the selectivity to CO_x was significant, CO₂ being the major product.

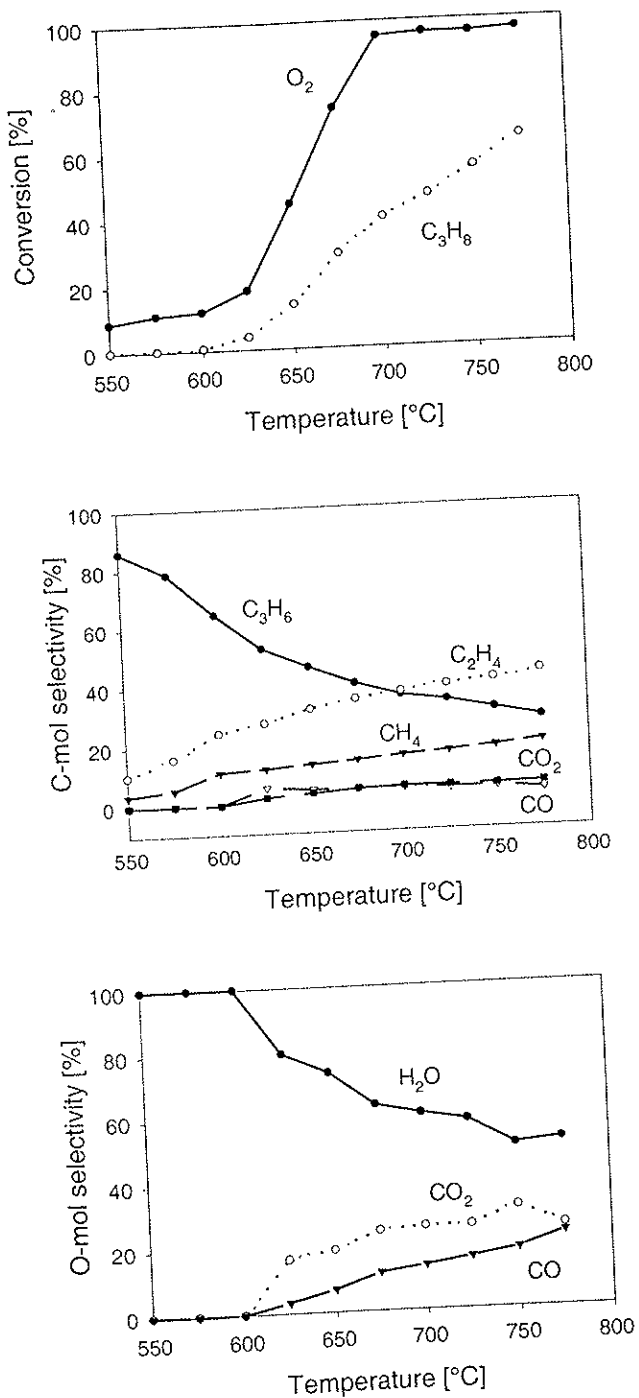


Figure 4.1.1. Conversions and selectivities over an empty reactor at various temperatures. Gas composition: 10 ml/min C₃H₈, 2 ml/min H₂ and 2 ml/min O₂.

4.2 VMgO catalyst

4.2.1 Catalyst characterization

The VMgO catalyst was characterized by BET, XRD and TPR. The surface area of the fresh catalyst was found by BET to be 38.0 m²/g, and the surface area of the catalyst after 40 hours on stream at 500°C was measured to 35.0 m²/g.

The XRD pattern is shown in Fig. 4.2.1. The reflections corresponding to MgO and Mg₃V₂O₈ (orthovanadate) crystalline phases are indicated in the figure. There are also indications of the existence of Mg₂V₂O₇ (pyrovanadate) crystallites in the XRD diffractogram (weak peaks at 2θ = 24, 25, 53, 58).

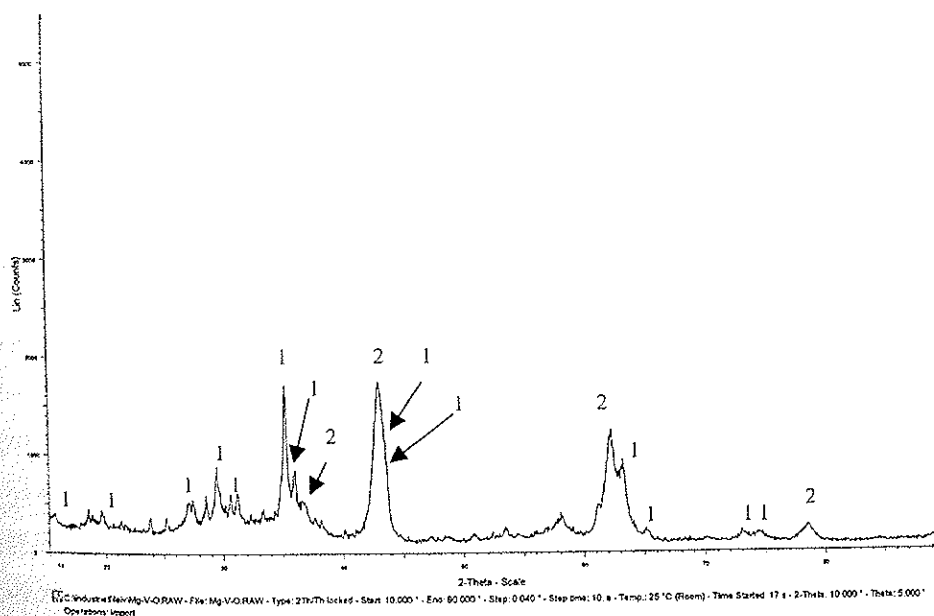


Figure. 4.2.1. XRD pattern of the fresh VMgO catalyst. (1) Mg₃(VO₄)₂, (2) MgO.

The TPR measurements for the VMgO catalyst is shown in fig 4.2.2.

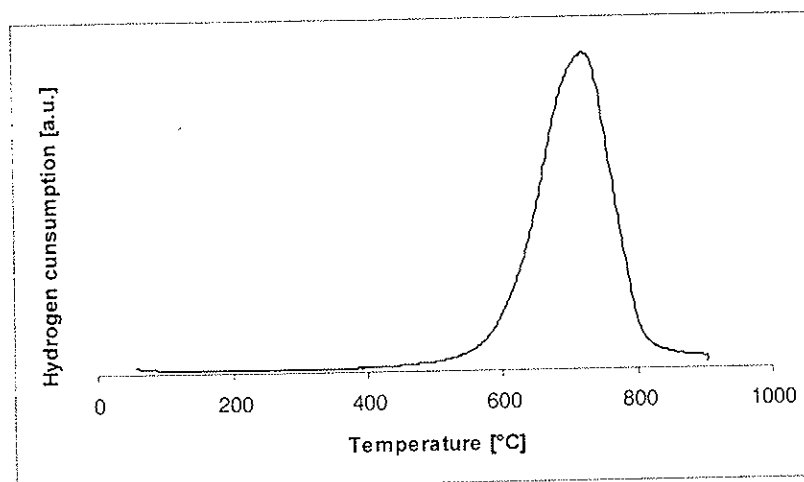


Figure 4.2.2. TPR measurements of the fresh VMgO catalyst. $W_{\text{cat}}=0.1$ g.

The TPR pattern of the VMgO catalyst indicates that there is only one reduction peak appearing between 600 and 800°C. The reduction is likely to be V^{5+} being reduced to V^{3+} . Corma et al. [Corma (1994)] found in a study of VMgO catalysts with varying vanadium content two separate reduction peaks within the temperature interval 300-800°C for all the catalysts. They also suggests that the more reducible peak (reduced at the lower temperature) is the one being responsible for the ODH of propane.

4.2.2 Effect of temperature on conversion and selectivities

The major products of the ODH of propane on VMgO were propene, CO_2 , CO and water. Traces of methane, ethane and ethene were also observed at high conversion, especially at high temperatures and high propane pressures. No oxygenates were detected. Fig 4.2.3 shows plots of reactant conversions, reaction rate of propane and product selectivities as a function of the temperature. Both the propane conversion and the oxygen conversion are strongly related to the temperature in the reactor. The selectivities to CO and CO_2 increase almost linearly, and the selectivity to propene decreases linearly as the temperature is raised from 475-550°C.

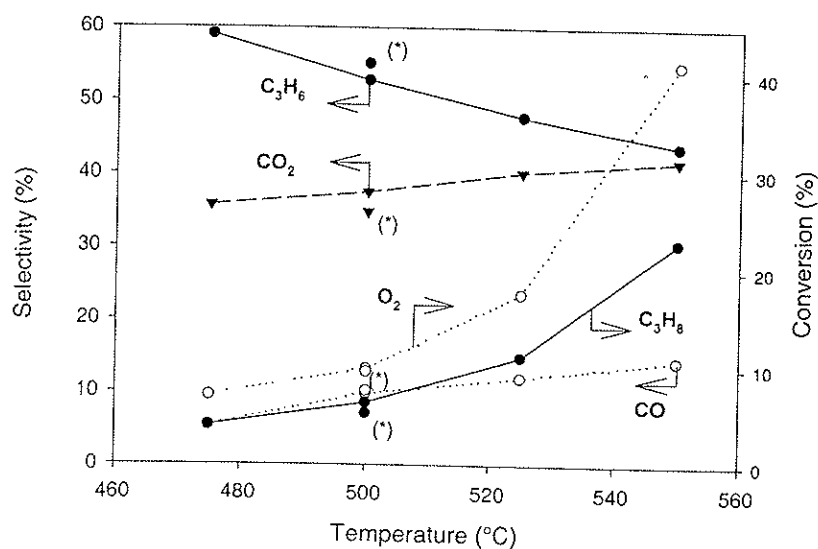


Figure 4.2.3. Conversions and selectivities as a function of reaction temperature. $C_3H_8/Air/He = 5/30/65$. $W_{cat} = 0.1g$. (The points labelled (*) is recorded about 5 hours later than the original point at 500°C)

Temperatures above 475°C seem to be needed for the activation of propane at these flow-rates. At temperatures lower than 475°C the conversion of propane is low (less than 4%). According to Bettahar et al. [Bettahar (1996)] propane activation needs a high reaction temperature (500°C compared to 400°C for propene) and, as a consequence, a strong activating (oxidising) phase such as vanadium. The difference of reactivity between propane and propene is linked to the strengths of the involved C-H bonds and to the stability of the corresponding radicals formed in the rate determining step by H abstraction: the less stable propyl radical (corresponding to the stronger C-H bond) needs a higher reaction temperature and a stronger oxidising phase to be produced than the most stable Π -allyl radical (corresponding to the weaker C-H bond breaking).

4.2.3 Catalyst stability

The VMgO system used here was quite stable over time with only a small degree of deactivation of the catalyst, at least at low conversions. The propane conversion dropped from 6.7 to 5.9% during 40 hours on stream. This is shown in Fig. 4.2.4 where the conversion of propane and oxygen as well as the selectivities to the products are shown as a function of time on stream.

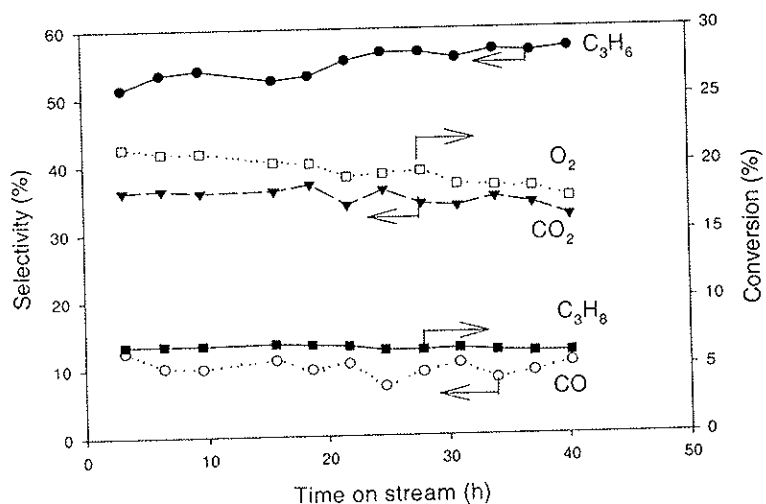


Figure 4.2.4. Catalytic stability of VMgO. $W_{\text{cat}}=0.10\text{g}$, $\text{C}_3\text{H}_8/\text{Air}/\text{He} = 10/30/60$ ml/min. $T=500^\circ\text{C}$.

From the figure it can be seen that the conversion of oxygen drops from 21 to 17.5% during the same period of time. The selectivities to the various products are changing as a function of time on stream. The propene selectivity increases from 51.1 to 58.3% and the CO₂ selectivity drops from 36.2 to 32.5% while the CO selectivity is more or less unchanged during the experiment. The catalyst seems to be more and more selective to the desired products with increasing time on stream. The surface area of the catalyst was measured after 40 hours on stream, and found to be $35\text{ m}^2/\text{g}_{\text{cat}}$, a reduction of about 9% compared to the fresh catalyst. This drop in surface area might

explain the decrease in propane conversion during the run. The results in Fig. 4.2.4, where the selectivity to propene increases with time on stream can be explained by the fact that the selectivity in the ODH is usually a strong function of conversion. This is shown in Fig. 4.2.5, which demonstrates the dependence of selectivity on conversion for VMgO catalysts. The extra set of data at 500°C in Fig. 4.2.3 also shows this effect. The extra data set is recorded about 5 hours later than the set original set, and shows that the propane conversions decrease and the selectivity to propene increases at the expense of CO_x as a function of time on stream. This conversion-selectivity dependence can also explain the results in fig 4.2.3, where the propene selectivity decreases as the temperature and propane conversion increases.

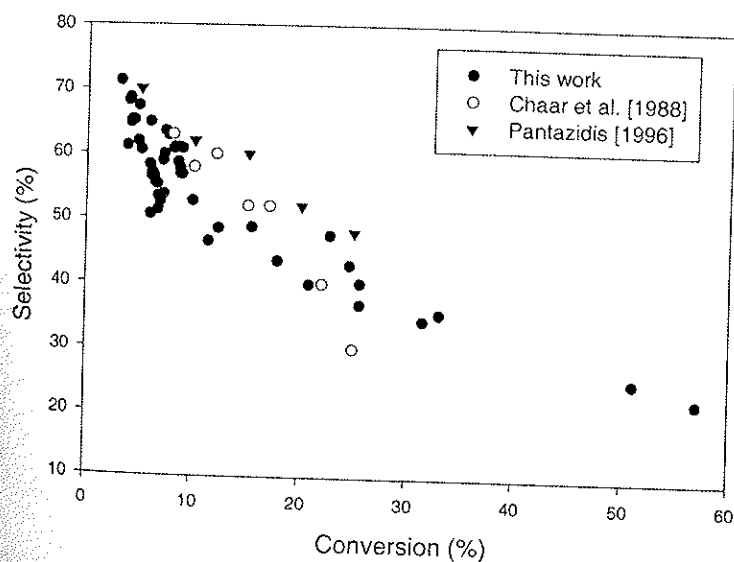


Figure 4.2.5. Selectivity to propene as a function of propane conversion.

The selectivity to propene decreases strongly with increasing conversion of propane. This is in good agreement with the results from other groups on similar catalytic systems [Pantazidis (1996), Chaar (1988)], also shown in the figure. The total yield of propene increases from about 5% at 10% propane conversion to 13% at 55% conversion. The results from Pantazidis and

Mirodatos [Pantazidis (1996)] were obtained on a catalyst with a similar composition, but a slightly higher surface area ($43 \text{ m}^2/\text{g}$). The observed differences in yields could be a consequence of this difference in catalyst surface area.

4.2.4 Reaction kinetics

The kinetics of the reaction was investigated at differential conditions (propane conversions kept below 10%). The absence of significant inter- or intra particle diffusion limitations was confirmed using the usual experiments: Decreasing the particle size was found to not change the reaction rate. Doubling the linear flow-rate at constant space velocity similarly gave no change in reaction rate. By varying the catalyst loading one can see from Fig. 4.2.6 that the reaction rate is constant up to a contact time (W/F) of $4 \text{ g}_{\text{cat}} \text{ h}/\text{mole-C}_3$ (0.1 g catalyst), but a further increase in the contact time lowers the reaction.

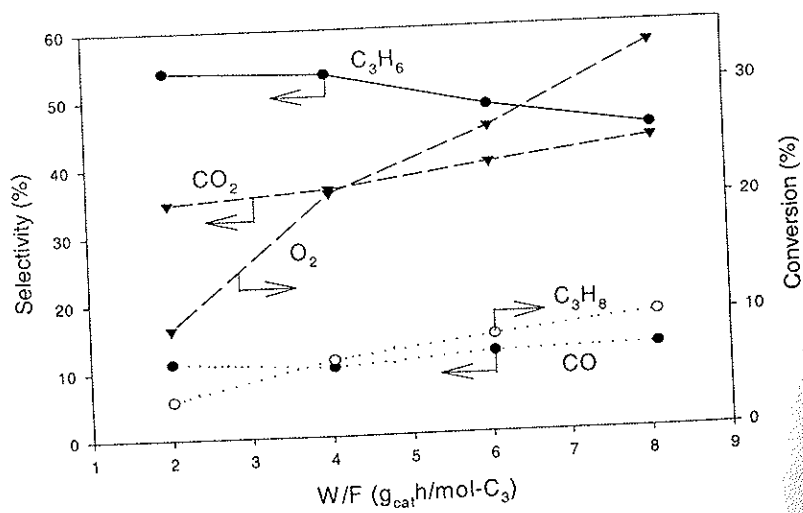


Figure 4.2.6. Influence of contact time on conversions, selectivities and reaction rate. $W_{\text{cat}} = 0.05 - 0.2 \text{ g}$, $\text{C}_3\text{H}_8/\text{Air}/\text{He} = 10/30/60 \text{ ml}/\text{min}$. $T = 500^\circ\text{C}$.

In Fig. 4.2.6 the reaction rate, product selectivities and the conversions of the reactants are plotted as a function of the contact time ($g_{\text{cat}} \text{ h/mole-C}_3$). The conversion of both oxygen and propane are increasing as the contact time is increased. The selectivity to propene drops from 54 to 45%, the CO_2 selectivity increases from 35 to 43% as the contact time is increased from 2 to 8 $g_{\text{cat}} \text{ h/mol-C}_3$. The selectivity to CO is more or less unaffected by the contact time. A decrease in reaction rate of propane from $27 \cdot 10^{-5}$ to $21 \cdot 10^{-5} \text{ mole/min-g}_{\text{cat}}$ is observed as the contact time is increased. In all the kinetic experiments reported here a contact time of 4 $g_{\text{cat}} \text{ h/mole-C}_3$ (catalyst loading of 0.1g) is used in order to operate at differential conditions. Corma et al. [Corma (1993)] have also studied the effect of contact time, but they found a linear correlation between contact time and conversion up to 30% propane conversion.

The rate of propane conversion was measured over a range of temperatures (Fig. 4.2.7). The apparent activation energy for the consumption of propane was estimated to be $122 \pm 6 \text{ kJ/mole}$ within the temperature range investigated (475-550°C). Patel et al. [Patel (1988)] found the activation energy on 40-VMgO (40 wt% V_2O_5) to be 140 kJ/mol (475-540°C), which is close to our results.

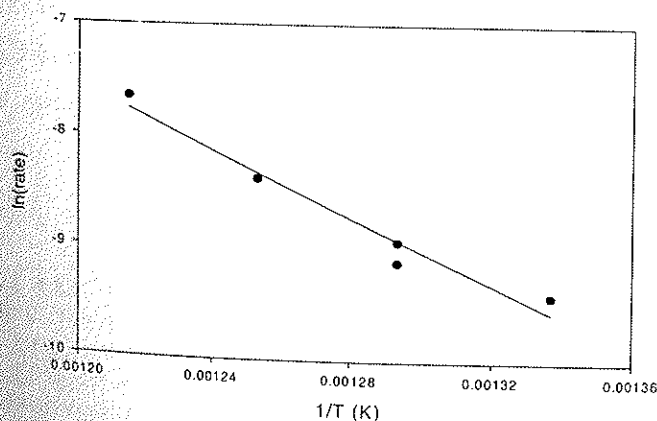


Figure 4.2.7. Activation energy. Temperature range 475-550°C, $\text{C}_3\text{H}_8/\text{Air/He} = 5/30/65 \text{ ml/min}$. $W_{\text{cat}} = 0.10\text{g}$.

Fig 4.2.8 gives results obtained with varying oxygen partial pressure. The product selectivities, conversions and the reaction rates of propane and oxygen are shown as a function of oxygen partial pressure in Fig 4.2.8a. The selectivities are only slightly affected by the partial pressure of oxygen. There is a small decrease in the selectivity to propene and a small increase in the selectivity to CO_2 as the partial pressure of oxygen increases, which is the same as observed by Stern and Grasselli [Stern (1997)]. The reaction rates of propane and oxygen as a function of oxygen pressure are shown in Fig 4.2.8b. Both rates increase as the oxygen pressure increases, but the oxygen partial pressure has a stronger influence on the rate of oxygen consumption than on the propane consumption. The rate of propane conversion increases by about 8% as the pressure of oxygen is doubled (from 0.04 to 0.08 atm). The oxygen reaction rate on the other hand increases by about 25% for the same oxygen pressure increment due to an increased selectivity to CO_2 . The reaction order for propane conversion with respect to oxygen is shown in Fig 4.2.8c and found to be 0.07. This result is in good agreement with findings of others, and orders in the range 0 - 0.13 are reported in the literature [Pantazidis (1996), Chaar (1988) and Michaels (1996)]. The apparent reaction orders for the formation of CO_2 , CO and C_3H_6 with respect to oxygen pressure were found to be 0.23 ± 0.05 , -0.27 ± 0.05 , 0.05 ± 0.01 , respectively. The results (with the exception of the order of CO) are in good agreement with Pantazidis and Mirodatos [Pantazidis (1996)] who found the orders of CO_2 , CO, and C_3H_6 to be 0.16, 0.23 and 0.0, respectively. However, for oxygen pressures below 0.05 atm they found the formation order to propene to be 0.11.

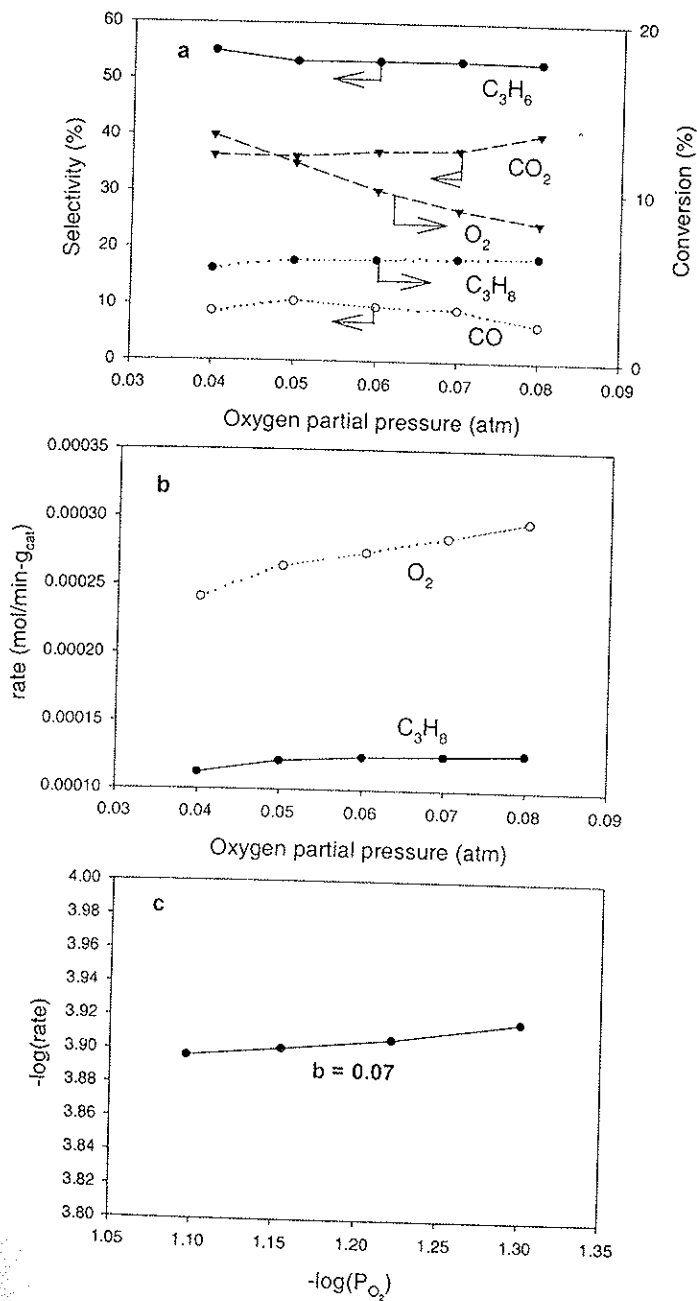


Figure 4.2.8. Results from experiments with varying oxygen partial pressure. $T = 500^\circ\text{C}$, 5 ml/min C_3H_8 , total flow: 100 ml.

a. Conversions and selectivities as a function of oxygen partial pressure.

b. Reaction rate of propane and oxygen as a function of oxygen partial pressure.

c. Reaction order of propane with respect to oxygen partial pressure.

The effect of propane pressures on the rates of propane consumption and products formation was also investigated. The results are reported in Fig 4.2.9. From Fig 4.2.9a it is evident that the selectivities to all products are constant as the partial pressure of propane increases. The conversion of propane is constant and the conversion of oxygen is increasing as the partial pressure of propane increases. Fig 4.2.9b shows that both the reaction rate of propane and oxygen consumption increases with increasing propane partial pressure. The apparent order for propane conversion is shown in Fig 4.2.9c and was found to be $1,0 \pm 0,1$ order with propane pressure. This is in agreement with others [Pantazidis (1996), Stern (1997)], but Chaar et al. [Chaar (1988)] reported the order of propane conversion to be 0.6 with respect to propane pressure. A strong dependence was obtained between product (and by-product) formation rates and propane pressure. The orders were found to be $0,96 \pm 0,08$, $1,1 \pm 0,2$ and $1,0 \pm 0,1$ for CO_2 , CO and C_3H_6 formation, respectively. The reaction orders of oxygen and propane seemed to be independent of the temperature of reaction, at least within the temperature interval studied here (500-550°C). Pantazidis and Mirodatos [Pantazidis (1996)] found the orders for the same components to be 0.78, 0.72 and 0.88 for CO , CO_2 and C_3H_6 , respectively.

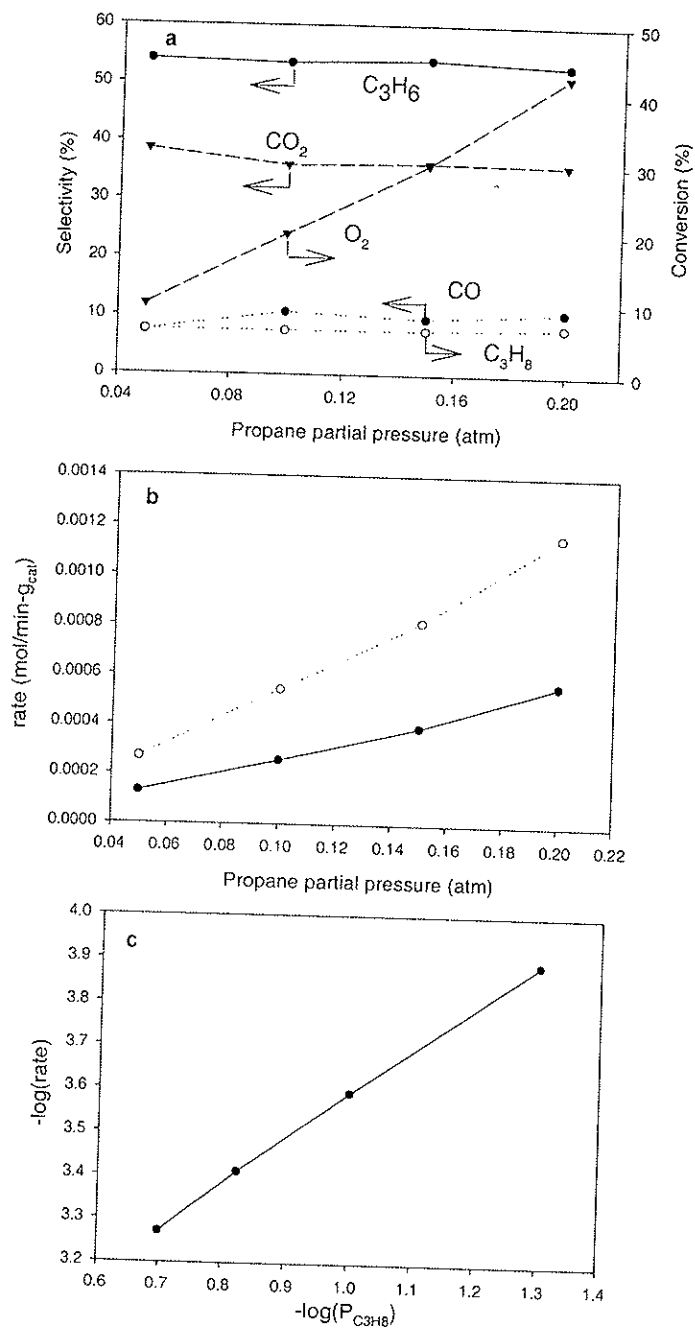


Figure 4.2.9. Results from experiments with varying propane partial pressure. $T = 500^\circ\text{C}$. 30 ml/min air, total flow: 100 ml/min.

a: Selectivity and conversion as a function of partial pressure of propane

b: Reaction rate of propane as a function of propane partial pressure.

c: Reaction order of propane with respect to propane partial pressure.

4.2.5 Adaptation to kinetic model

Attempts have been made to fit the experimental data into a kinetic model. Two different types of models have been tested; a power rate law and a Mars Van Krevelen expression. As already shown, the results can be fit by a power rate law:

$$-r_{C_3H_8} = k \cdot P_{C_3H_8}^\alpha \cdot P_{O_2}^\beta \quad [\text{mole/g-min}] \quad (4.2.1)$$

Where α and β are the consumption orders of propane and oxygen, respectively. k is found by curve fitting to be $0.0034 \text{ mole/g-min-atm}^{1.09}$ and the rate expression is found to be:

$$-r_{C_3H_8} = 0.0034 \cdot P_{C_3H_8}^{1.02} \cdot P_{O_2}^{0.07} \quad [\text{mole/g-min}] \quad (4.2.2)$$

In Fig 4.2.10 the model is plotted against the experimental results and from the figure it is evident that the model represents the data quite well.

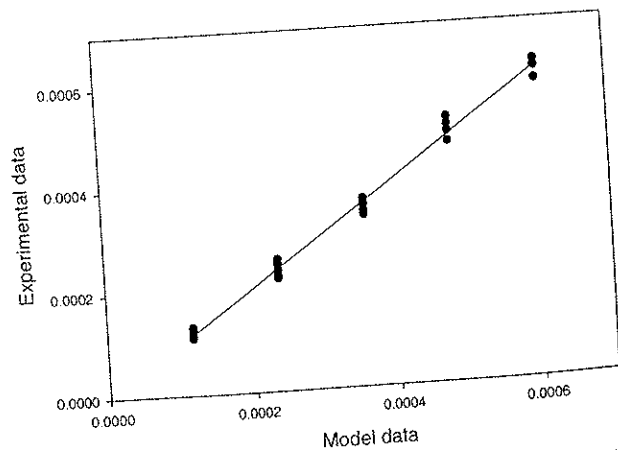


Figure 4.2.10. Cross plot of experimental results vs. model data (power rate law)

It is also possible to fit the data into a Mars Van Krevelen type expression [Bielanski (1991)]:

$$-r_{C_3H_8} = \frac{k_1 \cdot k_2 \cdot P_{C_3H_8} \cdot P_{O_2}^b}{k_1 \cdot P_{C_3H_8} + k_2 \cdot P_{O_2}^b} \quad [\text{mole/g-min}] \quad (4.2.3)$$

k_1 and k_2 are the rate constants for propane activation and for reoxidation of the catalyst, respectively, and b is the reaction order of oxygen. If reoxidation of the catalyst is much faster than the activation of hydrocarbons (which is assumed to be the rate limiting step of the reaction), then $k_2 \gg k_1$ and the rate expression can be reduced to:

$$-r_{C_3H_8} = k_1 \cdot P_{C_3H_8} \quad [\text{mole/g-min}] \quad (4.2.4)$$

This expression is very similar to the power rate law, but with a reaction order of zero with respect to oxygen. The rate constant, k , is found by curve fitting to be 0.0028 mole/g-min-atm. In Fig 4.2.11 the MVK model is plotted against the experimental results, and it can be seen that that the model represents the data quite well.

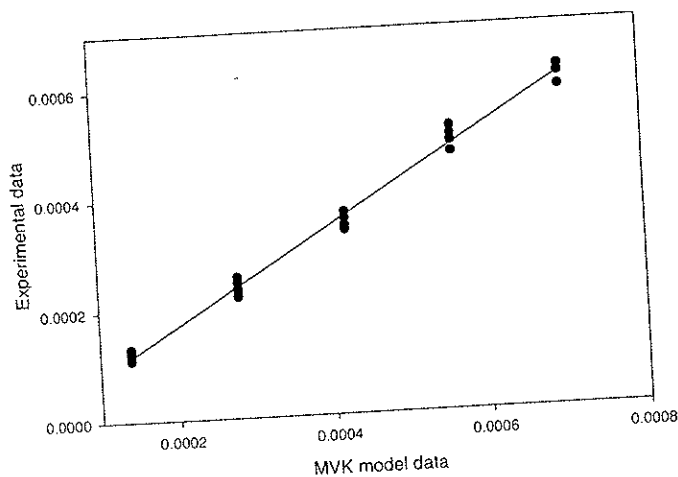


Figure 4.2.11. Cross plot of experimental data vs. model data (Mars van Krevelen).

4.2.6 Reaction pathways

Chaar et al. [Chaar (1988)] extrapolated their results to zero conversion and found that the initial products consisted of approximately 80% propene and 20% carbon oxides. Michaels et al. [Michaels (1996)] believe that propene is the only primary produced product, and that CO_x is produced largely by the sequential oxidation of the in situ produced intermediate propene, and to a lesser extent by a parallel route of direct deep oxidation of propane. They also indicate that the presence of two parallel pathways to CO_x is of some interest, as it suggests that partial and deep oxidation may occur at different surface sites or involve different forms of reactive oxygen. Chen et al. [Chen (1999)] suggests that CO only forms via secondary combustion of propene intermediates while CO_2 is formed via this reaction and also via the direct combustion of propane, at least for the $\text{V}_2\text{O}_5/\text{CrO}_2$ catalyst used in their study. By plotting the rate of CO_x formation as a function of $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ inlet pressure (holding the propane pressure constant and increasing the propene pressure), we found that the CO_x formation was directly proportional to the

amount of propene fed. This is shown in Fig. 4.2.12 and indicates that CO_x is formed mainly from propene, and not from propane, at least it indicates that the formation rate of CO_x from propene is much higher than from propane.

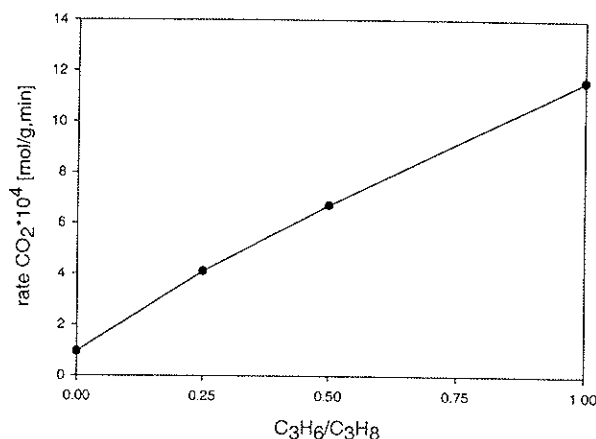


Figure 4.2.12. Plot of the formation rate of CO_2 as a function of $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ feed ratio. $T = 500^\circ\text{C}$. 10 ml/min propane, varying amount of propene, total flow: 100 ml/min.

It is well known that the reactivity of propene is much higher than that of propane. By substituting the propane gas in the ODH system with propene, we found that the reaction rate of propene to CO_x was about ten times higher than the case is for propane at 500°C . The relative reactivity between propene and propane can be even higher than 10, but the existence of possible diffusion limitations in the system with propene due to the high conversions of reactants can limit the reaction rate. The relative reaction rate can shift when mixtures of propane and propene are introduced instead of pure gases due to competitive reactions. The relative reaction rate between propene and propane it is more likely to shift to higher values than to a lower value. This high difference in reaction rate of propane and propene could explain the proportionality of CO_x formation with propene partial pressure since the CO_x formation rate from propane is about on tenth of the formation rate from propene.

4.3 Selective hydrogen combustion

The results from chapter 4.2 indicate that the main drawback with the ODH of propane over VMgO catalyst is the lack of selectivity with total oxidation being the main side reaction. In this chapter the focus is put on the selective hydrogen combustion (SHC) instead of the dehydrogenation in order to shift the equilibrium in the dehydrogenation reaction towards the alkene and provide heat for the dehydrogenation reaction. We have been studying the SHC properties using a gas mixture of propane, oxygen and hydrogen but we have also been interested in the selectivity in the presence of large amounts of propene (simulating high conversions). Results of catalysts that are only active as SHC-catalyst, and catalysts that are active as a DH/SHC- catalyst will be presented.

4.3.1 Catalyst characterization

Table 4.3.1 presents the surface areas (BET) and the XRD results of the fresh catalysts used in the experimental work.

Catalyst	Support	Surface area (BET) (m ² /g _{cat})	Crystalline phases (XRD)
SiO ₂	-	483	n.d.
Indium-oxide	SiO ₂	278	In ₂ O ₃ (cubic)
Bismuth-oxide	SiO ₂	242	Bi ₂ O ₃ (rhombohedral)
Bismuth-oxide	none	n.d.	n.d.
MgVO	none	38	MgO/Mg ₃ V ₂ O ₈
Lead-oxide	SiO ₂	120	PbO (amorphous)
Chromium-oxide	SiO ₂	330	Cr ₂ O ₃ (rhombohedral)
ZSM-5	none	n.d.	-
Pt	SiO ₂	415	-
PtSn	SiO ₂	428	-
Sn	SiO ₂	457	-

The XRD results for bismuth oxide and indium oxide are the same as observed by Grasselli et al. [Grasselli (1999)], but the result from the XRD on

PbO_x are not the same. They found a crystalline phase of Pb_3O_4 to be the active phase in the catalyst, while an amorphous was observed in this study. The preparation procedure used in this work was as close as possible the procedure Grasselli et al. [Grasselli (1999)] used in their work. The XRD-lines found for the MgVO catalyst were the same as those observed by Creaser and Andersson [10], but in our study there are also indications of magnesium pyrovanadate crystallites in the catalyst.

Temperature programmed data (TPR) for the catalysts are shown in Fig. 4.3.1.

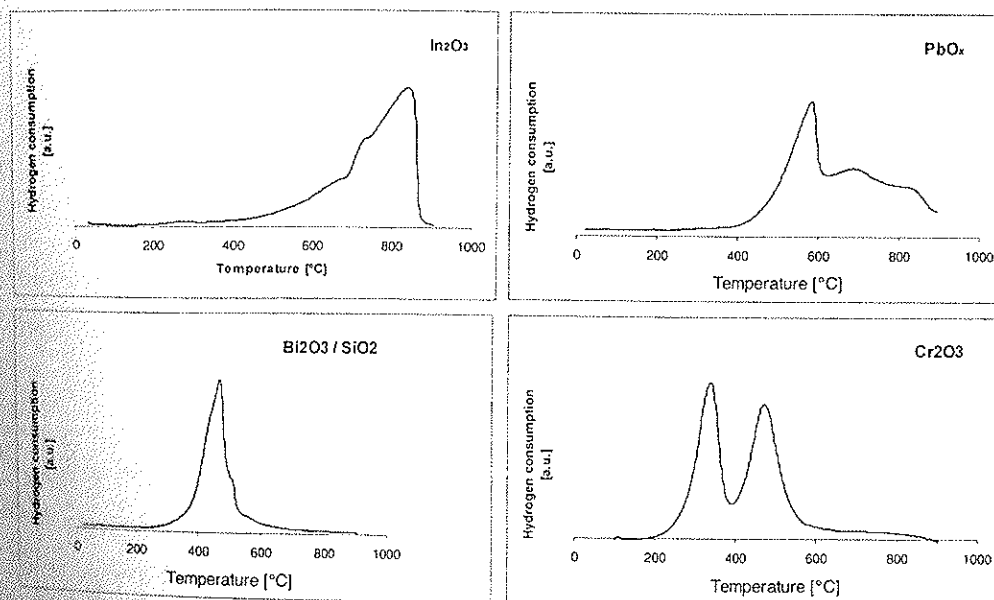


Figure 4.3.1. TPR profiles some of the catalyst tested in the SHC experiments. $W_{\text{cat}}=0.1\text{g}$.

The TPR data indicates that the catalysts are reduced at various temperatures, and will therefore exhibit different catalytic properties. In_2O_3 is reduced within the temperature interval 400-900°C. The reduction peaks probably correspond to In^{3+} being reduced to In^+ (700°C) and In^+ being reduced to In (800°C). Bismuth is reduced from 300 to 600°C, with a maximum around 450°C, probably corresponding to Bi^{3+} being reduced to Bi . The chromium catalyst is reduced within the temperature interval 200-600°C, and show two reduction

peaks at 300°C and 500°C, respectively. The peaks are likely to correspond to Cr^{3+} being reduced to Cr^{2+} and Cr^{2+} to Cr. Lead is reduced from 400 to 900°C. Pb^{2+} being reduced to Pb is the most likely reduction to occur.

4.3.2 Experiments with propane, hydrogen and air

Several catalysts, both metal and metal oxides were tested for their properties as SHC catalysts using a gas mixture of propane, hydrogen, air and He at 500 and/or 550°C. The exception is Pt, PtSn and Sn which are only tested at 550°C. A presentation of the catalyst screening is shown in this chapter. In the experiments, the conversion of oxygen and propane, and the selectivity to water, propene, CO_x and hydrocarbons are presented as a function of increasing oxygen flow. It can be noted that an oxygen flow of 1 ml/min corresponds to the stoichiometry of the H_2 - O_2 reaction, using the H_2 in the feed gas.

The results using the silica support as catalyst was about the same as observed for the empty reactor at 500°C, 3-7% conversion of oxygen and total conversion to water.

50 wt%- $\text{In}_2\text{O}_3/\text{SiO}_2$ was found to be the most active and selective oxide catalysts for the SHC under these conditions. In Fig. 4.3.2 the activity and selectivity data for the indium catalyst are shown as a function of oxygen flow for two temperatures. The oxygen conversion is above 90% until all the hydrogen is combusted, water (and propene) being the only products. If the oxygen flow was further increased (above the stoichiometry to water), some CO_2 was formed at 550°C. No CO was observed over this catalyst. The selectivity to water was 100% at 500°C, and above 90% for all oxygen flows at 550°C. The conversions of propane over the indium catalysts are also shown in the plot, and one can see that there was no conversion of propane at 500°C. There was some conversion in the range 1-2% at 550°C, giving ethene, propene, CO_2 and methane as the main products. The cracking of

propane to ethene and methane seems to be the main products from the propane conversion at high O_2 -flows.

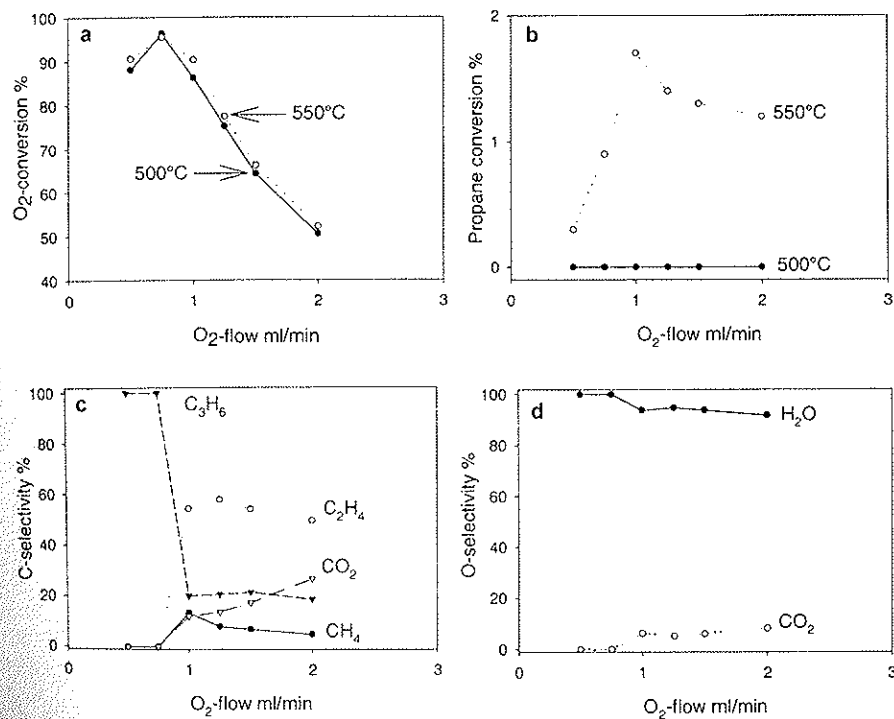


Figure 4.3.2. Catalytic combustion over In_2O_3/SiO_2 . a) O_2 conversion b) propane conversion c) C-selectivity d) O-selectivity. Conditions: 500°C (●), 550°C (○), 1 atm, 0.11g catalyst, Feed gas: 2 ml/min H_2 , 10 ml/min C_3H_8 , O_2 as shown in the figure, total flow 100 ml/min, balance is He.

In Fig. 4.3.3 are shown the data for the Bi_2O_3 catalysts (unsupported Bi_2O_3 and 50wt% $\text{Bi}_2\text{O}_3/\text{SiO}_2$) at 500°C and 550°C.

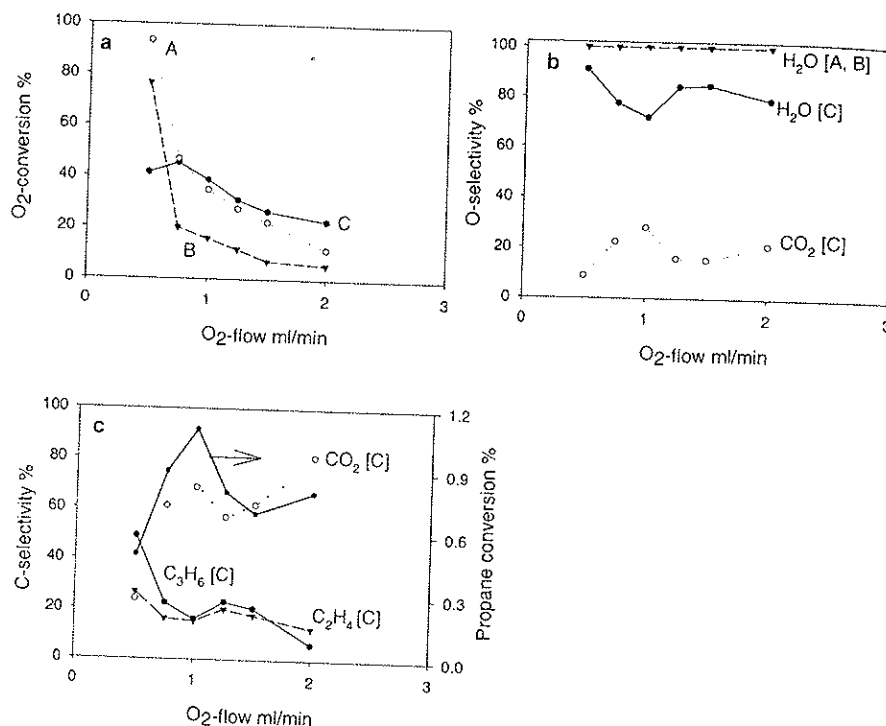


Figure 4.3.3. Catalytic combustion over bismuth-oxide. a) O₂ conversion b) O-selectivity/propane conversion. Conditions: 1 atm, 0.11g catalyst, Feed gas: 2 ml/min H₂, 10 ml/min C₃H₈, O₂ as shown in the figure, total flow 100 ml/min, balance is He.

A: Bi_2O_3 (no support), 550°C
 B: Bi_2O_3 (no support), 500°C
 C: 50 wt-% $\text{Bi}_2\text{O}_3/\text{SiO}_2$, 500°C

The unsupported Bi_2O_3 shows an excellent ability to preferentially attack hydrogen in the presence of propane, but its activity is not as high as is the case is for the indium catalyst. From Fig. 4.3.3a one can see that the drop in oxygen conversion is extensive with an increase in oxygen flow for both temperatures. Water is the only product formed over the unsupported bismuth at both temperatures, which means there is no conversion of propane over this catalyst. An experiment with 50wt% $\text{Bi}_2\text{O}_3/\text{SiO}_2$ at 500°C was also performed.

About 80% selectivity to water was obtained throughout the experiment (the rest being CO_2), compared to a 100% selectivity to water over the unsupported Bi_2O_3 . The oxygen flow was increased throughout the experiment, which means that the x-axis also indicates the oxygen conversion as a function of time on stream. It is thus possible that the different response to increased O_2 flow also reflects a difference in the deactivation of the supported/unsupported catalysts (Fig 4.3.3a, curve B and C). Pre-reduction of the catalyst gave no significant changes of the results.

Fig. 4.3.4 shows the results from an experiment catalyzed by ZSM-5. The oxygen conversion over this catalyst was low compared to the indium and bismuth catalysts. 100% oxygen-selectivity to water was observed over this catalyst. ZSM-5 does not show any substantial activity for converting propane, about 0.3% conversion was observed for this catalyst giving propene and the cracking products, C_2H_4 and CH_4 as the main products.

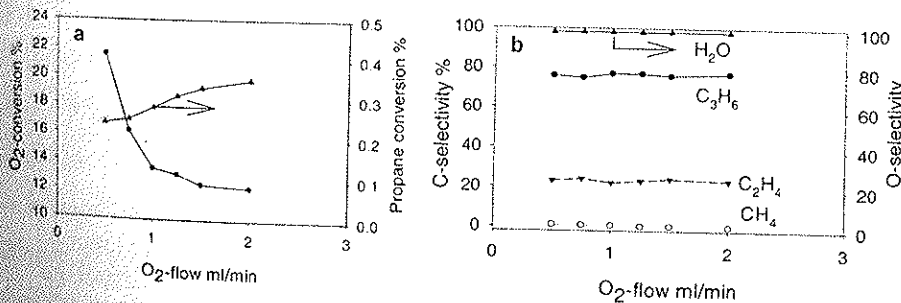


Figure 4.3.4. Catalytic combustion over ZSM-5. a) O_2 conversion/propane conversion b) C-selectivity/O-selectivity. Conditions: 500°C , 1 atm, 0.19g catalyst, feed gas: 2 ml/min H_2 , 10 ml/min C_3H_8 , O_2 as shown in the figure, total flow 100 ml/min, balance is He.

The results for 50wt% $\text{PbO}_x/\text{SiO}_2$ at 500°C are shown in Fig 4.3.5. This catalyst showed a low activity for oxygen conversion, and at the same time a relatively low selectivity to water. The selectivity to water is between 70 and

65%, the rest being CO_2 . As the oxygen flow increased the conversion dropped from 25 to 11% with increasing oxygen pressure still giving a total increase in the reaction rate of oxygen. There was no effect in pre-reducing the catalyst. Also for this catalyst a TPR pattern was collected (Fig. 4.3.1), and a reduction was found to take place between 500°C and 600°C . Since there was no effect in reducing the catalyst, again this indicates a spontaneous reoxidation of the catalyst as soon as oxygen was introduced to the system.

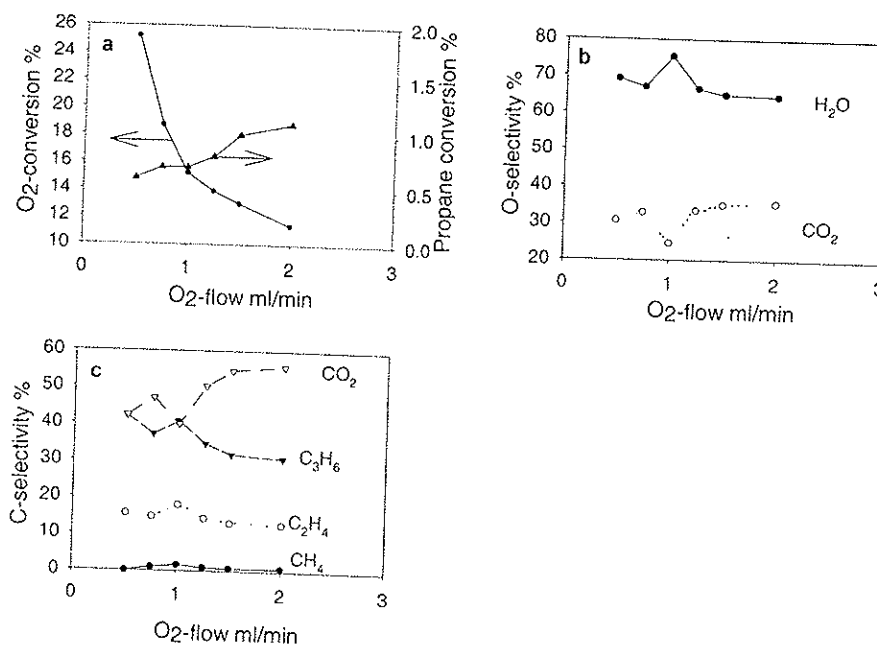


Figure 4.3.5. Catalytic combustion over 50 wt-% $\text{PbO}_x/\text{SiO}_2$. a) O_2 conversion/propane conversion b) O-selectivity c) C-selectivity. Conditions: 500°C , 1 atm, 0.11g catalyst, Feed gas: 2 ml/min H_2 , 10 ml/min C_3H_8 , O_2 as shown in the figure, total flow 100 ml/min, balance is He.

Two catalysts showed very poor SHC properties. Both chromium- and magnesium-vanadium oxide catalysts gave close to pure combustion of the propane, resulting in about 55% selectivity to CO_2 , 35% selectivity to water, and small amounts of CO (in the range 3-7%). The conversion of oxygen over the chromium catalyst was complete for all oxygen flows and the conversion of propane was increasing from about 5 to 15% as the oxygen flow increased.

No changes were observed in the product distribution during the run. There was no effect of pre-reducing the chromium catalyst. The oxygen conversion over the VMgO catalyst was somewhat lower than for the chromium catalyst, decreasing from 70 to 50% as the oxygen flow was increased from 0,5 to 1,5 ml/min, corresponding to an increase in the rate of oxygen consumption. It is obvious that MgVO and Cr₂O₃ are rather ineffective as SHC catalysts and can not be used for such a purpose.

Fig. 4.3.6 provides a summary of the results obtained at 550°C over Pt, PtSn and catalysts. No results are recorded at 500°C over these catalysts. From Fig. 4.3.6a it is evident that the O₂ conversion is high, but not complete for all cases for Pt and PtSn. The Sn catalyst was less active for oxygen conversion. Here the conversion is above 95% until the oxygen flow exceeds 1 ml/min, and at 1.5 ml O₂/min the conversion of oxygen has dropped to 82%. The excess oxygen reacts slowly with propane over the Sn catalyst and therefore the conversion of oxygen decreases when all the hydrogen is consumed. Fig. 4.3.6b shows the propane conversion over the three catalytic systems. The propane conversion initially increases when oxygen is introduced to the PtSn system. This is followed by a drop in the conversion from 5.6% at an oxygen content of 0.5 ml/min to a conversion of 4.0% at an oxygen flow of 1.5 ml/min. When the oxygen feed rate exceeds 1.5 ml/min, the propane conversion increases again. For Pt there is no such initial increase in conversion of propane when oxygen is introduced, but the same decrease in propane conversion as for PtSn is observed as the oxygen flow approaches 1 ml/min. This apparently complex relationship is probably the sum of the two main reactions: The drop in the propane conversion could be explained by deactivation of the catalysts. If the oxygen flow is further increased (above 1 ml/min) the propane conversion rises again. This is due to a steep increase in the formation rate of CO₂ above 1.0 ml/min of oxygen, and the sum of these reactions gives the observed overall consumption of propane.

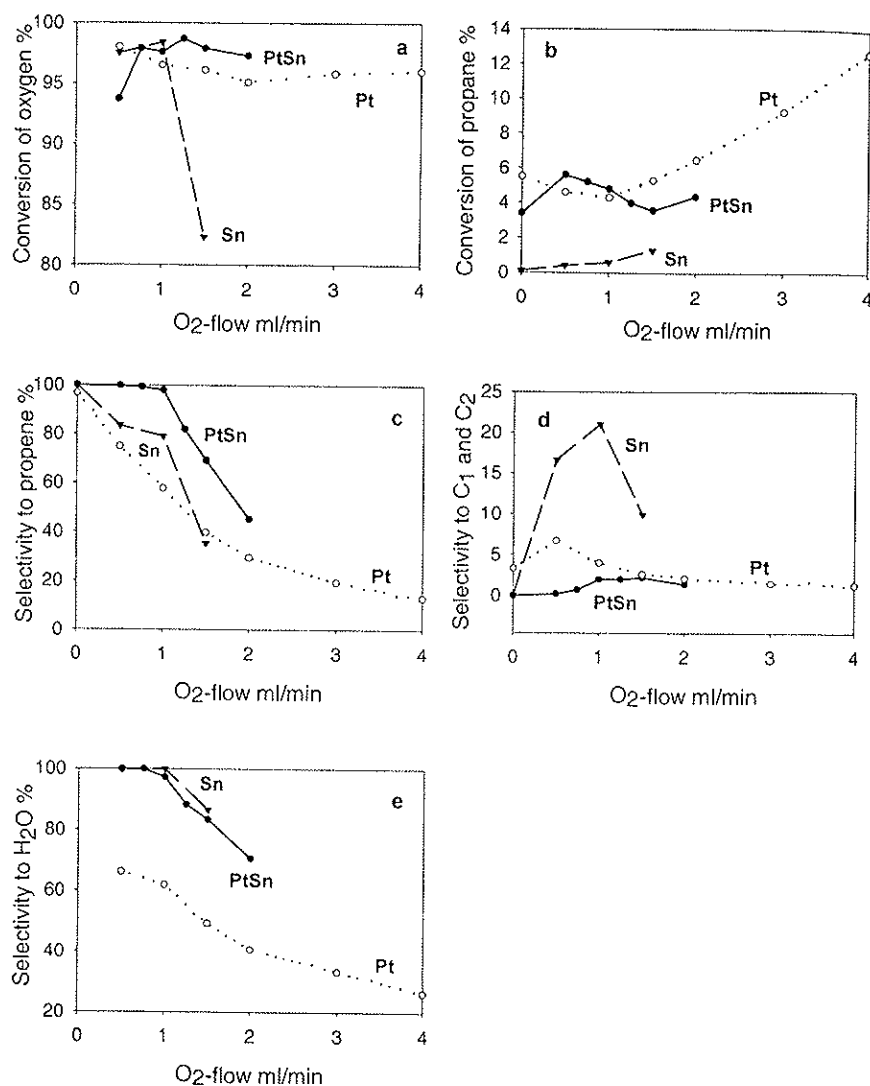


Figure 4.3.6. Catalytic combustion over Sn, Pt and PtSn catalysts. a) O₂ conversion b) propane conversion c) selectivity to propene d) Selectivity to C₁ and C₂ e) selectivity to H₂O. Conditions: 550 °C, 1 atm., 0.30 g catalyst, Feed gas: 2 ml/min H₂, 10 ml/min C₃H₈, O₂ as shown in the figure, total flow 100 ml/min, balance is He.

Sn is not a very active catalyst for converting propane, only about 0.5% (or less) of the propane is converted at oxygen flows lower than 1 ml/min. The selectivity to propene over PtSn (Fig. 4.3.6c) is almost complete up to 1 ml/min of O₂ in the feed gas, above this amount the carbon selectivity drops

due to the formation of CO and CO₂. Pt shows lower selectivity to propene than PtSn, and at 1 ml/min oxygen, the selectivity to propene is only 60% compared to almost 100% for PtSn. For Sn, the main product is propene, but significant amounts of cracking products are observed for this catalyst. From Fig. 4.3.6d one can see that the selectivity to C₁ and C₂ products are as high as 20% at stoichiometric (1 ml/min) amounts of oxygen, but the formation rate of cracking products is rather low since the activity of Sn for the conversion of propane is below 1%. Fig. 4.3.6e shows the selectivities to H₂O as a function of oxygen flow. Both PtSn and Sn show excellent properties towards producing water from hydrogen and oxygen without producing any CO_x, giving close to 100% selectivity to water as long as the oxygen flow is below 1 ml/min. Pt on the other hand is a less selective catalyst for water formation; at 1 ml/min oxygen the selectivity to water is only about 60%.

Fig. 4.3.7 shows the carbon and oxygen selectivities to CO₂ and CO for the same experiments as described in Fig. 4.3.6.

In line with the results shown above, the figure shows that no CO_x is formed for oxygen flow rates below 1 ml/min for PtSn and Sn catalysts. The results confirm that as long as the O₂ is fed to the reactor at a less than stoichiometric amount compared to the molecular hydrogen in the feed according to the reaction $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$, the O₂ reacts selectively with hydrogen to form water. When the oxygen flow is higher than 1 ml/min CO and CO₂ are formed and this becomes the major reaction pathway. The results indicate that O₂ reacts selectively with hydrogen only under certain conditions, i.e. under a surplus of hydrogen. As soon as this surplus hydrogen is converted, the excess O₂ will react with hydrocarbons in a non-selective manner leading to CO/CO₂, with a simultaneous drop in the selectivity to propene. The results in Fig. 4.3.7 also show that Pt does not show the same effect concerning selective hydrogen combustion. Already at oxygen flows of 0.5 ml/min significant amounts of CO₂ and CO are produced. The main product is always CO₂. Over

Pt the CO selectivity drops off with increasing O₂ flow, whereas for Sn and PtSn the trend is opposite. This could indicate a higher activity in the CO oxidation reaction over Pt, especially since the CO selectivity drops when excess O₂ is fed to the reactor (> 1 ml/min).

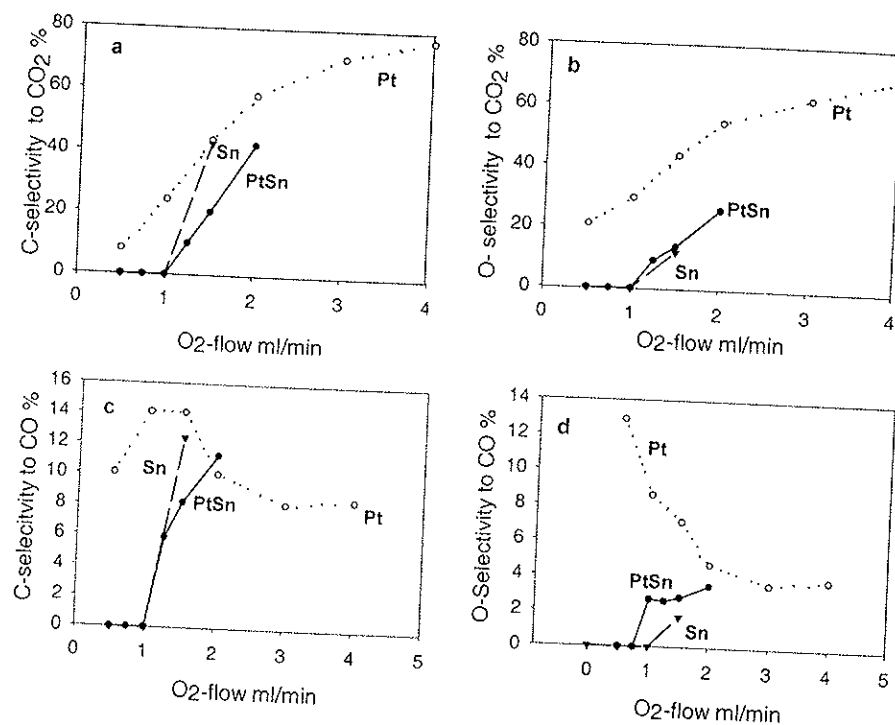


Figure 4.3.7. Catalytic combustion over Sn, Pt and PtSn catalysts. a) C-selectivity to CO₂ b) O-selectivity to CO₂ c) C-selectivity to CO d) O-selectivity to CO. Conditions: 550 °C, 1 atm., 0.30 g catalyst, Feed gas: 2 ml/min H₂, 10 ml/min C₃H₈, O₂ as shown in the figure, total flow 100 ml/min, balance is He.

4.3.3 Simulated high conversion over metal oxide based catalysts

Experiments with a mixture of propane, oxygen, hydrogen and a high concentration of propene over the most promising metal oxide catalysts presented in chapter 4.3.2 have been performed at 500°C in order to study the competitive reaction between hydrogen and propene towards oxygen. The catalysts tested at these conditions include $\text{In}_2\text{O}_3/\text{SiO}_2$, unsupported Bi_2O_3 , 50% $\text{Bi}_2\text{O}_3/\text{SiO}_2$ and $\text{PbO}_x/\text{SiO}_2$. The results for all the oxide catalysts are shown in Fig. 4.3.8.

$\text{In}_2\text{O}_3/\text{SiO}_2$ and 50% $\text{Bi}_2\text{O}_3/\text{SiO}_2$ give close to total conversion of oxygen for all oxygen flows. There is, however, some unconverted oxygen in the range 3-5% of the oxygen fed to the reactor. This could indicate a by-pass of some of the reactant gas through the catalyst bed, or as indicated by Beretta et al. [Beretta (1999)], that the oxygen conversion is limited by diffusion (although their results were obtained in an annular reactor with much higher flow-rates). In_2O_3 shows qualities of being a good SHC catalyst. 90% selectivity (based on oxygen) to water was obtained at low oxygen flows (0.5 ml/min) and an oxygen selectivity of 80% is obtained at stoichiometric amounts (1 ml/min) of oxygen. Indium is the only catalyst in which the selectivities to the products change as a function of the oxygen flow. As the oxygen flow increases, the production of CO_x becomes more and more pronounced.

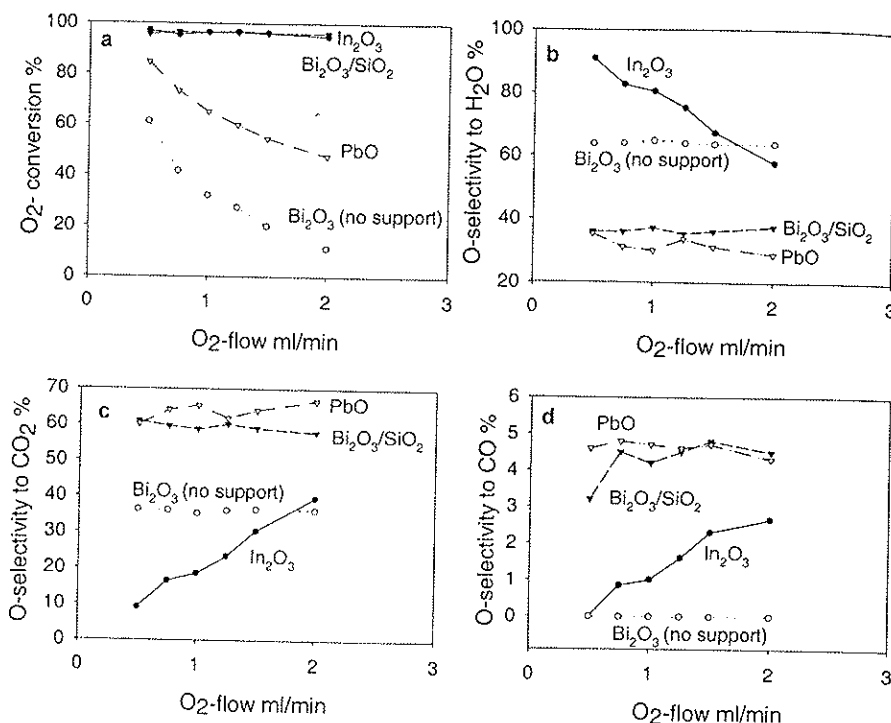


Figure 4.3.8. Catalytic combustion over In₂O₃/SiO₂, Bi₂O₃ (no support), 50 wt-% Bi₂O₃/SiO₂ and 50 wt-% PbO_x/SiO₂. a) O₂ conversion b) O-selectivity to H₂O c) O-selectivity to CO₂ d) O-selectivity to CO. Conditions: 500°C, 1 atm, 0.1 lg catalyst, Feed gas: 2 ml/min H₂, 5 ml/min C₃H₈, 8.4 ml/min C₃H₆, O₂ as shown in the figure, total flow 100 ml/min, balance is He.

All the other catalyst reported in Fig. 4.3.8. show close to constant selectivities for all oxygen flows and can said to be independent of the oxygen partial pressure. Unsupported Bi₂O₃ gives 65% selectivity to water and 35% selectivity to CO₂ for all oxygen flows for the simulated high conversion mixture of propane, propene and hydrogen. It follows that the rate of H₂ oxidation is higher than propene oxidation, and that the relative oxidation rates are constant throughout the experiment, irrespective of oxygen flows. 50% Bi₂O₃/SiO₂ and PbO_x/SiO₂ do not show any tendency towards the selective combustion of hydrogen preferentially to propene. About 60% selectivity to CO₂ is found for these catalysts, which indicates combustion of

propene. A complete combustion of propene gives according to Eq. 4.3.1 a 66% oxygen selectivity to CO₂ and 33% selectivity to H₂O. The corresponding partial oxidation to CO (Eq. 4.3.3) gives 50% CO and 50% H₂O from the oxygen balance. Since the selectivity to CO₂ is above 60% over the PbO_x and supported bismuth catalysts, and there also is some CO formed, the rate of hydrogen combustion must be close to zero over these catalysts. From Eq. 4.3.1- Eq. 4.3.3 and by using the product selectivities (Fig. 4.3.8) the contribution to the water production from each of the reactions was calculated. From Fig. 4.3.8b and Fig. 4.3.8d the selectivities of H₂O, CO₂ and CO over Bi₂O₃/SiO₂ at 1 ml/min oxygen are found to be 37%, 58% and 4, respectively.



From this it is calculated that 76% of the H₂O production can be related to Eq. 4.3.1, 13% related to Eq. 4.3.2 and the last 11% from Eq. 4.3.3. In other words, water production from total combustion of propene to CO₂ is about 6 times faster than the combustion of hydrogen over the Bi₂O₃/SiO₂ catalyst. Similar results are also calculated for the PbO_x/SiO₂ catalyst.

The reason for the different behaviour of the indium catalyst compared to the others is not yet understood. It has been suggested [Grasselli (1999)] that the SHC properties of the metal oxides are linked with a certain electron configuration. Our most selective catalyst, In₂O₃/SiO₂ does not have any free [s²] electron pairs in the outer shell [In has electron configuration Kr 4d¹⁰ 5s² 5p¹]. Pb²⁺ and Bi³⁺, on the other hand have free [s²] electronpairs in their oxidized state (Pb has electron configuration [Xe 4f¹⁴ 5d¹⁰ 5s² 5p²] and Bi [Xe 4f¹⁴ 5d¹⁰ 5s² 5p³]). It is therefore possible that the two free [5s²] electrons in Pb²⁺ and Bi³⁺ may affect the catalytic properties of the metals in a way that favour the adsorption and total combustion of propene over the combustion of

hydrogen. However, firm conclusions on these issues can only be drawn based on characterization of the oxidation state of these metals at reaction conditions.

A comparison of the simulated high conversion mixture with the experiment with only propane as the hydrocarbon feed is shown in Fig. 4.3.9.

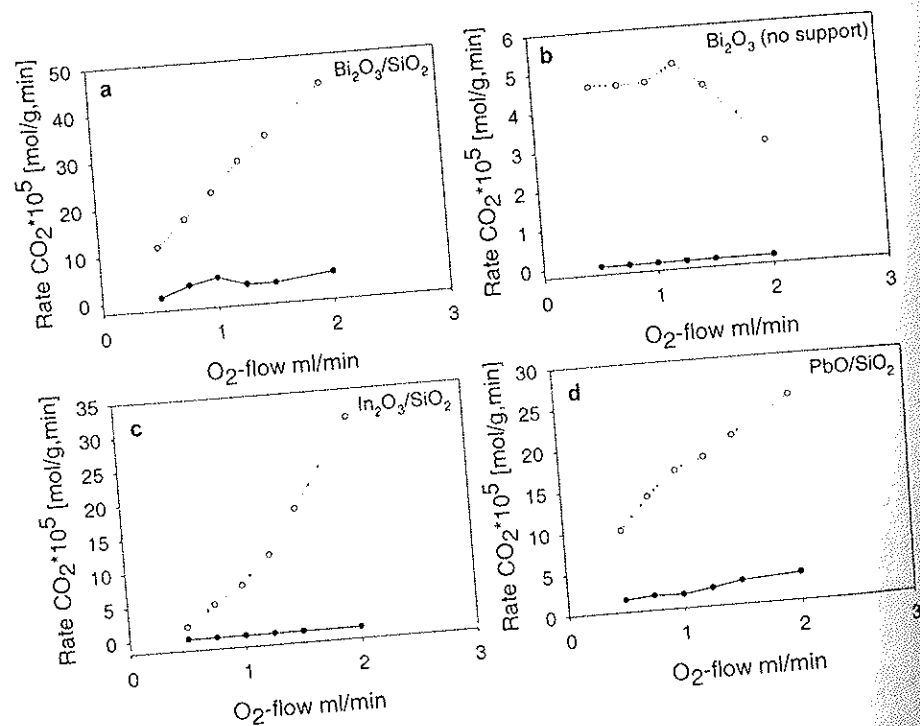


Figure 4.3.9. Rates for CO₂ formation. a) 50 wt-% Bi₂O₃/SiO₂ b) Bi₂O₃ (no support) c) In₂O₃/SiO₂ and d) 50 wt-% PbO/SiO₂. Conditions: 500°C, 1 atm, 0.11g catalyst. Feed gas with C₃H₆ in the feed (○): 2 ml/min H₂, 5 ml/min C₃H₈, 8.4 ml/min C₃H₆, O₂ as shown in the figure. Without C₃H₆ in the feed (●): 2 ml/min H₂, 10 ml/min C₃H₈, O₂ as shown in the figure. Total flow is always 100 ml/min, balance is He.

The figure shows the rates of CO₂ formation over the various catalysts. The results confirm that the alkene is more reactive towards oxygen than its corresponding alkane. The rate of CO₂ formation is also more sensitive to the oxygen partial pressure for the simulated high conversion mixture. The exception is the unsupported Bi₂O₃ in which the formation rate of CO₂ is more

or less independent of the oxygen partial pressure. The formation rate of CO_2 is, however, higher for the equilibrium mixture compared to the propane/hydrogen mixture also for this catalyst. Fig 4.3.9. also confirms that the formation rate of CO_2 over the indium catalyst is low for small oxygen flows. By comparing the formation rate of CO_2 over the indium to the $\text{Bi}_2\text{O}_3/\text{SiO}_2$ and $\text{PbO}_x/\text{SiO}_2$ catalysts, one can see that the formation rate at 0.5 ml/min is about 75% lower over the indium catalyst. The fact that the formation rate of CO_2 over $\text{Bi}_2\text{O}_3/\text{SiO}_2$ and $\text{PbO}_x/\text{SiO}_2$ increases with increasing oxygen flow, and the selectivities remains constant throughout the experiment, indicates a equal change in formation rate for CO_2 and H_2O . This indicates according to Eq. 4.3.1 a pure combustion of propene as the oxygen flow increases.

4.3.4 Simulated high conversion over Pt-based catalysts

Fig.4.3.10 (550°C) and Fig. 4.3.11 (500°C) show results obtained using a gas mixture containing a large fraction of propene, thus simulating a high conversion. The gas contained propane, propene and hydrogen in a ratio close to fulfilling the equilibrium criterion, to avoid any interchange of propane and propene due to hydrogenation.

The flow rate of oxygen was varied from zero to 4 ml/min. Fig. 4.3.10a and Fig. 4.3.11a show that the oxygen conversion is high at all conditions and similar for all the catalysts. The exception is for oxygen flows higher than 1 ml/min over Sn at 500°C, in which the conversion was lower than for the rest of the experiments. This shows that Sn as expected is a poor catalyst for hydrocarbon activation, as previously discussed for the system without propene in the feed (Fig. 4.3.6). The oxygen conversions were slightly higher for the propene-rich mixtures than for the system of propane, hydrogen and oxygen.

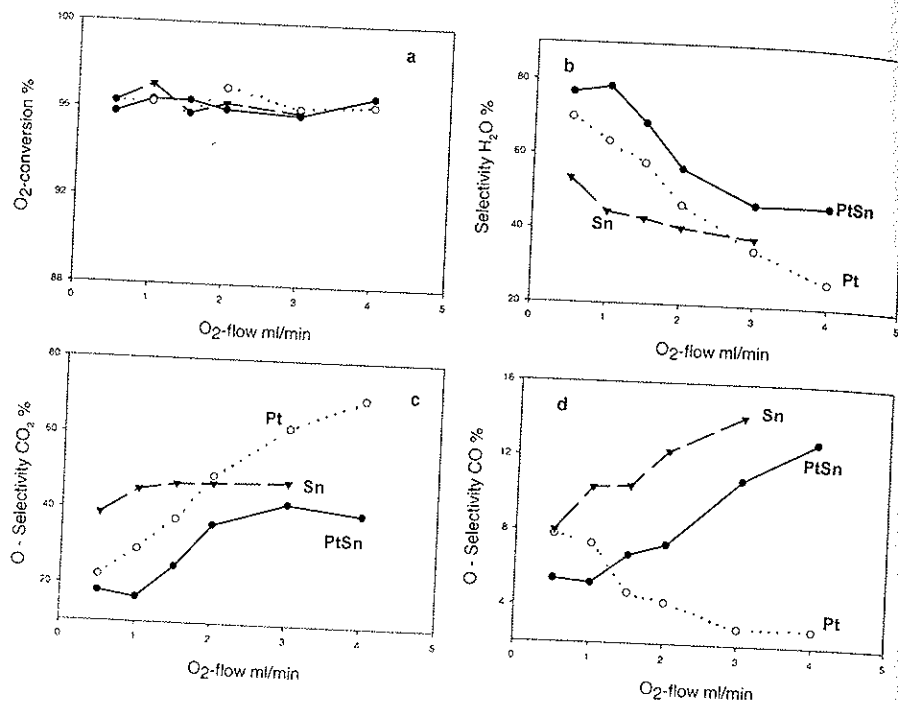


Figure 4.3.10. Catalytic combustion over Sn, Pt and PtSn catalysts. a) O₂-conversion b) O-selectivity to H₂O c) O-selectivity to CO₂ d) O-selectivity to CO. Conditions: 550°C, 1 atm., 0.30 g catalyst, Feed gas: 2 ml/min H₂, 5 ml/min C₃H₈, 28.2 ml/min C₃H₆, O₂ as shown in the figure, total flow 100 ml/min, balance is He.

However, also in this case (for all catalysts) is there some unconverted oxygen, in the range 4-6% of the oxygen fed to the reactor. Again, this could indicate a by-pass of some of the reactant gas through the catalyst bed, or that the oxygen conversion is limited by diffusion [Beretta (1999)]. Fig. 4.3.10b and Fig. 4.3.11b show the oxygen-selectivity to water formation. At low oxygen flows the selectivity decreases in the order PtSn > Pt > Sn for both temperatures. The selectivity falls dramatically when the oxygen flow is increased.

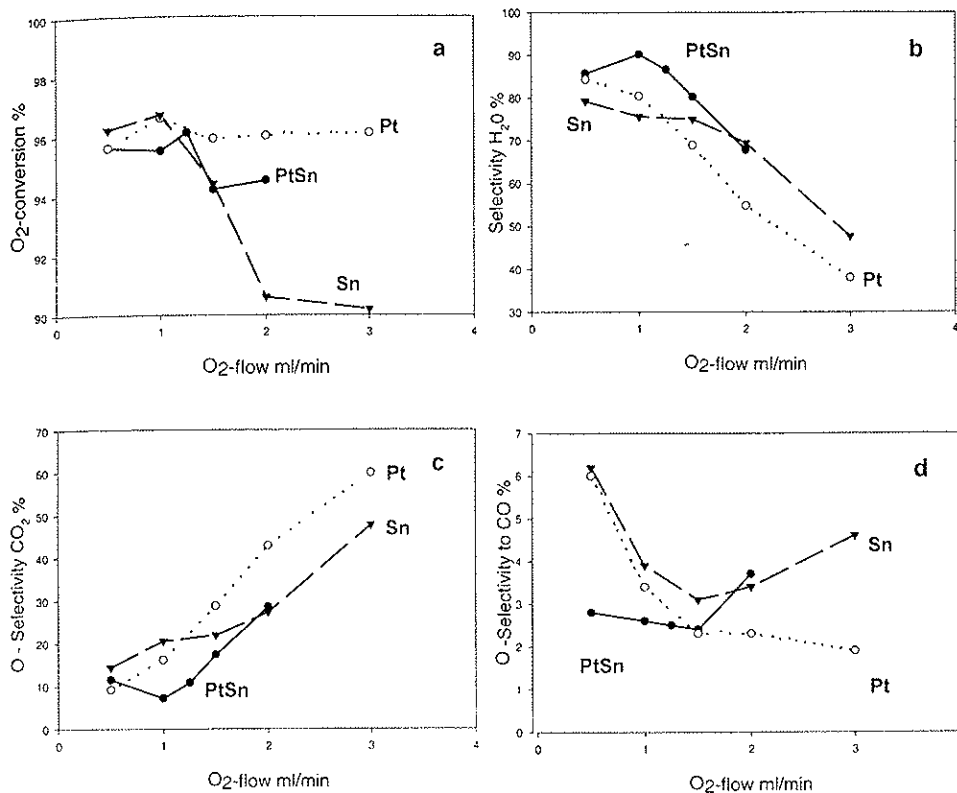


Figure 4.3.11. Catalytic combustion over Sn, Pt and PtSn catalysts. a) O₂-conversion b) O-selectivity to H₂O c) O-selectivity to CO₂ d) O-selectivity to CO. Conditions: 500°C, 1 atm., 0.30 g catalyst, Feed gas: 2 ml/min H₂, 5 ml/min C₃H₈, 8.4 ml/min C₃H₆, O₂ as shown in the figure, total flow 100 ml/min, balance is He.

The difference between Pt and PtSn remains constant throughout, whereas for the Sn catalyst the drop in selectivity is less severe. Above 2 ml/min O₂ feed-rate the selectivity to water is in the range 40 - 50% at 550°C and slightly higher at 500°C, which indicates that the hydrocarbons are being combusted, e.g.: C₃H₆ combustion would give a H₂O selectivity (based on consumed O₂) of 33 %. At low oxygen flows (less than 1 ml/min), a close to 80% selectivity to water is observed over PtSn at 550°C. A 90% selectivity to water is observed at 500°C over the same catalyst. Sn and Pt are less selective hydrogen combustion catalysts compared to the PtSn catalyst for both temperatures, 500°C giving higher selectivity to water for both catalysts. Fig. 4.3.10c-d and Fig 4.3.11c-d show the selectivities to CO₂ and CO at 550°C and 500°C, respectively. The main product is always CO₂. As the case was for

the experiments without propene in the feed (Fig. 4.3.7), the CO selectivity drops off with increasing O₂ flow over Pt, whereas for Sn and PtSn the trend is opposite. This could again indicate a higher activity in the CO oxidation reaction over Pt.

Due to the composition of the feed gas is the main dehydrogenation reaction (Eq. 2.1.1) close to equilibrium, and there is only limited conversion. However, due to side-reactions, mainly cracking/hydrogenolysis type of reactions, and possibly due to different reactivities towards oxygen the hydrocarbon composition is somewhat changed at the reactor outlet. There was no clear trend in the cracking product distribution. It could however be observed over Sn and PtSn that the selectivity to methane in most cases was lower than what would be expected if the C₂ products were formed by a simple C-C bond scission (expect C-selectivity $S_{CH_4} : S_{C_2H_4} = 1:2$). A possible explanation is that the C₁-species is oxidised to carbon oxides, leaving a C₂-unit as a hydrocarbon product. In Table 4.3.2 are listed the product distribution of C₁ and C₂ products for the different catalysts at 550 and 500°C. Since methane is the most stable hydrocarbon, it is clear that the C₁ species can not desorb as methane, but has to react directly (from an adsorbed state) after the C-C bond cleavage of the propane/propene. The selectivity to methane over the Pt catalyst at 550°C is higher than what would be expected from a C-C bond cleavage, which is the opposite trend from Sn and PtSn. The explanation for this must be that ethene formed as cracking product is further reacted to CO_x.

Table 4.3.2

Product distribution (% C-mole selectivity) to methane and ethene over PtSn, Pt and Sn catalysts. Conditions: 1 atm., 0.30 g catalyst, Feed gas: 2 ml/min H₂, 5 ml/min C₃H₈, 28.2 ml/min C₃H₆ (550°C) and 8.4 ml/min C₃H₆ (500°C), O₂ as shown in the table, total flow 100 ml/min, balance is He. For conversions and other selectivities see Fig. 2 (550°C) and Fig. 3 (500°C).

Temp (°C)	O ₂ -flow (ml/min)	Sn		Pt		PtSn	
		CH ₄	C ₂ H ₄	CH ₄	C ₂ H ₄	CH ₄	C ₂ H ₄
550	0	0	0	1.0	1.0	5.2	6.3
	0.5	2.8	7.8	5.9	5.7	1.3	7.6
	1.0	1.6	4.4	2.8	3.0	1.0	4.0
	1.5	1.2	3.9	2.0	2.0	1.6	6.8
	2.0	1.3	3.8	1.0	1.4	1.3	4.5
	3.0	0.9	3.4	0.6	1.0	1.0	3.0
	4.0	-	-	0.5	0.9	1.0	3.3
500	0	0	0	2.1	3.7	0	0
	0.5	1.6	7.5	3.5	6.5	1.1	9.0
	1.0	1.7	5.4	2.0	2.6	1.4	12.7
	1.25	-	-	-	-	1.2	9.9
	1.5	1.0	4.4	0.8	1.8	0.9	5.2
	2.0	0.8	3.3	0.3	1.0	0	2.5
	3.0	0.3	1.4	0	0.6	-	-

It is intuitively obvious to suggest that the alkene is more reactive towards oxygen than its corresponding alkane. A comparison of the simulated high conversion mixture with the experiments with only propane as the hydrocarbon feed (the results shown in Fig. 4.3.10 and Fig. 4.3.7) over PtSn confirms this and is shown in Fig. 4.3.12. With increasing O₂-feedrate, a clear difference in the behaviour is observed. With only propane as the hydrocarbon in the feed, the rate of formation of carbon oxides is negligible up to a point where all the hydrogen feed is consumed. (The oxygen conversion is always close to 95%). Only at the situation where excess O₂ is fed is there a measurable CO/CO₂ formation rate. This is contrasted by the experiments with high concentrations of propene in the feed (see also Fig. 4.3.10 and Fig. 4.3.11). The CO and CO₂ formation is high and important as soon as O₂ is introduced in the feed gas. It is well known that the high reactivity of propene towards oxygen is the main problem with this type of process. With low propene concentrations, a selective reaction between H₂ and O₂ is possible.

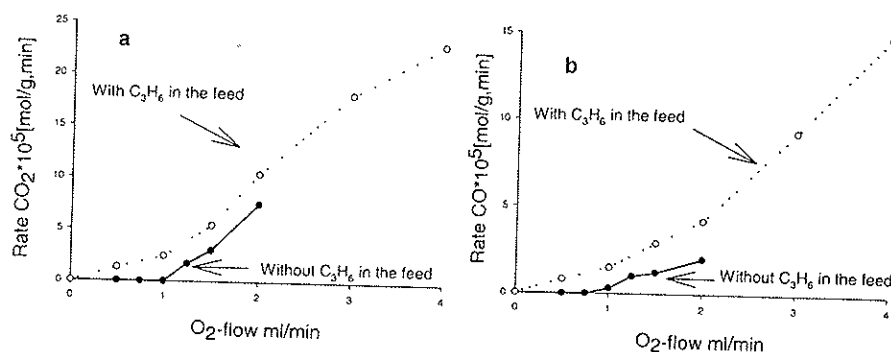


Figure 4.3.12. Rates of CO₂ (a) and CO (b) formation at 550°C. Conditions: 1 atm., 0.30 g Pt-Sn catalyst. Feed gas with C₃H₆: 2 ml/min H₂, 5 ml/min C₃H₈, 28.2 ml/min C₃H₆, O₂ as shown in the figure, without C₃H₆: 2 ml/min H₂, 10 ml/min C₃H₈, O₂ as shown in the figure. Total flow is always 100 ml/min, balance is He.

Only when all the H₂ is consumed will O₂ attack the hydrocarbons and form CO and CO₂. This must be a catalytic oxidation (the gas-phase reaction will not be selective), and the lower than expected selectivity to CH₄ indicates that the oxygen also picks up a C₁-species from the surface, leaving a C₂ unit which can desorb as a product.

The explanation to why PtSn (and to a certain extent Sn) gives higher selectivity to propene and combusts hydrogen with a higher perfection than does Pt is not clear. The two main side reactions that usually compete with dehydrogenation are hydrogenolysis and coke formation [Yang (1992)]. These two undesired reactions are more sensitive to the structure of the metal surface than is dehydrogenation [Yang (1992)]. The reason why PtSn preferentially combusts hydrogen and Pt does not could as an analogy be speculated to be due to a dilution of the Pt ensembles in PtSn. Sn act as a diluent, and reduces the formation rate of structure sensitive side products as coking which require large ensembles of Pt. Possibly, the same feature of the surface favours the adsorption and activation of hydrogen in competition with the hydrocarbons. Another possible explanation is that the addition of Sn provides an electronic effect on the catalyst. The conversion of alkanes is low over pure Sn, which

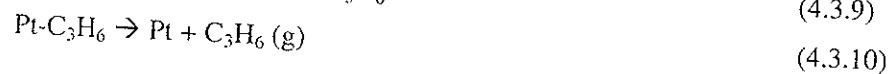
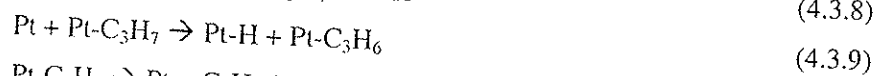
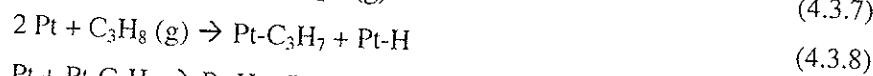
indicates that Sn does not adsorb alkanes in the same extent as Pt. Pure Pt gives high conversions of alkanes, hydrogen and oxygen, especially in the initial parts of the experiments. The conversion of alkanes over Pt drops off as a function of time, probably due to coke formation. A too strong hydrocarbon adsorption on Pt can explain the low selectivity to the desired products. When a hydrocarbon molecule approaches the catalyst surface of the pure Pt, it adsorbs dissociatively and reacts to produce water and an allylic specie which can desorb to produce an alkene. Instead of desorbing as an alkene, the strongly adsorbed intermediate is further oxidized to CO_x . When Sn is added to the Pt catalyst, the adsorption strength between the adsorbent and the catalyst surface is lowered, and at the same time the size of the Pt ensembles are reduced. In this way the desired product can more easily desorb from the catalyst surface. The discussion above is based on the assumption that the reaction involves only adsorbed species. This is however not clear.

We assume that oxygen is strongly adsorbed on Sn, as the case is for the Pt catalyst [King (1982)]. Then hydrogen can react directly from the gas phase (Eley-Rideal (ER) mechanism) or from an adsorbed state (Langmuir-Hinshelwood (LH) mechanism). It is, however, difficult to see how a gas-phase attack on adsorbed oxygen should give a complete selectivity towards H_2 combustion. We further assume that alkanes do not adsorb on Sn, since the propane conversion is low over this catalyst, and water is the only oxygenated product as long as there are no alkenes in the system.

For Pt we know that oxygen is strongly adsorbed [Holmen (1996)] and then there is a competitive adsorption between hydrogen and hydrocarbons. We assume a LH type of mechanism also for the Pt catalyst. In this catalytic system there are larger ensembles of Pt, which are required for coking and hydrogenolysis to take place. A possible too strong adsorption of the desired product causes a further reaction to undesired products. All this together results in a catalyst with low selectivity to the desired products.

On the PtSn system some of the undesired reactions are inhibited by the presence of Sn: Alkanes do not adsorb on Sn, which means that the production of water is favoured, and at the same time the size of the Pt ensembles are reduced by Sn, which results in reduced amount of coking and hydrogenolysis. The electronic properties of the catalyst are modified by the Sn addition to the Pt catalyst. This results in an increased amount of desired products. When propene is added to the feed, Sn is no longer able to selectively combust hydrogen, which indicates that also propene adsorb on the Sn surface, and the result is lower selectivities to the desired products.

Summarizing some of these arguments, a possible reaction mechanism for the reactions taking place on the PtSn catalyst surface is proposed in the following section:



To explain the selectivity effect the following assumptions are necessary. Oxygen will adsorb on Pt in preference to Sn as long as there is Pt available in the system. Sn does not have an active participation in the catalytic process, but reduces the Pt ensembles and the adsorption strength of the Pt. On pure Sn reactions (4.3.4)-(4.3.7) will be the same as for Pt, while reactions (4.3.8)-(4.3.10) do not take place over this catalyst. A too strong hydrocarbon adsorption to the pure Pt explains the low selectivity to the desired products on this catalyst.

5 Conclusions

A study of the oxidative dehydrogenation of propane over a vanadium-magnesium-oxide catalyst showed that the main problem with this system is the lack of selectivity due to complete combustion. Selectivity to propene up to about 60% was obtained at 10% conversion at 500°C, but the selectivity decreased with increasing conversion. No oxygenates were detected, the only by-products were CO and CO₂. The selectivity to propene is a strong function of the conversion of propane. The reaction rate of propane was found to be 1.0 ± 0.1 order in propane and 0.07 ± 0.02 order in oxygen. The kinetic results are in agreement with a Mars van Krevelen mechanism with the activation of the hydrocarbons as the rate-determining step. The rate of propene oxidation to CO₂ was studied and found to be significantly higher than that of propane.

Another possible process involves the simultaneous equilibrium dehydrogenation of propane to propene and combustion of part of the hydrogen formed to provide the in situ heating as well as shift the equilibrium dehydrogenation reaction further to the product propene. The selective combustion of hydrogen in the presence of propane was found to be possible under certain reaction conditions over some metal oxide catalysts. In₂O₃/SiO₂, unsupported Bi₂O₃ and ZSM-5 show the ability to combust hydrogen in a gas mixture with propane and oxygen with good selectivity. Bi₂O₃/SiO₂ and PbO/SiO₂ show moderate properties as selective hydrogen combustion catalysts, and Cr₂O₃/SiO₂ and VMgO are ineffective as SHC catalysts. If propene is added to the gas mixture, Bi₂O₃/SiO₂ and PbO/SiO₂ are no longer able to selectively combust hydrogen. In₂O₃/SiO₂, on the other hand, combusts hydrogen with 90% selectivity at low oxygen flows, and with 80% selectivity at stoichiometric amounts (to water) of oxygen. Bi₂O₃ (no support) combusts hydrogen with 60% selectivity independent of the oxygen flow. In₂O₃/SiO₂ and Bi₂O₃/SiO₂ are found to be the most active catalysts for the conversion of oxygen.

The selective combustion of hydrogen in the presence of propane/propene over Pt-based catalysts was also found to be possible at some reaction conditions. It seems like tin has a stabilising effect on the catalyst activity, PtSn being more stable than Pt. Both Sn and PtSn seem to be able to selectively combust hydrogen in a gas mixture with propane and oxygen. Pt does not show this quality. If propene is added to the gas mixture, Sn is no longer able to selectively combust hydrogen. PtSn on the other hand combust hydrogen with about 80% selectivity at 550°C and 90% selectivity at 500°C as long as the oxygen flow is less than half the amount of hydrogen. As soon as the oxygen flow exceeds half the amount of hydrogen, the selectivity to CO_x increases at the expense of water.

A Langmuir-Hinshelwood type of reaction mechanism is proposed over the Pt, Sn and PtSn catalysts. It is also proposed that oxygen is strongly adsorbed on both Pt and Sn, but the adsorption on Pt is preferred to Sn as long as there is Pt available in the system. Alkanes are strongly adsorbed on Pt, but do not adsorb on Sn, in contrast to alkenes that adsorb on all the catalysts. Sn reduces the Pt ensembles and the adsorption strength of the Pt, and as a consequence reduces the formation of the undesired products.

References

- Agaskar, P. A., U. S. Pat., 5,430,209 (1995)
- Alkhazov, T. G. and Lisovskii A. E., Oxidative dehydrogenation of hydrocarbons (in Russian), Khimia, Moscow, 1980
- Anderson, L. S. T., Appl. Catal. A, General 112, 209 (1994)
- Beretta, A., Gasperini, M. E., Trepiedi, G., Piovesan, L. and Forzatti, P., Stud. Surf. Sci. Cat., 119, (1998)
- Beretta, A., Piovesan L. and Forzatti P., J. Catal., 184 455 (1999)
- Berg, R. C., Vora, B. V., Mowry, J. R., Oil Gas J., Now 10, 191 (1980)
- Bettahar, M. M., Costentin, G., Savary, L. and Lavalley, J. C., Appl. Catal. A: General 145, 1 (1996)
- Bielanski, A., Haber, J., Oxygen in Catalysis, Dekker, New York, 145 (1991)
- Blekkan, E. A., Holmen, A., Vada, S., Acta Chemia Scandinavica, 47, 275 (1993)
- Bond, G.C, Heterogeneous Catalysis: Principles and Applications, Clarendon Press, Oxford, (1987)
- BP Amoco, "Statistical Review of World Energy", (2000)
- Bricker, J. C., Imai, T., Mackowiak, D. E., U. S. Patent, 4,717,779 (1988)

- Buiten, J., *J. Catal.*, 10, 188 (1968)
- Burch, R., Crabb, E. M., *Appl. Catal. A*, 100, 111 (1993)
- Cavani, F., Trifiro, F., *Scienza E Tecnologia*, 76, 708 (1994)
- Cavani, F., Trifiro, F., *Appl. Catal. A*: 157, 195 (1997)
- Centi, G., Perathoner, S., Trifiro, F., *Appl. Catal. A*: 157, 143 (1997)
- Centi, G., Cavani, F., Trifiro, F., "Selective oxidation by heterogeneous catalysis", New York 2001.
- Chaar, M. A., Patel, D. and Kung, M. C., Kung, H. H., *J. Catal. A*, 105, 483 (1988)
- Chaar, M. A., Patel, D. and Kung, H. H., *J. Catal. A*, 109, 463 (1988)
- Chen K., Khodakov A., Yang J., Bell A.T. and Iglesia E., *Journal of Cat.*, 186, 325 (1999)
- Cherrak, A., Hubaut, R., Barboux, Y., Mairesse, G., *Catal. Lett.*, 15, 377 (1992)
- Corma, A., Lopez-Nieto, J. M., Paredes, N., Perez, M., Shen, Y., Cao, H., Suib, S. L., *Stud. Surf. Sci. Catal.*, 72, 213 (1992)
- Corma, A., Lopez-Nieto, J. M., Paredes, N., *J. Catal.*, 144, 425 (1993)
- Corma, A., Lopez-Nieto, J. M., Paredes, N., Dejoz, A., Vazques, I., *Stud. Surf. Sci. Catal.*, 82 113 (1994)

Creaser D., Andersson B., Appl. Catal. A, 141, 131 (1996)

Creaser D., Andersson B., Hudgins R.R., Silveston., Appl. Catal. A:Gen. 187, 147 (1999)

Dahl, I. M., Grande, K., Jens, K. J., Rytter, E, Slagtern, A., Appl. Catal., 77, 163(1991)

de Morais, J., PhD Thesis University of Lyon (F), (1995)

Fox, D. B., Lee, E. H., Chem. Tech., 186 (1973)

Fujimoto, I., Nakamura, K., Yotota, K., Zeolites, 9, 120 (1989)

Gao, X., Ruiz, P., Xin, Q., Guo, X., Delmon, B., Catal. Lett., 23, 321 (1994)

Gao, X., Ruiz, P., Xin, Q., Guo, X., Delmon, B., J. Catal., 148, 56 (1994)

Gates, B.C., Catalytic Chemistry, John Wiley & Sons., Inc., New York, (1992)

Graselli, R. K., Stern, D. L., Tsikoyiannis, J. G., Appl. Catal. A: General, 189, 1 (1999)

Graselli, R. K., Stern, D. L., Tsikoyiannis, J. G., Appl. Catal. A: General, 189, 9 (1999)

Holmen, A., Student compendium 'Heterogen Katalyse', Department of Industrial Chemistry, NTNU, Trondheim, Norway,(1996)

- Imai, T., U. S. Pat. 4,435,607 (1984)
- Imai, T., Bricker, J. C., U. S. Pat. 4,812,597 (1989)
- Imai, T., Jan, D.-Y., U. S. Pat. 4,788,371 (1988)
- King, D. A. and Woodruff, D. P., " The Chemical Physics of solid surfaces and heterogeneous catalysis", Volume 4, Elsevier scientific publishing company, (1982)
- Kung, M. C., Kung, H. H., J. Catal. 134, 668 (1992)
- Kung, H. H. and Kung, M. C., Appl. Catal. A., General 157, 105 (1997)
- Lin, C.-H., Lee, K.-C., Wan, B.-Z., Appl. Catal. 164, 59 (1997)
- Læg Reid, T., Rønnekleiv, M. and Solbakken, Å., Ber. -Dtsch, Wis. Ges. Erdoel, Erdgas Kohle, Tagungsber. 9395, 147 (1993)
- Mamedov, E. A., Cortes Corberan, V., Appl. Catal. A: General 127, 1 (1995)
- Mazzocchia, C., Aboumard, C., Diagne, D., Temesti, E., Herrmann, J. M., Thomas, G., Cat. Lett., 10, 181 (1991)
- Michaels, J. N., Stern, D. L. and Grasselli, R. K., Catalyst Letters, 42, 139 (1996)
- Miller J. E., Jackson N. B., Evans L, Sault A. G., Gonzales M. M., Cat. Letters 58, 147 (1999)
- Nguyen, K. T., Kung, H. H., Ind. Eng. Chem. Res., 30, 352 (1991)

Pantazidis, A. and Mirodatos, C., 11th International Congress on Catalysis-40th Anniversary, Studies in Surface Science and Catalysis, 101, 1029 (1996)

O'Hara, M. J., Imai, T., Bricker, J. C., Mackowiak, D. E., U. S. Patent, 4,565,898 (1986)

Pantazidis, A., Mirodatos, C., Stud. Surf. Sci. Catal., 101, 1029 (1996)

Pantazidis, A., Bucholz, S. A., Zanthoff, H. W., Schuurmann, Y., Mirodatos, C., Catalysis Today, 40, 207 (1998)

Patel, D., Kung, M. C. and Kung, H. H., Proc. 9th Int. Congr. Catal., 4, 463 (1988)

Pujado, P. R., Vora, B. V., Chem. Econ. Eng. Rev., 15(5), 16 (1983)

Resasco, D. E. and Haller D. L., Catalysis (London) 11, 379 (1994)

Resetarits, M. R., Agnello, J., Lockett, M. J., Kirkpatrick, H. L., Oil Gas J., June 6, 54 (1988)

Rokstad, O. A. and Lindvåg, O. A., 'Gaskromatografisk analyse. Beregning av sammensetninger', Avdeling teknisk kjemi, SINTEF, Trondheim (1998)

Shenoy, M. S., Rao, J., Chem. Tech. Biotech., 36, 95 (1986)

Shenoy, M. S., Rao, J., Chem. Tech. Biotech., 36, 110(1986)

Siew Hew Sam, D., Soenen, V., Volta, J. C., J. Catal., 123, 417 (1990)

- Smits, R. H. H., Sheshan, K, Ross, J. R. H., Stud. Surf. Sci. Catal., 72, 221 (1992)
- Smits, R. H. H., PhD Thesis University of Twente (NL), (1994)
- Singh, J. K., Gehlwat, M. S., Rao, J., Chem. Tech. Biotech., 47, 127 (1990)
- Statoil, " Statoil Faktahefte 1996/97", (1997)
- Stephenson, Introduction to the chemical Process Industries, Reinhold, New York, (1966)
- Stern, D. L. and Grasselli, R. K., J. Catal. 167, 560 (1997)
- Sulikowski, B., Krysciak, J., Valenzuela, R. X., Cortes-Coberan, V., Stud. Surf. Sci. Catal., 82, 133 (1994)
- Tagamolila, C. P., U. S. Pat., 5,043,500 (1991)
- Takita, H., Yamashita, K., Moritaka, K., Chem. Lett., 10, 1973 (1989)
- Ted Oyama, S., Am. Chem. Soc., (1996)
- The Norwegian Ministry of Petroleum and Energy, "Norwegian Petroleum Activity", (2000)
- Tsikoyiannis, D. G., Stern, D. L., Grasselli, R. K., Journal of Catalysis, 184, 77 (1999)
- Trimm, D.L., Rokstad, O.A., Cooper B.J., "Compendium Petrochemistry 1", Laboratory of Industrial Chemistry, NTH, Trondheim, Norway, (1988)

Ushkov, S. B., Osipova, Z. G., Sokolovskii, V. D., Ketchik, S. V., Kinet.
Katal., 29, 222 (1988)

Vatcha, S. R., Catalytica Highlights, 19(2), 1 (1993)

Vora, B., Marker, T. L., Barger, P. T., Nilsen, H. R., Kvisle, S. and Fuglerud,
T., Stud. Surf. Sci. Catal., 107, 87 (1997)

Appendices

Appendix 1: Calculation procedures for conversions, selectivities and reaction rates.

Appendix 2: Paper I

Appendix 3: Paper II

Appendix 4: Paper III

Appendix 5: Paper IV

Appendix 1: Calculation procedures for conversions, selectivities and reaction rates.

This chapter describes the calculation procedures used for the calculation of the mass balances from the GC chromatograms.

A.1.1 Calculations by using internal standard

Most of the theory in chapter A.1.1 is written by Rokstad [Rokstad (1998)]
The method of internal standard is used for the calculation of the amount of O₂, CO and CO₂ out of the reactor. Nitrogen is used as the internal standard since nitrogen is inert and natural fed to the reactor as a component in air. It is assumed that the air consists of 78.084% nitrogen, the rest being oxygen. The amount of nitrogen fed to the reactor can then be calculated by the gas law:

$$n_{N_2} = \frac{0,78084 \cdot P \cdot F_{air,mm}}{R \cdot T} \quad (\text{A.1.1})$$

Where:

P = pressure [atm.]

F = flow rate [ml/min]

T = temperature [K]

R = gas constant [cm³ atm K⁻¹ mol⁻¹]

The molar amounts of the other gases fed to the reactor are also found from the gas law.

The amount of nitrogen can also be calculated from eqn. A.1.2

$$n_{N_2} = f_{N_2} \cdot A_{N_2} \quad (\text{A.1.2})$$

Where:

n_{N_2} = number of moles of nitrogen

f_{N_2} = molar response factor of nitrogen

A_{N_2} = response area of nitrogen

The other product gases can be calculated from eqn. A.1.3

$$n_i = f_i \cdot A_i \quad (\text{A.1.3})$$

From eqn. A.1.2 and eqn. A.1.3:

$$\frac{n_i}{n_{N_2}} = \frac{f_i}{f_{N_2}} \cdot \frac{A_i}{A_{N_2}} \quad (\text{A.1.4})$$

The relative response factor for component i is defined as:

$$f_{i/N_2} = \frac{f_i}{f_{N_2}} \quad (\text{A.1.5})$$

The relative response factor for the internal standard is then 1.

By combining eqn. A.1.4 and eqn. A.1.5 the number of moles of component i is found:

$$n_i = n_{N_2} \cdot f_{i/N_2} \cdot \frac{A_i}{A_{N_2}} \quad (\text{A.1.6})$$

The number of mole of CO:

$$n_{CO} = n_{N_2} \cdot f_{CO,N_2} \cdot \frac{A_{CO}}{A_{N_2}} \quad (A.1.7)$$

Number of mole of CO₂ :

$$n_{CO_2} = n_{N_2} \cdot f_{CO_2,N_2} \cdot \frac{A_{CO_2}}{A_{N_2}} \quad (A.1.8)$$

Number of mole of O₂:

$$n_{O_2} = n_{N_2} \cdot f_{O_2,N_2} \cdot \frac{A_{O_2}}{A_{N_2}} \quad (A.1.9)$$

The relative response factors for CO and CO₂ is found from Rokstad [Rokstad (1998)] to be 1.00 and 0.85, respectively. The response factor for O₂ is found by the relative ratio between nitrogen and oxygen by analyzing several GC samples of air.

The amount of hydrocarbons is calculated with the assumption that the molar response factors for the FID detector are proportional to the number of C-atoms in the molecule.

A.1.2 Calculation of conversions, selectivities and reaction rates

There are two sets of equations used in the calculations: one set when only propane is used as hydrocarbon feed and one set for an equilibrium mixture of propane, propene and hydrogen. These sets are described in detail in the following chapters.

A.1.2.1 Only propane in the feed

Number of C-atoms, n(HC), in the hydrocarbons is found from eqn. A. 1.10:

$$n(\text{HC}) = 3n(\text{C}_3\text{H}_8)_{\text{inn}} - n(\text{CO}) - n(\text{CO}_2) \quad (\text{A.1.10})$$

$n(\text{CO})$ and $n(\text{CO}_2)$ are found from eqn. A.1.7 and eqn. A.1.8.

The number of C-atoms in the hydrocarbons can also be calculated from the following equation:

$$n(\text{HC}) = 3n(\text{C}_3\text{H}_8)_{\text{out}} + 3n(\text{C}_3\text{H}_6) + 2n(\text{C}_2\text{H}_6) + 2n(\text{C}_2\text{H}_4) + n(\text{CH}_4) \quad (\text{A.1.11})$$

The GC- areas for all the hydrocarbons are proportional to the number of C-atoms in the molecule. The amount of propene can be calculated from eqn. A.1.12:

$$n(\text{C}_3\text{H}_6) = n(\text{C}_3\text{H}_8) \cdot \frac{A(\text{C}_3\text{H}_6)}{A(\text{C}_3\text{H}_8)} \quad (\text{A.1.12})$$

The procedure for all hydrocarbons is equivalent with that of propene.

ethane :

$$n(\text{C}_2\text{H}_6) = \frac{3}{2} \cdot n(\text{C}_3\text{H}_8) \cdot \frac{A(\text{C}_2\text{H}_6)}{A(\text{C}_3\text{H}_8)} \quad (\text{A.1.13})$$

ethene :

$$n(\text{C}_2\text{H}_4) = \frac{3}{2} \cdot n(\text{C}_3\text{H}_8) \cdot \frac{A(\text{C}_2\text{H}_4)}{A(\text{C}_3\text{H}_8)} \quad (\text{A.1.14})$$

methane :

$$n(\text{CH}_4) = 3 \cdot n(\text{C}_3\text{H}_8) \cdot \frac{A(\text{CH}_4)}{A(\text{C}_3\text{H}_8)} \quad (\text{A.1.15})$$

Equation A.1.11 can then be reformed to:

$$n(\text{HC}) = 3n(\text{C}_3\text{H}_8)_m \cdot \left(1 + \frac{A(\text{C}_3\text{H}_6)}{A(\text{C}_3\text{H}_8)} + \frac{A(\text{C}_2\text{H}_6)}{A(\text{C}_3\text{H}_8)} + \frac{A(\text{C}_2\text{H}_4)}{A(\text{C}_3\text{H}_8)} + \frac{A(\text{CH}_4)}{A(\text{C}_3\text{H}_8)} \right) \quad (\text{A.1.16})$$

By combining eqn. A.1.16 and eqn. A.1.10 the amount of propane out of the reactor can be found. When the amount of propane is known the rest of the hydrocarbons can be calculated from eqn. A.1.12 – A.1.15.

The amount of H₂O produced can be calculated from the oxygen balance:

$$n(\text{H}_2\text{O}) = 2n(\text{O}_2)_{\text{in}} - 2n(\text{O}_2)_{\text{out}} - n(\text{CO}) - 2n(\text{CO}_2) \quad (\text{A.1.17})$$

In the calculations it is assumed that there is no production of oxygenates or other products that will result in a loss of oxygen.

Conversion

The conversions of propane and oxygen are calculated by eqn. A.1.18 and A.1.19:

$$\eta_{\text{C}_3\text{H}_8} = \frac{n(\text{C}_3\text{H}_8)_{\text{in}} - n(\text{C}_3\text{H}_8)_{\text{out}}}{n(\text{C}_3\text{H}_8)_{\text{in}}} \cdot 100\% \quad (\text{A.1.18})$$

$$\eta_{O_2} = \frac{n(O_2)_{in} - n(O_2)_{out}}{n(O_2)_{in}} \cdot 100\% \quad (\text{A.1.19})$$

Selectivity

The selectivities to the various products, on carbon basis, are calculated by eqn.

A.1.20- A.1.25:

$$S(CH_4) = \frac{n(CH_4)}{3 \cdot n(C_3H_8)_{in} - 3 \cdot n(C_3H_8)_{out}} \cdot 100\% \quad (\text{A.1.20})$$

$$S(C_2H_6) = \frac{2n(C_2H_6)}{3n(C_3H_8)_{in} - 3n(C_3H_8)_{out}} \cdot 100\% \quad (\text{A.1.21})$$

$$S(C_2H_4) = \frac{2n(C_2H_4)}{3n(C_3H_8)_{in} - 3n(C_3H_8)_{out}} \cdot 100\% \quad (\text{A.1.22})$$

$$S(C_3H_6) = \frac{3n(C_3H_6)}{3n(C_3H_8)_{in} - 3n(C_3H_8)_{out}} \cdot 100\% \quad (\text{A.1.23})$$

$$S(CO_2) = \frac{n(CO_2)}{3n(C_3H_8)_{in} - 3n(C_3H_8)_{out}} \cdot 100\% \quad (\text{A.1.24})$$

$$S(CO) = \frac{n(CO)}{3n(C_3H_8)_{in} - 3n(C_3H_8)_{out}} \cdot 100\% \quad (A.1.25)$$

The oxygen selectivities, $S_O(i)$, are calculated in a similar way :

$$S_O(CO) = \frac{n(CO)}{2n(O_2)_{in} - 2n(O_2)_{out}} \cdot 100\% \quad (A.1.26)$$

$$S_O(CO_2) = \frac{2n(CO_2)}{2n(O_2)_{in} - 2n(O_2)_{out}} \cdot 100\% \quad (A.1.27)$$

$$S_O(H_2O) = \frac{n(H_2O)}{2n(O_2)_{in} - 2n(O_2)_{out}} \cdot 100\% \quad (A.1.28)$$

The reaction rate for propane conversion:

$$r(C_3H_8) = \frac{(n(C_3H_8)_{in} - n(C_3H_8)_{out})}{W_{cat}} \quad (A.1.29)$$

The formation rate for a carbon containing component, i , is given by:

$$r(i) = r(C_3H_8) \cdot S(i) \cdot n_C / 100 \quad (A.1.30)$$

Where n_{C_i} is the ratio of number of carbon atoms in propane in comparison to component i . (i.e. $n_{C_i} = 3$ for CO).

Reaction rate for conversion of oxygen:

$$r(O_2) = \frac{(n(O_2)_{in} - n(O_2)_{out})}{W_{cat}} \quad (A.131)$$

For an oxygen containing component the formation rate is calculated by eqn. A.1.32:

$$r(i) = r(O_2) \cdot S_O(i) \cdot n_{O_i}/100 \quad (A.1.32)$$

where n_{O_i} is the ratio of number of O-atoms in dioxygen in to the number of o-atoms in component i .

A.1.2.2 Equilibrium mixture of propane, propene and hydrogen

Both propane and propene are converted when an equilibrium mixture is fed, and the calculations of the mass balances are more complicated.

Equation A.1.10 has to be corrected for the amount of propene fed:

$$n(HC) = 3n(C_3H_8)_{in} + 3n(C_3H_6)_{in} - n(CO) - n(CO_2) \quad (A.1.33)$$

The amounts of hydrocarbons and H₂O are calculated by eqn. A.1.11 – A.1.17. The conversions of propane and oxygen is found from eqn. A.1.18 and A.1.19, while the conversion of propene is calculated from the following eqn:

$$\eta_{C_3H_6} = \frac{n(C_3H_6)_{in} - n(C_3H_6)_{out}}{n(C_3H_6)_{in}} \cdot 100\% \quad (A.1.34)$$

The calculations of C-selectivities of CO and CO₂ are calculated in different ways dependent on whether propane, propene or both are being converted.

If only propane is converted eqn A.1.20 – A.1.25 are used. If only propene is used, the denominator in eqn A.1.20 – A.1.25 is changed:

$$\text{from } (3n(C_3H_8)_{in} - 3n(C_3H_8)_{out}) \text{ to } (3n(C_3H_6)_{in} - 3n(C_3H_6)_{out}) \quad (A.1.35)$$

If both propane and propene are converted the denominator in eqn A.1.20 – A.1.25 are changed to:

$$((3n(C_3H_8)_{in} - 3n(C_3H_8)_{out}) + (3n(C_3H_6)_{in} - 3n(C_3H_6)_{out})) \quad (A.1.36)$$

In the latter case, no selectivities can be calculated.

The reaction rates for conversion of propane and oxygen are given by eqn A.1.29 and A.1.31. For propene it is calculated from eqn A.1.37:

$$r(C_3H_6) = \frac{(n(C_3H_6)_{in} - n(C_3H_6)_{out})}{W_{cat}} \quad (A.1.37)$$

The reaction rate for a carbon containing component, i , is calculated from eqn A.1.30 if only propane is converted. If only propene is converted the rate is calculated by eqn A.1.38.

$$r(i) = r(C_3H_6) \cdot S(i) \cdot n_{C_i}/100 \quad (\text{A.1.38})$$

If both propane and propene are converted the rate is calculated by eqn A.1.39:

$$r(i) = (r(C_3H_8) + r(C_3H_6)) \cdot S(i) \cdot n_{C_i}/100 \quad (\text{A.1.39})$$

The reaction rate (on oxygen basis) is calculated by eqn A.1.32.

Papers

Paper I

Oxidative Dehydrogenation of Propane Over a VMgO Catalyst

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Abstract

The reaction kinetics of the oxidative dehydrogenation of propane was studied at 475-550°C over V-Mg-O catalysts. Vanadium-magnesium-oxides are among the most selective and active catalysts for the dehydrogenation of propane to propene. Selectivity to propene up to about 60% was obtained at 10% conversion, but the selectivity decreased with increasing conversion. No oxygenates were detected, the only by-products were CO and CO₂ (and water). The reaction rate of propane was found to be first order in propane and zero order in oxygen, which fits to a Mars van Krevelen mechanism with the activation of the hydrocarbons as the rate determining step. The activation energy of the conversion of propane was found to be 122±6 kJ/mole.

Keywords

Propane, oxidative dehydrogenation, V-Mg-O

Introduction

The dehydrogenation of alkanes to alkenes is a potentially important route to convert low-value paraffinic feedstocks (C₃-C₄) into more useful chemicals. Although steam-cracking is the most important route to light alkenes, this process has limitations, especially in the production of propene and higher alkenes. The current commercial catalytic process use promoted Pt(Sn)/support or Cr₂O₃/ Al₂O₃ [1,2] for the direct dehydrogenation in which alkanes are converted to unsaturated hydrocarbons and hydrogen. The disadvantage of the direct dehydrogenation route is that it is a strongly endothermic and equilibrium limited reaction, and the severe conditions required (high temperatures and low pressures) lead to coke formation on the catalyst. These features dominate the reactor design, which has to allow for the transfer of the heat as well as allow for frequent decoking and regeneration of the catalyst.

The oxidative dehydrogenation (ODH) of lower alkanes is an interesting alternative to the conventional dehydrogenation of LPG, owing to the possibility of working at lower reaction temperatures. This reaction is not limited by the thermodynamic equilibrium, and catalyst deactivation is usually not a problem since coke and its precursors can be efficiently removed by oxygen. Short contact time ODH has the attractive potential of being performed in very small-size reactors, as well as the possibility of autothermal operation. However, since the formation of carbon oxides is more favourable thermodynamically than the formation of olefins, it is necessary to intercept the desired products kinetically. For this reason, catalysts must increase the formation rate of the desired products [3]. This reaction has been much studied over recent years, the main drawback being the lack of selectivity at high conversions, with total oxidation to CO₂ and H₂O being the main side reactions.

Much research has concentrated on vanadium-oxide based catalysts for oxidative dehydrogenation. In particular vanadium-magnesium-oxide (VMgO) catalysts have demonstrated a promising yield for alkenes and have been studied by several groups [3-6]. By analogy with other oxidation reactions, the ODH reaction has been proposed to proceed via a Mars-van Krevelen redox sequence [6, 8], in which alkanes react with lattice oxygen and the resulting vacancies react with dissociatively adsorbed O_2 . These mechanistic proposals have been largely based on agreement between proposed sequences of elementary steps and experimental power-law kinetic rate expressions, with limited independent evidence for specific elementary steps [9]. In this work we present kinetic data obtained over a VMgO catalyst.

Experimental

Catalyst preparation

The V-Mg-O catalyst was prepared by impregnating $Mg(OH)_2$ (Fluka) with an aqueous solution of NH_4VO_3 (Merck). The vanadium: magnesium atomic ratio was 0.32. The catalyst was calcined at $550^\circ C$ for 9 hours with a ramp rate of $5^\circ C/min$ from room temperature using an airflow of 50 ml/min (GHSV = 0.30 l/g h). The surface area (BET) was found to be 38 m^2/g .

Catalytic test

The reaction was investigated in a fixed bed quartz micro-reactor (U-type) with an inner diameter of 3,5 mm at atmospheric pressure using air as the oxidant. The temperature was varied between 500 and 550°C. The total gas flow rate was 100 ml/min with varying composition: The flow of propane was varied from 5 to 25 ml/min and the flow of air was varied from 10 to 40 ml/min, the balance being helium. The catalyst loading was in the range 0.05-0.2 g with a particle size of 270-450 μm . The product gas was analysed by on-line gas chromatography (hydrocarbons and carbon oxides). The chromatograph used was a Perkin Elmer autosystem XL equipped with a TCD (Carbosieve SII, 10 ft, mesh 80) and a FID (PoraPLOT Q, 27,5m, i.d. 0.53mm).

The conversion of propane in the empty reactor was negligible (<0.5%) even at 575°C. Under the same conditions, a reactor filled with quartz wool showed lower conversion than an empty reactor. Water and hydrogen productions are not analysed by the GC but were calculated through mass balances.

Results and discussion

The major products of the ODH of propane on VMgO were propene, CO_2 , CO and water. Traces of methane, ethane and ethene were also observed at high conversion, especially at high temperatures and high propane pressures. No oxygenates were detected. Fig. 1 shows plots of reactant conversion and product selectivities as a function of temperature. Both propane conversion and oxygen conversion are strongly related to the temperature in the

reactor. The selectivities to CO and CO₂ increase almost linearly, and the selectivity to propene decreases linearly as the temperature is increased from 475-550°C. Temperatures above 475°C seem to be needed for the activation of propane at these flow-rates. At temperatures lower than 475°C the conversion of propane is low (less than 4%). According to Lavalley et al.[10] propane activation needs a high reaction temperature (500°C compared to 400°C for propene) and, as a consequence, a strong activating (oxidising) phase such as vanadium. The difference of reactivity between propane and propylene is linked to the strengths of the involved C-H bonds and to the stability of the corresponding radicals formed in the rate determining step by H abstraction: the less stable propyl radical (corresponding to the stronger C-H bond) needs a higher reaction temperature and a stronger oxidising phase to be produced than the most stable Π- allyl radical (corresponding to the weaker C-H bond breaking).

The VMgO system used here was quite stable over time with only a small degree of deactivation of the catalyst, at least at low conversions. The propane conversion dropped from 6.7 to 5.9% during 40 hours on stream. This is shown in Fig. 2 where the conversion of propane and oxygen as well as the selectivities to the products are shown as a function of time on stream. From the figure it can be seen that the conversion of oxygen drops from 21 to 17.5% during the same period of time. The selectivities to the various products show a small change during the experiment. The propene selectivity increases from 51.1 to 58.3% and the CO₂ selectivity drops from 36.2 to 32.5% while the CO selectivity is more or less unchanged during the experiment. The catalyst seems to be more and more selective to the desired products with increasing time on stream. The surface area of the catalyst was measured after 40 hours on stream, and found to be 35 m²/g_{cat}, a reduction of about 9% compared to the fresh catalyst. This drop in surface area explains the decrease in propane conversion during the run. The results in Fig. 2, where the selectivity to propene increases with time on stream can be

explained by the fact that the selectivity in the ODH is usually a strong function of conversion. This is shown in Fig. 3, which demonstrates the dependence of selectivity on conversion for VMgO catalysts. The extra set of data at 500°C in Fig. 1 also shows this effect. The extra data set is recorded about 5 hours later than the original set, and shows that the propane conversion decrease and the selectivity to propene increases at the expense of CO_x as a function of time on stream. This conversion-selectivity dependence can also explain the results in Fig 1, where the propene selectivity decreases as the temperature and propane conversion increases. The selectivity to propene decreases strongly with increasing conversion of propane. The selectivity to propene is decreasing from about 70% at a conversion of 4% to 22% at a conversion of propane of 57%. This is in good agreement with the results from other groups on similar catalytic systems [3, 4], also shown in the figure. No temperature effects on the selectivities are observed over the catalyst. For a fixed propane conversion (various temperature and catalyst loading) the product selectivity remained constant. The total yield of propene increases from about 5% at 10% propane conversion to 13% at 55% conversion. The results from Pantazidis and Mirodatos [3] were obtained on a catalyst with a similar composition, but a slightly higher surface area (43 m²/g). The observed differences in yields could be a consequence of this difference in catalyst surface area. The catalyst preparation method is important for the activity of the catalyst and the selectivity of the products. The active phases for the ODH are assumed to be magnesium orthovanadate [11, 12] and magnesia pyrovanadate [13]. An XRD experiment of the fresh catalyst was performed in order to identify the active phase of the VMgO catalyst. The reflections corresponding to MgO and Mg₃V₂O₈ (orthovanadate) crystalline phases are indicated in the Fig. 4. There are also indications of the existence of magnesium pyrovanadate from the XRD diffractogram.

The kinetics of the reaction was investigated at differential conditions (conversions kept below 10%). The absence of significant inter- or intra particle diffusion limitations was confirmed

using the usual experiments: Decreasing the particle size was found to not change the reaction rate. Doubling the linear flowrate at constant space velocity similarly gave no change in reaction rate. By varying the catalyst loading one can see from Fig. 5 that the reaction rate is constant up to a contact time (W/F) of $4 \text{ g}_{\text{cat}} \text{ h/mole-C}_3$ (0.1 g catalyst), but a further increase in the contact time lowers the reaction. In Fig. 5 the product selectivities and the conversions of the reactants are plotted as a function of the contact time ($\text{g}_{\text{cat}} \text{ h/mole-C}_3$). The conversion of both oxygen and propane are increasing as the contact time is increased. The selectivity to propene drops from 54 to 45%, the CO_2 selectivity increases from 35 to 43% as the contact time is increased from 2 to $8 \text{ g}_{\text{cat}} \text{ h/mole-C}_3$. The selectivity to CO is more or less unaffected by the contact time. A decrease in reaction rate of propane from $27 \cdot 10^{-5}$ to $21 \cdot 10^{-5} \text{ mole/min-g}_{\text{cat}}$ is observed as the contact time is increased. In all the kinetic experiments reported here a contact time of $4 \text{ g}_{\text{cat}} \text{ h/mole-C}_3$ (catalyst loading of 0.1g) is used in order to operate at differential conditions. Corma et al.[14] have also studied the effect of contact time, but they found a linear correlation between contact time and conversion up to 30% propane conversion.

The rate of propane conversion was measured over a range of temperatures (Fig.6). The apparent activation energy for the consumption of propane was estimated to be $122 \pm 6 \text{ kJ/mole}$ within the temperature range investigated ($475\text{-}550^\circ\text{C}$). Kung et al.[6] found the activation energy on 40-VMgO (40 wt% V_2O_5) to be 140 kJ/mol ($475\text{-}540^\circ\text{C}$), which is close to our results.

Fig 7 gives results obtained with varying oxygen partial pressure. The product selectivities, conversions and the reaction rates of propane and oxygen are shown as a function of oxygen partial pressure in Fig 7a. The selectivities are only slightly affected by the partial pressure of oxygen. There is a small decrease in the selectivity to propene and a small increase in the

selectivity to CO_2 as the partial pressure of oxygen increases, which is the same as observed by Stern and Graselli [15]. The reaction rates of propane and oxygen as a function of oxygen pressure are shown in Fig 7b. Both rates increase as the oxygen pressure increases, but the oxygen partial pressure has a stronger influence on the rate of oxygen consumption than on the propane consumption. The rate of propane conversion increases by about 8% as the pressure of oxygen is doubled (from 0.04 to 0.08 atm). The oxygen reaction rate on the other hand increases by about 25% for the same oxygen pressure increment due to an increased selectivity to CO_2 . The reaction order for propane conversion with respect to oxygen is shown in Fig 7c and found to be 0.07. This result is in good agreement with findings of others, and orders in the range 0 - 0.13 are reported in the literature [3,4,7]. The apparent reaction orders for the formation of CO_2 , CO and C_3H_6 with respect to oxygen pressure were found to be 0.23 ± 0.05 , -0.27 ± 0.05 , 0.05 ± 0.01 , respectively. The results (with the exception of the order of CO) are in good agreement with Pantazidis and Mirodatos [3] who found the orders of CO_2 , CO, and C_3H_8 to be 0.16, 0.23 and 0.0, respectively. However, for oxygen pressures below 0.05 atm they found the formation order to propene to be 0.11.

The effect of propane pressures on the rates of propane consumption and products formation was also investigated. The results are reported in Fig 8. From Fig 8a it is evident that the selectivities to all products are constant as the partial pressure of propane increases. The conversion of propane is constant and the conversion of oxygen is increasing as the partial pressure of propane increases. Fig 8b shows that both the reaction rate of propane and oxygen consumption increases with increasing propane partial pressure. The apparent order for propane conversion is shown in Fig 8c and was found to be 1.0 ± 0.1 order with propane pressure. This is in agreement with others [3, 15], but Kung et al. [4] reported the order of propane conversion to be 0.6 with respect to propane pressure. A strong dependence was

obtained between product (and by-product) formation rates and propane pressure. The orders were found to be $0,96 \pm 0,08$, $1,1 \pm 0,2$ and $1,0 \pm 0,1$ for CO_2 , CO and C_3H_6 formation, respectively. The reaction orders of oxygen and propane seemed to be independent of the temperature of reaction, at least within the temperature interval studied here ($500\text{--}550^\circ\text{C}$). Pantazidis and Mirodatos [3] found the orders for the same components to be 0.70, 0.72 and 0.88 for CO , CO_2 and C_3H_6 , respectively.

Attempts have been made to fit the experimental data into a kinetic model. Two different types of models have been tested; a power rate law and a Mars Van Krevelen expression. As already shown, the results can be fit by a power rate law:

$$-r_{\text{C}_3\text{H}_8} = k \cdot P_{\text{C}_3\text{H}_8}^\alpha \cdot P_{\text{O}_2}^\beta \quad [\text{mole/g-min}] \quad (1)$$

Where α and β are the consumption orders of propane and oxygen, respectively.

k is found by curve fitting to be $0.0034 \text{ mole/g-min-atm}^{1.09}$ and the rate expression is found to be:

$$-r_{\text{C}_3\text{H}_8} = 0.0034 \cdot P_{\text{C}_3\text{H}_8}^{1.02} \cdot P_{\text{O}_2}^{0.07} \quad [\text{mole/g-min}] \quad (2)$$

In Fig 9A the model is plotted against the experimental results and from the figure it is evident that the model represents the data quite well.

It is also possible to fit the data into a Mars Van Krevelen type expression [16]:

$$-r_{\text{C}_3\text{H}_8} = \frac{k_1 \cdot k_2 \cdot P_{\text{C}_3\text{H}_8} \cdot P_{\text{O}_2}^b}{k_1 \cdot P_{\text{C}_3\text{H}_8} + k_2 \cdot P_{\text{O}_2}^b} \quad [\text{mole/g-min}] \quad (3)$$

k_1 and k_2 are the rate constants for propane activation and for reoxidation of the catalyst, respectively, and b is the reaction order of oxygen. If reoxidation of the catalyst is much faster

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than the activation of hydrocarbons (which is assumed to be the rate limiting step of the reaction), then $k_2 \gg k_1$ and the rate expression can be reduced to:

$$-r_{C_3H_8} = k_1 \cdot P_{C_3H_8} \quad [\text{mole/g-min}] \quad (4)$$

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This expression is very similar to the power rate law, but with a reaction order of zero with respect to oxygen. The rate constant, k , is found by curve fitting to be 0.0028 mole/g-min-atm. In Fig 9B the MVK model is plotted against the experimental results, and it can be seen that that the model represents the data quite well.

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Kung et al.[4] extrapolated their results to zero conversion and found that the initial products consisted of approximately 80% propene and 20% carbon oxides. Grasselli et al.[7] believe that propene is the only primary produced product, and that CO_x is produced largely by the sequential oxidation of the in situ produced intermediate propene, and to a lesser extent by a parallel route of direct deep oxidation of propane. They also indicate that the presence of two parallel pathways to CO_x is of some interest, as it suggests that partial and deep oxidation may occur at different surface sites or involve different forms of reactive oxygen. Iglesia et al.[17] suggests that CO only forms via secondary combustion of propene intermediates while CO_2 is formed via this reaction and also via the direct combustion of propane, at least for the V_2O_5/ZrO_2 catalyst used in their study. By plotting the rate of CO_x formation as a function of C_3H_6/C_3H_8 inlet pressure (holding the propane pressure constant and increasing the propene pressure), we found that the CO_x formation was directly proportional to the amount of propene fed. This is shown in Fig 10 and indicates that CO_x is formed mainly from propene, and not from propane, at least it indicates that the formation rate of CO_x from propene is much higher than from propane. It is well known that the reactivity of propene is much higher than that of propane. By substituting the propane gas in the ODH system with propene, we found that the

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reaction rate of propene to CO_x was about ten times higher than the case is for propane at 500°C . The relative reactivity between propene and propane can be even higher than 10, but the existence of possible diffusion limitations in the system with propene due to the high conversions of reactants can limit the reaction rate. The oxygen conversion at $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ inlet pressure of 1 is about 95%, which means that all the oxygen fed to the reactor is reacted. The relative reaction rate can shift when mixtures of propane and propene are introduced instead of pure gases due to competitive reactions. The relative reaction rate between propene and propane it is more likely to shift to higher values than to a lower value. This high difference in reaction rate of propane and propene could explain the proportionality of CO_x formation with propene partial pressure since the CO_x formation rate from propane is about on tenth of the formation rate from propene.

Summary and conclusions

Vanadium-magnesium-oxides are among the most selective and active catalysts for the dehydrogenation of propane to propene. Selectivity to propene up to about 60% was obtained at 10% conversion, but the selectivity decreased with increasing conversion. No oxygenates were detected, the only by-products were CO and CO₂. The selectivity to propene is a strong function of the conversion of propane. The VMgO catalyst seems quite stable as a function of time, except from a small initial activity drop during the first 3 hours on stream. The reaction rate of propane was found to be 1.0 ± 0.1 order in propane and 0.07 ± 0.02 order in oxygen. The activation energy of the conversion of propane was found to be 122 ± 6 kJ/mole. The kinetic results are in agreement with a Mars van Krevelen mechanism with the activation of the hydrocarbons as the slow step. The rate of propene oxidation to CO₂ was studied and found to be significantly higher than that of propane.

Acknowledgements

Financial support from the Norwegian Research Council through the Natural Gas Conversion Programme is gratefully acknowledged.

References

- [1] O. A. Bariãs, A. Holmen and E. A. Blekkan, *J. Catal.*, 158(1), 1 (1996)
- [2] M. Larsson, M. Hultèn, E. A. Blekkan and B. Andersson, *J. Catal.*, 164(1), 44 (1996)
- [3] A. Pantazidis and C. Mirodatos, 11th International Congress on Catalysis- 40th Anniversary, *Studies in Surface Science and Catalysis*, 101, 1029 (1996)
- [4] M. A. Chaar, D. Patel and H. H. Kung, *J. Catal.*, 109, 463 (1988)
- [5] H. H. Kung, M. C. Kung, *Appl. Catal. A, General* 157, 105 (1997)
- [6] D. Patel, M. C. Kung, H. H. Kung, *Proc. Int. Congr. Catal.*, 9th, 4, 463(1988)
- [7] J. N. Michaels, D. L. Stern and R. K. Grasselli, *Catalyst Letters*, 42, 139 (1996)
- [8] D. Creaser and B. Andersson, *Appl. Catal. A*, 141, 131 (1996)
- [9] L. S. T. Anderson, *Appl. Catal. A, General* 112, 209 (1994)
- [10] M. M. Bettahar, G. Costentin, L. Savary, J. C. Lavalley, *Appl. Catal. A*, 145, 1 (1996)
- [11] K. T. Nguyen and H. H. Kung, *Ind. Eng. Chem. Res.*, 30, 352 (1991)
- [12] D. Patel, P. J. Anderson and H. H. Kung, *J. Catal.*, 125, 132 (1990)
- [13] D. Siew Hew Sam, V. Soenen and J. C. Volta, *J. Catal.*, 123, 417 (1990)
- [14] A. Corma, J. M. Lopez Nieto and N. J. Paredes, *J. Catal.*, 144, 425 (1993)
- [15] D. L. Stern and R. K. Grasselli, *J. Catal.* 167, 560 (1997)
- [16] A. Bielanski and J. Haber, *Oxygen in Catalysis*, ISBN 0-8247-8320-4 (1991)
- [17] K. Chen, A. Khodakov, J. Yang, A. T. Bell and E. Iglesia, *J. Catal.*, 186, 325 (1999)

Legends for figures

Figure 1: Conversions, selectivities and reaction rate as functions of reaction temperature.

$W_{\text{cat}} = 0.1\text{g}$, $\text{C}_3\text{H}_8/\text{Air}/\text{He} = 5/30/65\text{ ml/min}$. (The points labelled (*) is recorded about 5 hours later than the original point at 500°C)

Figure 2: Catalytic stability of VMgO. $W_{\text{cat}} = 0.10\text{g}$, $\text{C}_3\text{H}_8/\text{Air}/\text{He} = 10/30/60\text{ ml/min}$.

$T = 500^\circ\text{C}$.

Figure 3: Selectivity to propene as a function of propane conversion

Figure 4: XRD pattern of the fresh VMgO catalyst. (1) $\text{Mg}_3(\text{VO}_4)_2$ (2) MgO

Figure 5: Influence of contact time on conversions, selectivities and reaction rate.

$W_{\text{cat}} = 0.05 - 0.2\text{ g}$, $\text{C}_3\text{H}_8/\text{Air}/\text{He} = 10/30/60\text{ ml/min}$. $T = 500^\circ\text{C}$.

Figure 6: Activation energy. Temperature range $475 - 550^\circ\text{C}$, $\text{C}_3\text{H}_8/\text{Air}/\text{He} = 5/30/65\text{ ml/min}$.

$W_{\text{cat}} = 0.10\text{g}$

Figure 7: Results from experiments with varying oxygen partial pressure. $T = 500^\circ\text{C}$.

$5\text{ ml/min C}_3\text{H}_8$, total flow: 100 ml/min . $W_{\text{cat}} = 0.10\text{g}$

a: Conversions and selectivities as a function of oxygen partial pressure.

b: Reaction rate of propane and oxygen as a function of oxygen partial pressure.

c: Reaction order of propane with respect to oxygen partial pressure

Figure 8: Results from experiments with varying propane partial pressure. $T = 500^{\circ}\text{C}$. 30 ml/min Air, total flow: 100 ml/min. $W_{\text{cat}} = 0.10\text{g}$

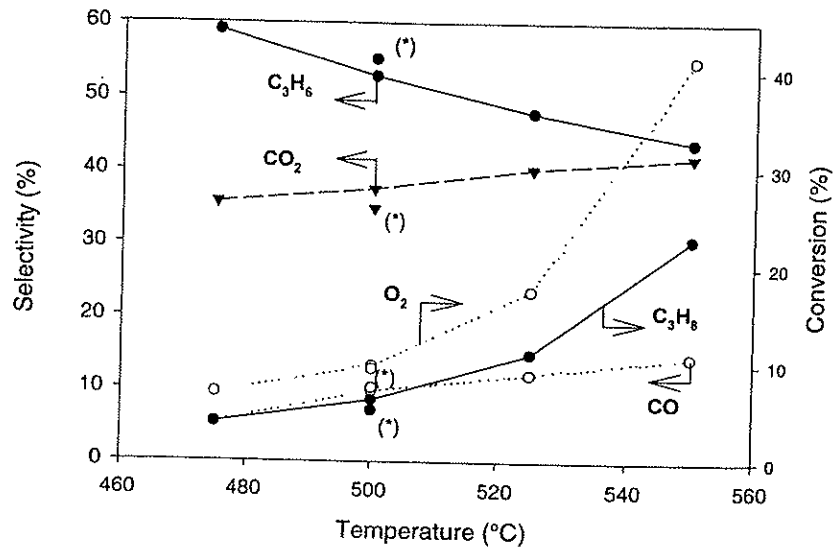
- a: Selectivity and conversion as functions of partial pressure of propane.
- b: Reaction rate of propane and oxygen as a function of propane partial pressure.
- c: Reaction order of propane with respect to propane partial pressure.

Figure 9: Cross plot of experimental results vs. model data

- a: Power-rate law
- b: Mars van Krevelen

Figure 10: Plot of the formation rate of CO_2 as a function of $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ feed ratio. $T=500^{\circ}\text{C}$. 10 ml/min propane, varying amount of propene, total flow: 100ml/min. $W_{\text{cat}} = 0.10\text{g}$

Figure 1



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Figure 2

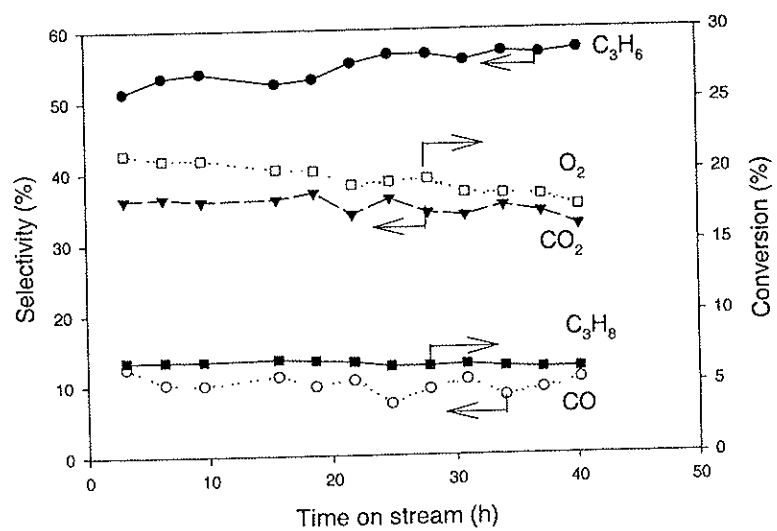


Figure 3

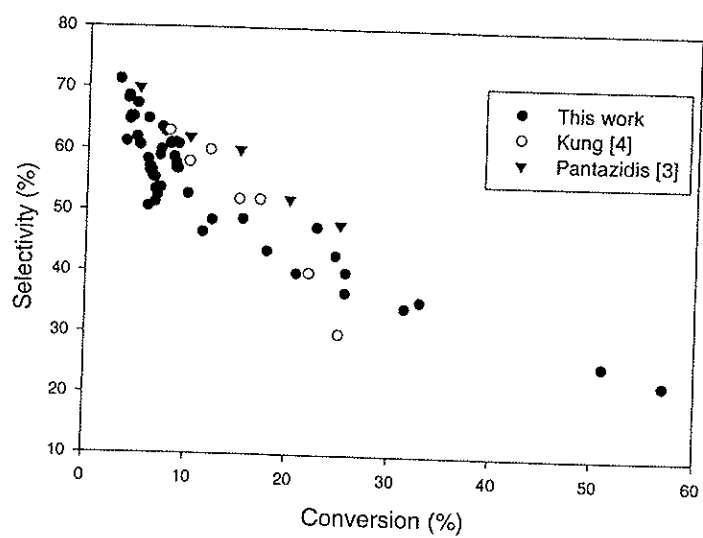


Figure 4

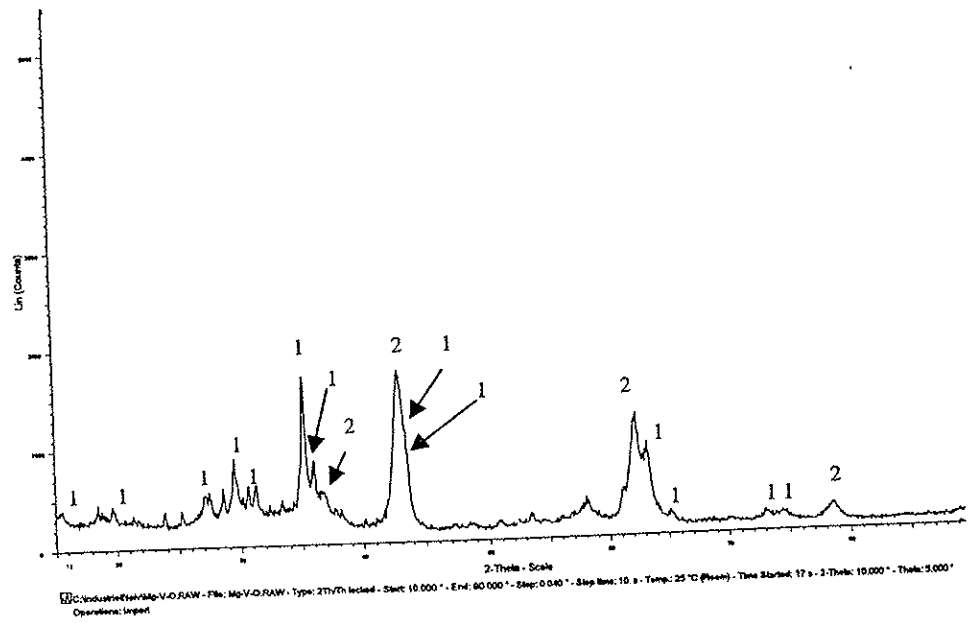


Figure 5

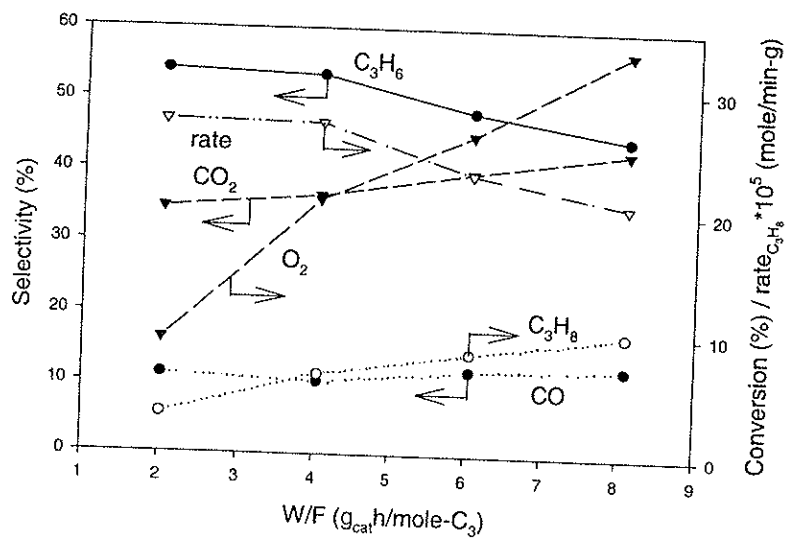


Figure 6

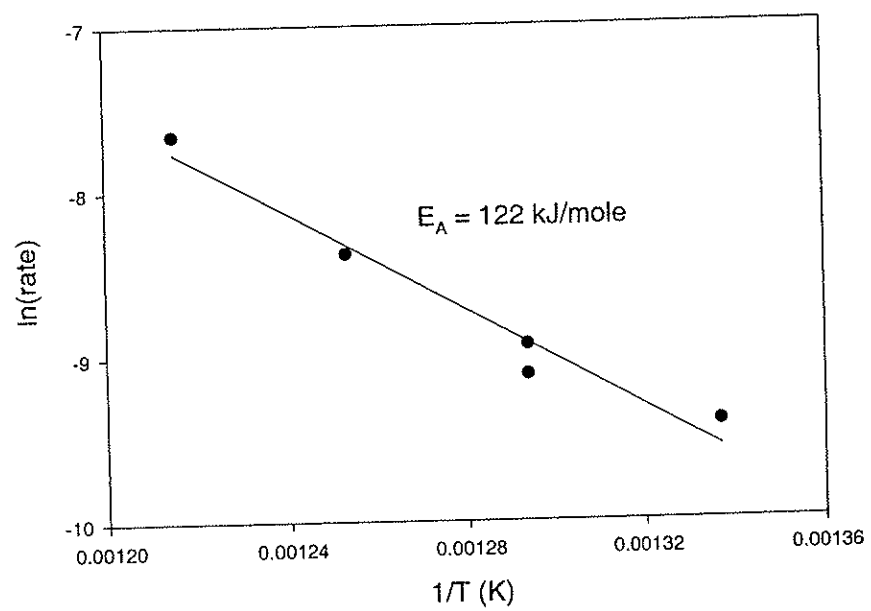


Figure 7

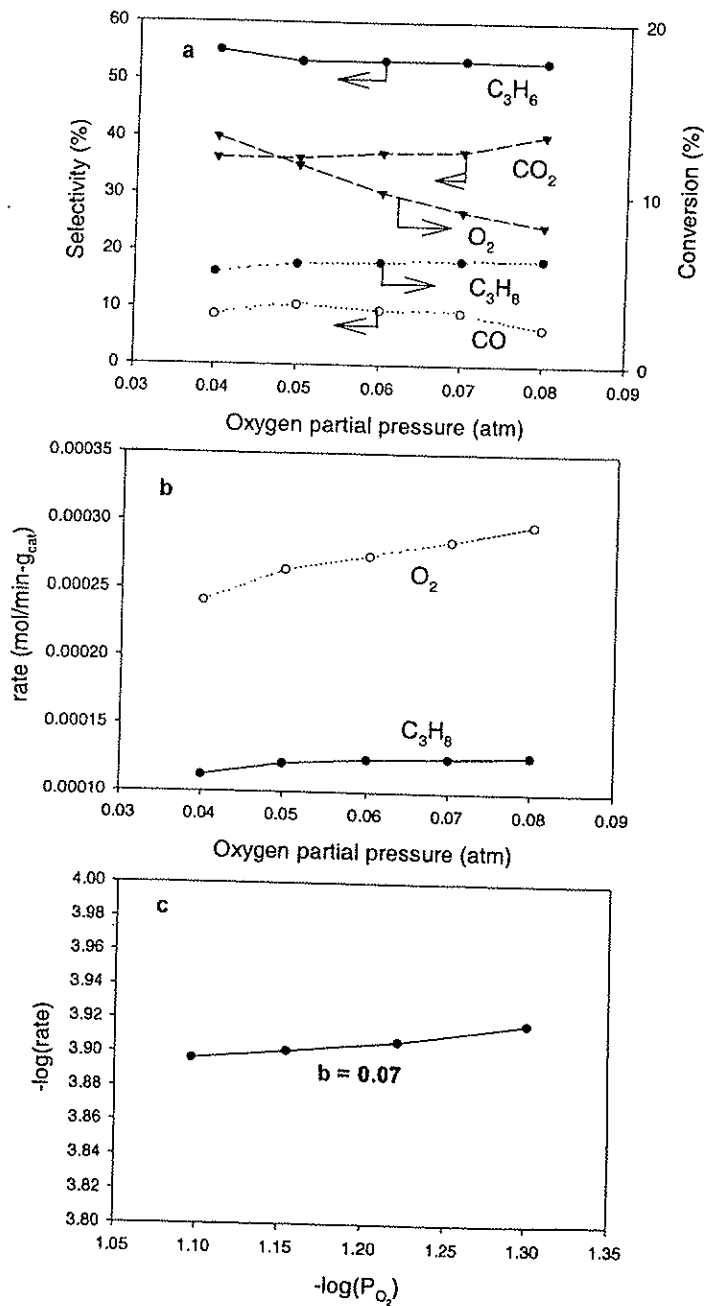


Figure 8

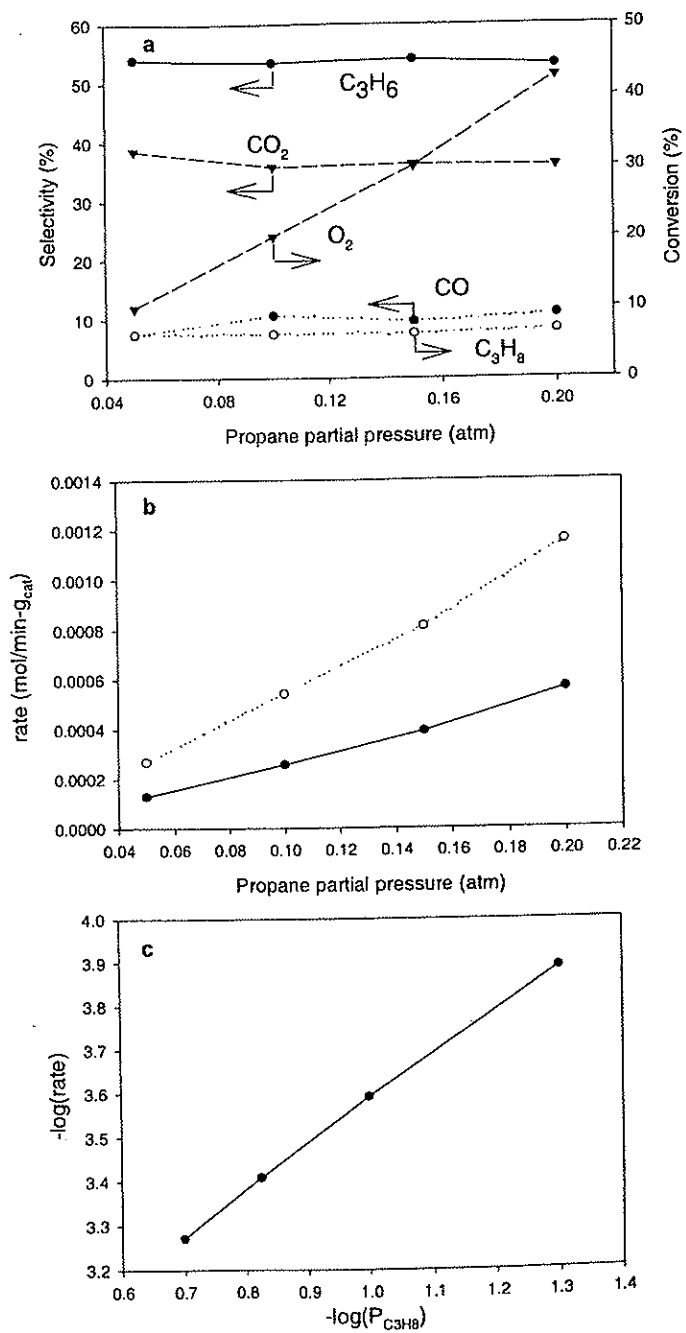


Figure 9

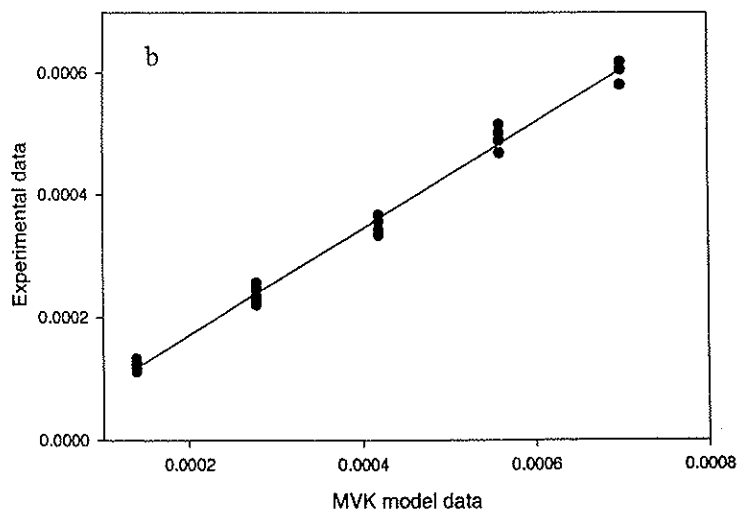
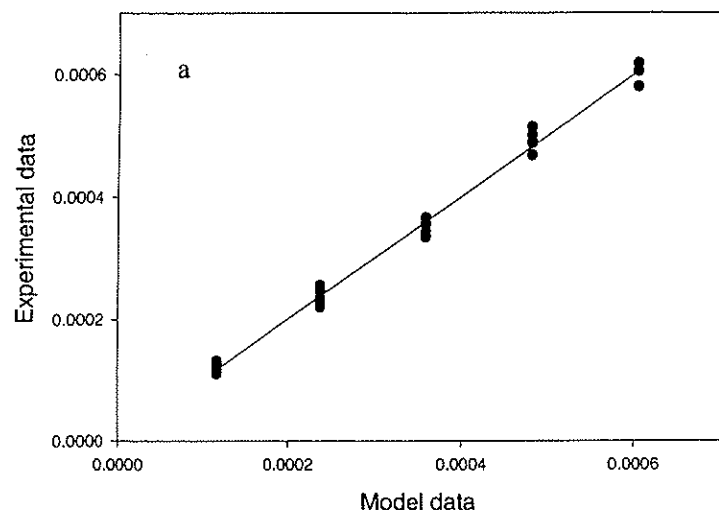
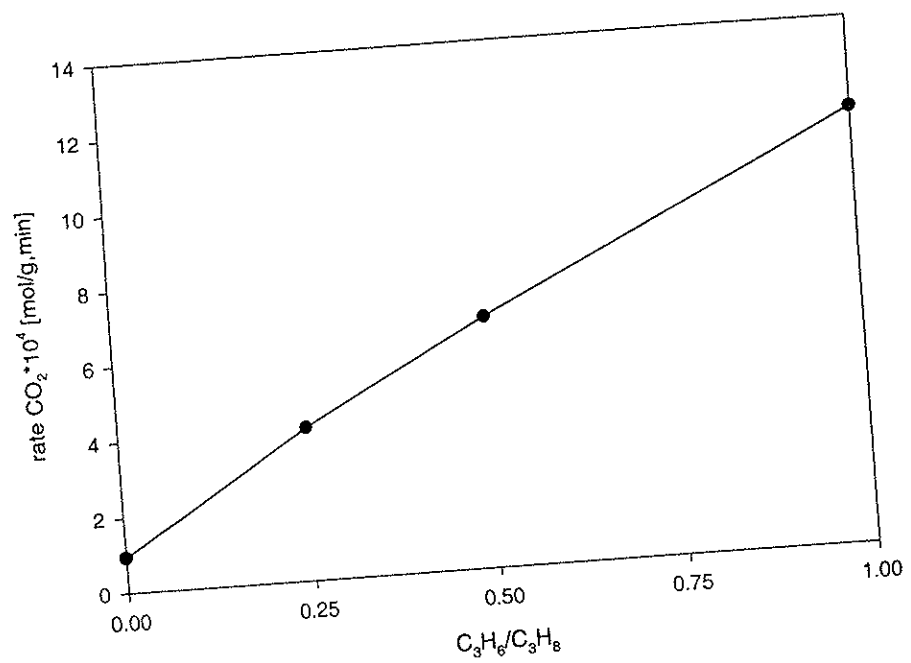


Figure 10



Paper II is not included due to copyright.

Papers

Paper III

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Selective combustion of hydrogen in the presence of hydrocarbons

1. Pt-based catalysts

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Abbreviated title: SHC over Pt-based catalysts

Keywords: Pt, PtSn, propane, dehydrogenation, selective hydrogen combustion

Abstract

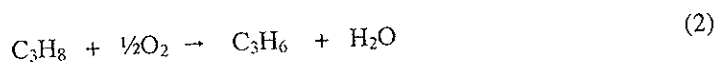
In this communication we present experimental results showing that under certain reaction conditions the selective combustion of hydrogen in the presence of light hydrocarbons over a PtSn/SiO₂ catalysts is possible. This reaction is of importance in the development of new dehydrogenation technology based on partial combustion of hydrogen to provide *in situ* heat generation to the endothermic dehydrogenation processes. Both Sn and PtSn seem to be able to selectively combust hydrogen in a gas mixture with propane and oxygen, whereas Pt alone is less selective. If propene is added to the gas mixture, Sn is no longer able to selectively combust hydrogen. PtSn on the other hand can combust hydrogen with about 80% selectivity at 550°C and 90% selectivity at 500°C as long as the oxygen flow is less than half the amount of hydrogen (stoichiometry to water formation). As soon as the oxygen flow exceeds half the amount of hydrogen, the selectivity to CO_x increases at the expense of water.

Introduction

The catalytic dehydrogenation of light alkanes like propane and butane is growing in importance, in the case of propane due to an imbalance between the growth in demand for propene and ethene. The selective production of propene via catalytic dehydrogenation, reaction (1), is difficult to do economically using the existing process technology.



The strong endothermic character of the equilibrium limited reaction (1) ($\Delta H_{873\text{K}}^0 = 124$ kJ/mole) demands a high reaction temperature, low pressure or strong dilution (often with steam) to achieve high conversions. In addition is the propane - propene separation difficult and energy consuming due to a small boiling-point difference, thus making the recycling of unconverted reactant more expensive. Oxidative dehydrogenation according to eq. (2), which is exothermic and without equilibrium limitations at normal conditions has been studied as an alternative, but so far there has been no breakthrough in the search for catalysts providing the necessary yield of propene [1].



The main problem is the lack of selectivity due to complete combustion, especially of the more reactive alkene. A recently adapted idea as an alternative to the ODH for obtaining olefin yields higher than equilibrium and for making the total process heat balanced or exothermic is the selective hydrogen combustion (SHC) [2-7]. If the process operation is adiabatic and heat balanced it can be called autothermal dehydrogenation (ADH) [3]. The principal idea of ADH of propane is to supply the heat by combustion of about half of the hydrogen formed in the dehydrogenation reaction in the reactor itself. One proposal [3] is to use alternating zones of dehydrogenation (DH) and selective hydrogen combustion (SHC) over the same catalyst. Over a Sn-Pt-Cs/ZnAl₂O₄ catalyst at 600°C, 95% selectivity to propene was achieved at a 38% conversion of propane [3]. Grasselli et al. [5-7] studied the SHC over metal oxides of Bi, Bi-Mo, Sb, In and W among other catalysts, and reported promising SHC properties for several of the metal oxides. Among the best catalysts for SHC are [5] Bi₂O₃, Bi₂Mo₃O₁₂, In₂Mo₃O₁₂, Sb₂O₄, In₂O₃ and WO₃. They used either alternating zones of a Pt-Sn/ZSM-5 (DH) and the SHC catalysts or a physical mixture of the same catalysts for the total dehydrogenation process. In this paper we will show results of experiments performed with the aim of exploring the possibility of feeding oxygen to a conventional catalytic dehydrogenation system, with particular emphasis on the conditions leading to the formation of the undesired carbon oxides. We have been particularly interested in the selectivity in the presence of large amounts of propene (simulating high conversions). We have focused on Pt-based catalysts, which are well known to be both active in the dehydrogenation as well as good combustion catalysts. The effect of tin, a promoter often used to reduce coking of the catalyst was also studied.

Experimental

Catalyst preparation

The catalysts were prepared by aqueous incipient wetness impregnation of silica (Merck Kieselgel 60, $S_{\text{BET}} = 483 \text{ m}^2/\text{g}$, particle size 0.063 - 0.2 mm), using $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. The dissolution of the tin salt was aided by addition of HNO_3 . Three catalysts were used, Sn/SiO_2 (1.0 wt% Sn), Pt/SiO_2 (1.0 wt% Pt) and PtSn/SiO_2 (0.35 - 1.0 wt%). All reported loadings are nominal values. The catalysts will be termed Sn, Pt and PtSn, respectively. The catalysts were calcined at 600°C for 12 hours with a ramp rate of $5^\circ\text{C}/\text{min}$ from room temperature using an airflow of 50 ml/min (GHSV = 0.30 l/g h). The surface areas (BET) of the catalysts were found to be: $\text{Sn}/\text{SiO}_2 = 457 \text{ m}^2/\text{g}$, $\text{Pt}/\text{SiO}_2 = 415 \text{ m}^2/\text{g}$ and $\text{PtSn}/\text{SiO}_2 = 428 \text{ m}^2/\text{g}$.

Catalytic test

The reactions were studied in a fixed bed quartz micro-reactor (U-shaped) with an inner diameter of 3.5 mm. The reactions were carried out at atmospheric pressure using air as the oxidant. The catalyst loading was 0.3g for all experiments. The reactor was placed in an electrical furnace, and the temperature controlled using external and internal thermocouples in the range from ambient to 775°C . The total flow rate was 100 ml/min with varying compositions of propane, air, propene, hydrogen, the balance being helium. Gases were premixed and fed to the reactor using electronic mass flow controllers (Bronkhurst). The product gas was analysed for hydrocarbons ($\text{C}_1 - \text{C}_4$) and for permanent gases (O_2 , N_2 , CO , CO_2) by GC. In the experiments the catalyst was prereduced for two hours with hydrogen (15 ml/min) with a heating rate of $10^\circ\text{C}/\text{min}$ from ambient to 500°C . The chromatograph used was a Perkin Elmer autosystem XL equipped with a TCD (Carbosieve SII, 10ft, mesh 80) and a FID (PoraPLOT Q, 27.5 m, i.d. 0.53mm). From the composition data the fractional conversion of propane and oxygen were calculated. The selectivities were calculated based on moles propane converted to CO/CO_2 (C-selectivity) or number of moles dioxygen converted to CO/CO_2 or H_2O (O-selectivity).

Water and hydrogen in the exit gas was not analysed by the GC, but the amounts were calculated through mass balances.

Results and discussion

There was no significant conversion of propane at temperatures below 600°C for the empty reactor when a gas mixture of propane (10%), oxygen (2%) and hydrogen (2%) was fed. A gradual increase of the oxygen conversion was observed as the temperature increased from 30°C, and at temperatures of about 550°C the conversion was about 10%. The results are in good agreement with what Beretta et al. [8, 9] have observed, but somewhat different from the results of Burch and Crabb [10], who observed conversions in the empty reactor already at 550°C. The difference could be due to the different gas composition of our experiments compared to the results of the other groups, is that we had a co-injection of hydrogen in the feed.

The results using the silica support as catalyst was about the same as observed for the empty reactor at 500°C, 3-7% conversion of oxygen and total conversion to water.

Fig. 1 shows typical developments of the activity in propane dehydrogenation over the platinum based catalysts with respect to time.

In Fig. 1a the catalytic stability of the PtSn is shown for the different gas mixtures (propane, propane/H₂, propane/O₂ and propane/H₂/O₂). The propane conversion is lower with oxygen present in the feed than the case is for the gas mixtures without oxygen, but oxygen appears to lead to a more stable catalyst. The reason for this could be that oxygen (or the water formed in the reaction) continuously removes coke or coke precursors deposited on the catalyst. Co-fed hydrogen also seems to stabilise the catalytic activity to some extent. When only propane is present in the feed, the initial conversion is higher, but the drop in activity over the first few hours on-stream is pronounced.

In Fig. 1b the catalytic stability of the Pt is shown for the same gas mixtures. A comparison of the behaviour of the Pt catalyst to the PtSn catalyst shows that the Pt is much more active initially, but deactivates much faster compared to the PtSn catalyst, as also observed previously in the conventional dehydrogenation system [11]. Here the same effect is shown also in the presence of O₂. Sn appears to have a stabilising effect on the activity of the catalyst. In the experiment with propane and H₂, the Pt shows a much higher activity than the case is for the other gas compositions. It seems like H₂ addition enhances the activity of this catalyst. This was not the case for the PtSn catalyst. Sn alone is not a very active catalyst for the dehydrogenation or combustion of hydrocarbons. At 550°C the conversion of propane is less than 1% when 1% Sn/SiO₂ is used as a catalyst (not shown).

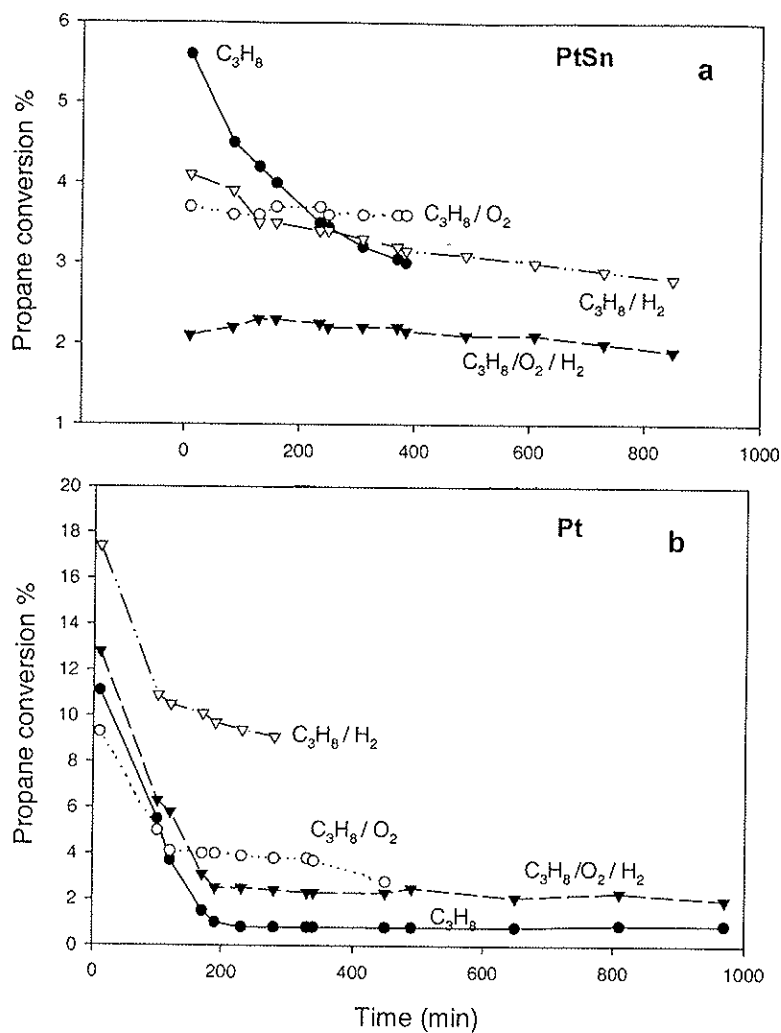


Figure 1. Catalytic stability during propane dehydrogenation in different gas mixtures: propane (●), propane/O₂ (10/1) (○), propane/O₂/H₂ (10/1/2) (▼) and propane/H₂ (10/4) (▽). Conditions: 500 °C, 1 atm., 0.30 g catalyst, Feed gas: Always 10 ml/min C₃H₈, H₂ and O₂ as indicated by the ratios, total flow 100 ml/min, balance is He.

a: PtSn/SiO₂

b: Pt/SiO₂

Fig. 2 provides a summary of some results obtained at 550°C over the different catalysts when increasing amounts of oxygen were added to a propane/hydrogen feed.

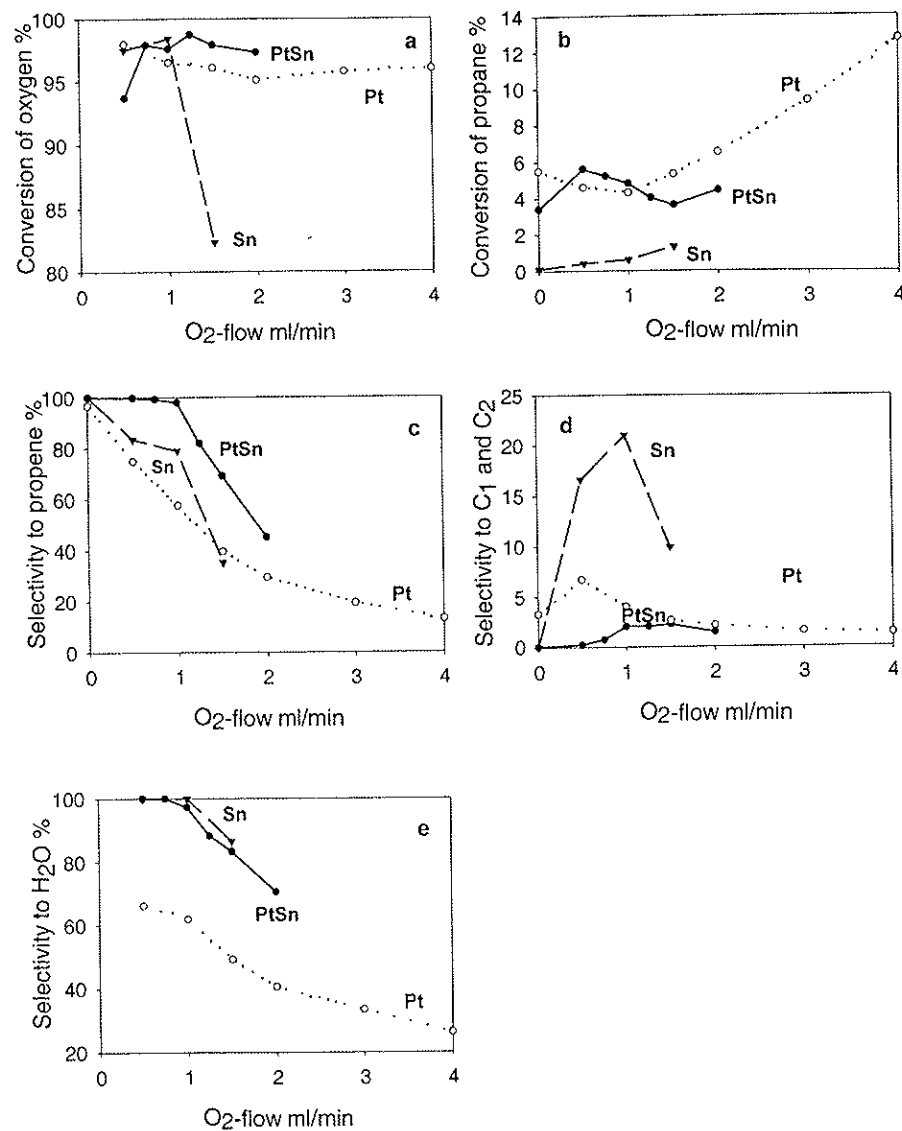


Figure 2. Catalytic combustion over Sn, Pt and PtSn catalysts. a) O₂ conversion b) propane conversion c) selectivity to propene d) Selectivity to C₁ and C₂ e) selectivity to H₂O. Conditions: 550 °C, 1 atm., 0.30 g catalyst, Feed gas: 2 ml/min H₂, 10 ml/min C₃H₈, O₂ as shown in the figure, total flow 100 ml/min, balance is He.

The experiments were conducted with a small amount (2.0 ml/min) of gaseous H_2 in the reactor feed gas to reduce the deactivation and to study the reaction pathway of oxygen in the system.

From Fig. 2a it is evident that the O_2 conversion is high, but not complete for all cases for Pt and PtSn. There is some unconverted oxygen, in the range 4-6% of the oxygen fed to the reactor, and this number is constant, independent of the feed rate and catalyst. This could indicate a by-pass of some of the reactant gas through the catalyst bed, or as indicated by Beretta et al. [8], that the oxygen conversion is limited by diffusion (although their results were obtained in an annular reactor with much higher flow-rates). An empty reactor gave a low oxygen conversion at the same conditions (< 10%). The Sn catalyst was less active for oxygen conversion. Here the conversion is above 95% until the oxygen flow exceeds 1 ml/min, and at 1.5 ml O_2 /min the conversion of oxygen has dropped to 82%. The excess oxygen reacts slowly with propane over the Sn catalyst and therefore the conversion of oxygen decreases when all the hydrogen is consumed.

Fig. 2b shows the propane conversion over the three catalytic systems. The propane conversion initially increases when oxygen is introduced to the PtSn system. This is followed by a drop in the conversion from 5.6% at an oxygen content of 0.5 ml/min to a conversion of 4.0% at an oxygen flow of 1.5 ml/min. When the oxygen feed rate exceeds 1.5 ml/min, the propane conversion increases again. For Pt there is no such initial increase in conversion of propane when oxygen is introduced, but the same decrease in propane conversion as for PtSn is observed as the oxygen flow approaches 1 ml/min. This apparently complex relationship is probably the sum of the two main reactions: The drop in the propane conversion could be explained by deactivation of the catalysts. If the oxygen flow is further increased (above 1 ml/min) the propane conversion rises again. This is due to a steep increase in the formation rate of CO_2 above 1.0 ml/min of oxygen, and the sum of these reactions gives the observed overall consumption of propane.

Sn is not a very active catalyst for converting propane, only about 0.5% (or less) of the propane is converted at oxygen flows lower than 1 ml/min. The selectivity to propene over PtSn (Fig. 2c) is almost complete up to 1 ml/min of O_2 in the feed gas, above this amount the carbon selectivity drops due to the formation of CO and CO_2 . Pt shows lower selectivity to propene than PtSn, and at 1 ml/min oxygen, the selectivity to propene is only 60% compared to almost 100% for PtSn. For Sn, the main product is propene, but significant amounts of cracking products are observed for this catalyst.

In Fig. 2d a selectivity to C_1 and C_2 products as high as 20% at stoichiometric (1 ml/min) amounts of oxygen is reported, but the formation rate of cracking products is rather low since the activity of Sn for the conversion of propane is below 1%. The selectivity to cracking products over Pt and PtSn is much lower than the case is for Sn, the maximum selectivity to cracking products over the Pt catalyst is at 0.5 ml/min oxygen about 7%. For the PtSn catalyst the maximum selectivity to cracking is 2% at oxygen flow rates above 1 ml/min.

Fig. 2e shows the selectivities to H_2O as a function of oxygen flow. Both PtSn and Sn show excellent properties towards producing water from hydrogen and oxygen without producing any CO_x , giving close to 100% selectivity to water as long as the oxygen flow is below 1 ml/min. Pt on the other hand is a less selective catalyst for water formation; at 1 ml/min oxygen the selectivity to water is only about 60%.

Fig. 3 shows the carbon and oxygen selectivities to CO_2 and CO for the same experiments as described in Fig. 2.

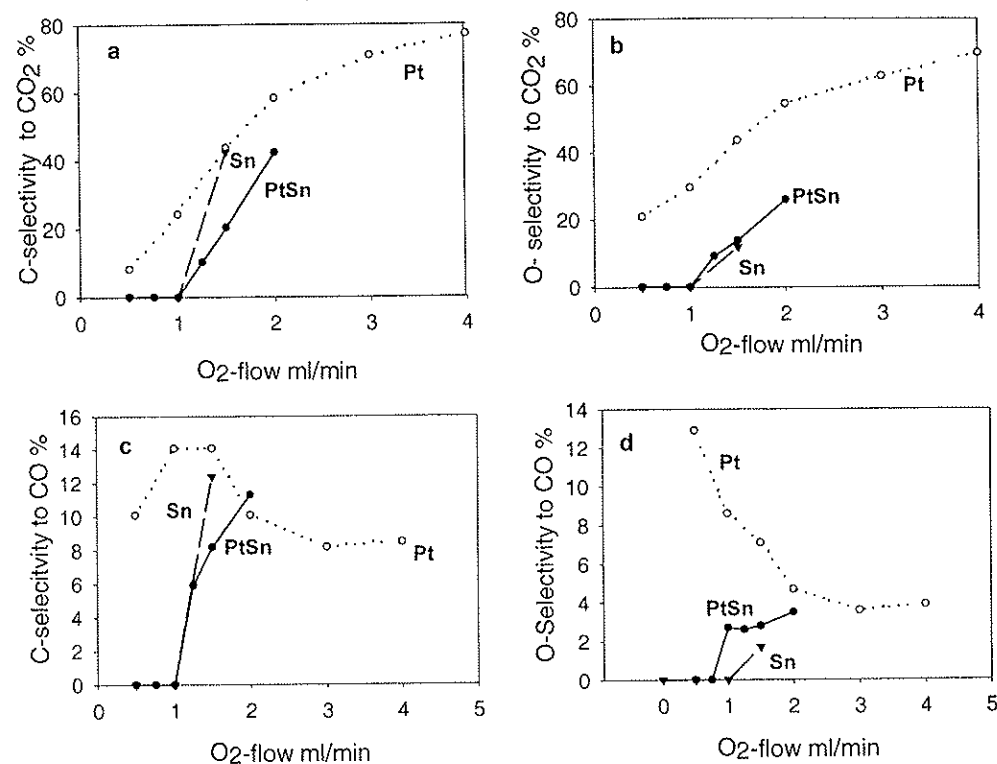


Figure 3. Catalytic combustion over Sn, Pt and PtSn catalysts. a) C-selectivity to CO₂ b) O-selectivity to CO₂ c) C-selectivity to CO d) O-selectivity to CO. Conditions: 550 °C, 1 atm., 0.30 g catalyst, Feed gas: 2 ml/min H₂, 10 ml/min C₃H₈, O₂ as shown in the figure, total flow 100 ml/min, balance is He.

In line with the results shown above, the figure shows that no CO_x is formed for oxygen flow rates below 1 ml/min for PtSn and Sn catalysts. It can again be noted that an oxygen flow of 1 ml/min corresponds to the stoichiometry of the H₂ - O₂ reaction with the H₂ added to the feed. The results confirm that as long as the O₂ is fed to the reactor at a less than stoichiometric amount compared to the molecular hydrogen in the feed according to the reaction $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$, the O₂ reacts selectively with hydrogen to form water. When the oxygen flow is higher than 1 ml/min CO and CO₂ are formed and this eventually becomes the

major reaction pathway. The results indicate that O_2 reacts selectively with hydrogen only under certain conditions, i.e. under a surplus of hydrogen. As soon as this surplus hydrogen is converted, the excess O_2 will react with hydrocarbons in a non-selective manner leading to CO/CO_2 , with a simultaneous drop in the selectivity to propene.

The results in Fig. 3 a-d also show that Pt does not show the same effect concerning selective hydrogen combustion. Already at oxygen flows of 0.5 ml/min significant amounts of CO_2 and CO are produced. The main product is always CO_2 . Over Pt the CO selectivity drops off with increasing O_2 flow, whereas for Sn and PtSn the trend is opposite. This could indicate a higher activity in the CO oxidation reaction over Pt, especially since the CO selectivity drops when excess O_2 is fed to the reactor (> 1 ml/min).

Fig. 4 (550°C) and Fig. 5 (500°C) show results obtained using a gas mixture containing a large fraction of propene, thus simulating a high conversion.

The gas contained propane, propene and hydrogen in a ratio close to fulfilling the equilibrium criterion, to avoid any interchange of propane and propene due to hydrogenation. The flow rate of oxygen was varied from zero to 4 ml/min.

Fig. 4a and Fig. 5a shows that the oxygen conversion is high at all conditions and similar for all the catalysts. The exception is for oxygen flows higher than 1 ml/min over Sn at 500°C, in which the conversion was lower than for the rest of the experiments. This shows that Sn as expected is a poor catalyst for hydrocarbon activation, as previously discussed for the system without propene in the feed (Fig. 2). The oxygen conversions were slightly higher for the propene-rich mixtures than for the system of propane, hydrogen and oxygen. However, also in this case (for all catalysts) is there some unconverted oxygen, in the range 4-6% of the oxygen fed to the reactor. Again, this could indicate a by-pass of some of the reactant gas through the catalyst bed, or that the oxygen conversion is limited by diffusion [8].

Fig. 4b and Fig. 5b show the oxygen-selectivity to water formation. At low oxygen flows the selectivity decreases in the order PtSn $>$ Pt $>$ Sn for both temperatures. The selectivity to water falls dramatically when the oxygen flow is increased. The difference between Pt and PtSn remains constant throughout, whereas for the Sn catalyst the drop in selectivity is less severe. Above 2 ml/min O_2 feed-rate the selectivity to water is in the range 40 - 50% at 550°C and slightly higher at 500°C, which indicates that the hydrocarbons are being combusted, e.g.: C_3H_6 combustion would give a H_2O selectivity (based on consumed O_2) of 33%. At low oxygen flows (less than 1 ml/min), a close to 80% selectivity to water is observed over PtSn at 550°C. A 90% selectivity to water is observed at 500°C over the same catalyst. Sn and Pt are less selective hydrogen combustion catalysts compared to the PtSn catalyst for both temperatures, 500°C giving higher selectivity to water for both catalysts.

Fig. 4c and 4d and Fig 5c and 5d show the selectivities to CO_2 and CO at 550°C and 500°C, respectively. The main product is always CO_2 . As the case was for the experiments without propene in the feed (Fig. 3), the CO selectivity drops off with increasing O_2 flow over Pt, whereas for Sn and PtSn the trend is opposite. This could again indicate a higher activity in the CO oxidation reaction over Pt also at these conditions.

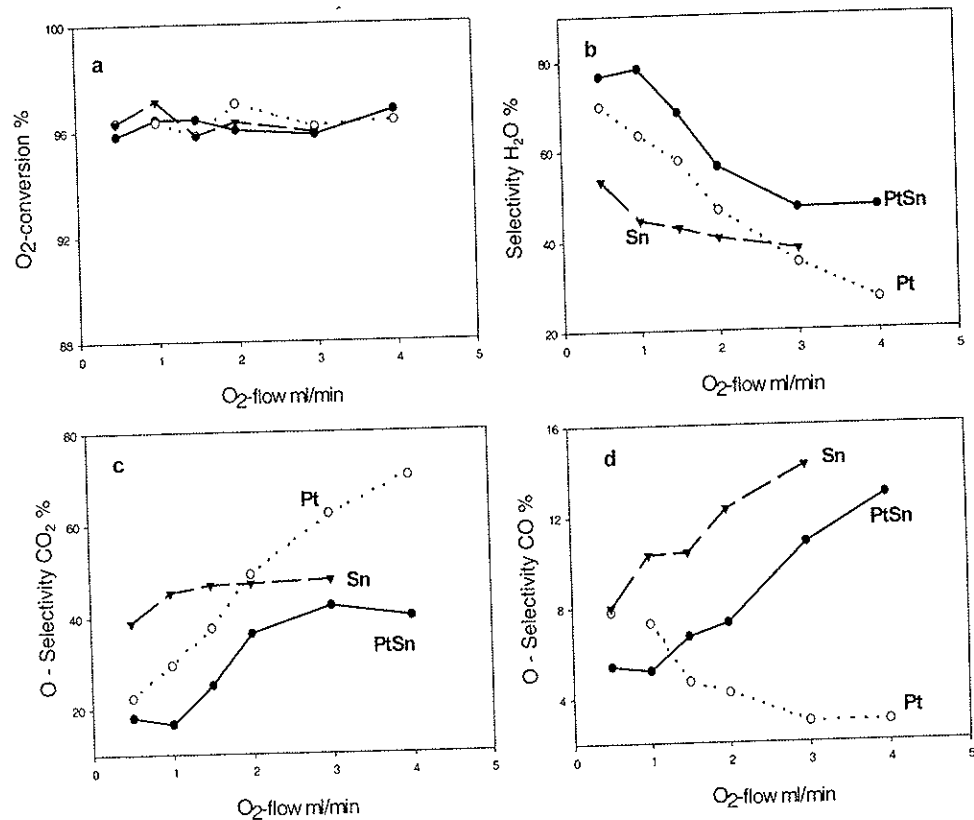


Figure 4. Catalytic combustion over Sn, Pt and PtSn catalysts. a) O₂-conversion b) O-selectivity to H₂O c) O-selectivity to CO₂ d) O-selectivity to CO. Conditions: 550°C, 1 atm., 0.30 g catalyst, Feed gas: 2 ml/min H₂, 5 ml/min C₃H₈, 28.2 ml/min C₃H₆, O₂ as shown in the figure, total flow 100 ml/min, balance is He.

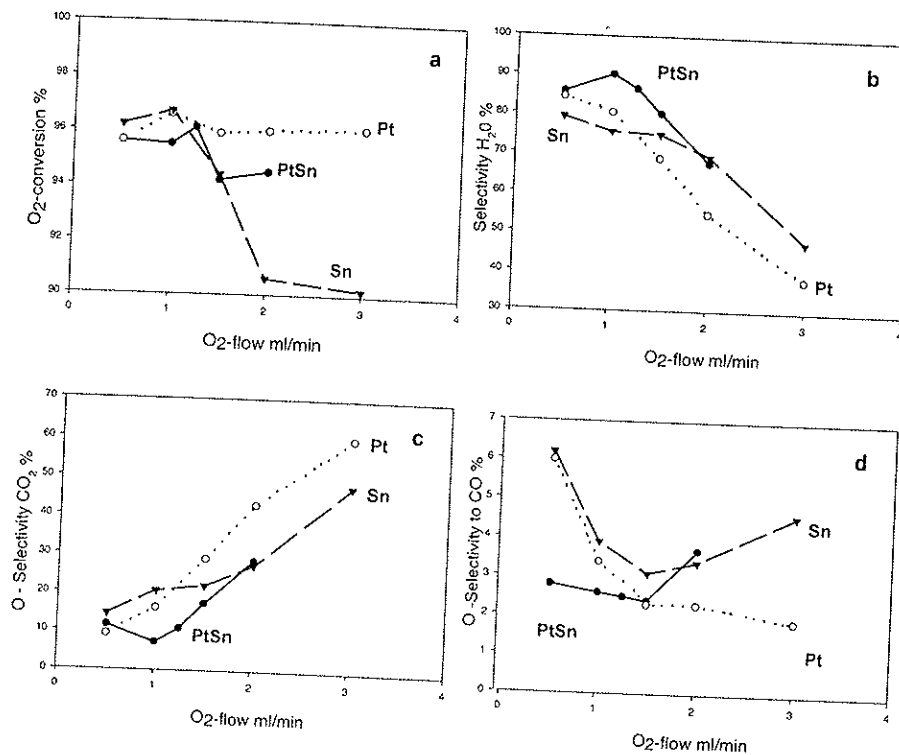


Figure 5. Catalytic combustion over Sn, Pt and PtSn catalysts. a) O₂-conversion b) O-selectivity to H₂O c) O-selectivity to CO₂ d) O-selectivity to CO. Conditions: 500°C, 1 atm., 0.30 g catalyst, Feed gas: 2 ml/min H₂, 5 ml/min C₃H₈, 8.4 ml/min C₃H₆, O₂ as shown in the figure, total flow 100 ml/min, balance is He.

Due to the composition of the feed gas is the main dehydrogenation reaction (1) close to equilibrium, and there is only limited conversion. However, due to side-reactions, mainly cracking/hydrogenolysis type of reactions, and possibly due to different reactivities towards oxygen the hydrocarbon composition is somewhat changed at the reactor outlet. There was no clear trend in the cracking product distribution. It could however be observed over Sn and PtSn that the selectivity to methane in most cases was lower than what would be expected if the C₂ products were formed by a simple C-C bond scission (expect C-selectivity $S_{CH_4} : S_{C_2H_4} = 1:2$). A possible explanation is that the C₁-species is oxidised to carbon oxides, leaving a C₂-unit as a hydrocarbon product.

In Table 1 are listed the product distribution of C₁ and C₂ products for the different catalysts at 550 and 500°C, respectively. Since methane is the most stable hydrocarbon, it is clear that the C₁ species can not desorb as methane, but has to react directly (from an adsorbed

state) after the C-C bond cleavage of the propane/propene. The selectivity to methane over the Pt catalyst at 550°C is higher than what would be expected from a C-C bond cleavage, which is the opposite trend from Sn and PtSn. The explanation for this must be that ethene formed as cracking product is further reacted to CO_x.

Table 1

Product distribution (% C-mole selectivity) to methane and ethene over PtSn, Pt and Sn catalysts. Conditions: 1 atm., 0.30 g catalyst, Feed gas: 2 ml/min H₂, 5 ml/min C₃H₈, 28.2 ml/min C₃H₆ (550°C) and 8.4 ml/min C₃H₆ (500°C), O₂ as shown in the table, total flow 100 ml/min, balance is He. For conversions and other selectivities see Fig. 2 (550°C) and Fig. 3 (500°C).

Temp (°C)	O ₂ - flow (ml/min)	Sn		Pt		PtSn	
		CH ₄	C ₂ H ₄	CH ₄	C ₂ H ₄	CH ₄	C ₂ H ₄
550	0	0	0	1.0	1.0	5.2	6.3
	0.5	2.8	7.8	5.9	5.7	1.3	7.6
	1.0	1.6	4.4	2.8	3.0	1.0	4.0
	1.5	1.2	3.9	2.0	2.0	1.6	6.8
	2.0	1.3	3.8	1.0	1.4	1.3	4.5
	3.0	0.9	3.4	0.6	1.0	1.0	3.0
	4.0	-	-	0.5	0.9	1.0	3.3
500	0	0	0	2.1	3.7	0	0
	0.5	1.6	7.5	3.5	6.5	1.1	9.0
	1.0	1.7	5.4	2.0	2.6	1.4	12.7
	1.25	-	-	-	-	1.2	9.9
	1.5	1.0	4.4	0.8	1.8	0.9	5.2
	2.0	0.8	3.3	0.3	1.0	0	2.5
	3.0	0.3	1.4	0	0.6	-	-

The explanation to why PtSn (and to a certain extent Sn) gives higher selectivity to propene and combusts hydrogen more selectively than does Pt is not clear.

The two main side reactions that usually compete with dehydrogenation are hydrogenolysis and coke formation [12]. These two undesired reactions are more sensitive to the structure of the metal surface than is dehydrogenation [12]. The reason why PtSn preferentially combust hydrogen and Pt does not could as an analogy be speculated to be due to a dilution of the Pt ensembles in PtSn. Sn acts as a diluent, and reduces the formation rate of structure sensitive side products as coking which require large ensembles of Pt. Possibly, the same feature of the surface favours the adsorption and activation of hydrogen in competition with the hydrocarbons.

Another possible explanation is that the addition of Sn provides an electronic effect on the catalyst. The conversion of alkanes is low over pure Sn, which indicates that Sn does not adsorb alkanes in the same extent as Pt. Pure Pt gives high conversions of alkanes, hydrogen and oxygen, especially in the initial parts of the experiments. The conversion of the hydrocarbons over Pt drops off as a function of time, probably due to coke formation. A too strong hydrocarbon adsorption on Pt can explain the low selectivity to the desired products. When a hydrocarbon molecule approaches the catalyst surface of the pure Pt, it adsorbs

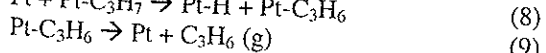
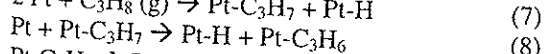
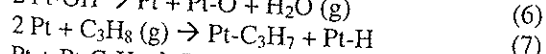
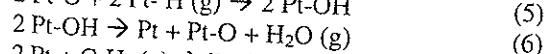
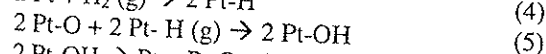
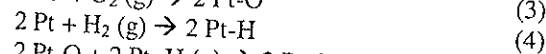
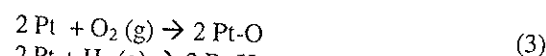
dissociatively and reacts to produce water and an allylic specie which can desorb to produce an alkene. Instead of desorbing as an alkene, the strongly adsorbed intermediate is further oxidized to CO_x . When Sn is added to the Pt catalyst, the adsorption strength between the adsorbent and the catalyst surface is lowered, and at the same time the size of the Pt ensembles are reduced. In this way the desired product can more easily desorb from the catalyst surface. The discussion above is based on the assumption that the reaction involves only adsorbed species. This is however not clear.

We assume that oxygen is strongly adsorbed on Sn, as the case is for the Pt catalyst [14]. Then hydrogen can react directly from the gas phase (Eley-Rideal (ER) mechanism) or from an adsorbed state (Langmuir-Hinshelwood (LH) mechanism). It is, however, difficult to see how a gas-phase attack on adsorbed oxygen should give a complete selectivity towards H_2 combustion. We further assume that alkanes do not adsorb on Sn, since the propane conversion is low over this catalyst, and water is the only oxygenated product as long as there are no alkenes in the system.

For Pt we know that oxygen is strongly adsorbed [13] and then there is a competitive adsorption between hydrogen and hydrocarbons. We assume a LH type of mechanism also for the Pt catalyst. In this catalytic system there are larger ensembles of Pt, which are required for coking and hydrogenolysis to take place. A possible too strong adsorption of the desired product causes a further reaction to undesired products. All this together results in a catalyst with low selectivity to the desired products.

On the PtSn system some of the undesired reactions are inhibited by the presence of Sn: Alkanes do not adsorb on Sn, which means that the production of water is favoured, and at the same time the size of the Pt ensembles are reduced by Sn, which results in reduced amount of coking and hydrogenolysis. The electronic properties of the catalyst are modified by the Sn addition to the Pt catalyst. This results in an increased amount of desired products. When propene is added to the feed, Sn is no longer able to selectively combust hydrogen, which indicates that also propene adsorb on the Sn surface, and the result is lower selectivities to the desired products.

A possible reaction mechanism for the reactions taking place on the PtSn catalyst surface is proposed in the following section:



To explain the selectivity effect the following assumptions are necessary. Oxygen will adsorb on Pt in preference to Sn as long as there is Pt available in the system. Sn does not have an active participation in the catalytic process, but reduces the Pt ensembles and the adsorption strength of the Pt. On pure Sn reactions (3)-(6) will be the same as for Pt, while

reactions (7)-(9) do not take place over this catalyst. A too strong hydrocarbon adsorption to the pure Pt explains the low selectivity to the desired products on this catalyst.

Summary and conclusions

The results show that under certain reaction conditions the selective combustion of hydrogen in the presence of light hydrocarbons over Pt-based catalysts is possible. It seems like tin has a stabilising effect on the catalyst activity, PtSn being more stable than Pt. Both Sn and PtSn seem to be able to selectively combust hydrogen in a gas mixture with propane and oxygen. Pt does not show this quality. If propene is added to the gas mixture, Sn is no longer able to selectively combust hydrogen. PtSn on the other hand combust hydrogen with about 80% selectivity at 550°C and 90% selectivity at 500°C as long as the oxygen flow is less than half the amount of hydrogen. As soon as the oxygen flow exceeds half the amount of hydrogen, the selectivity to CO_x increases at the expense of water. A Langmuir-Hinshelwood type of reaction mechanism is proposed over the Pt, Sn and PtSn catalysts. It is also proposed that oxygen is strongly adsorbed on both Pt and Sn, but the adsorption on Pt is preferred to Sn as long as there is Pt available in the system. Alkanes are strongly adsorbed on Pt, but do not adsorb on Sn, in contrast to alkenes that adsorb on all the catalysts. Sn reduces the Pt ensembles and the adsorption strength of the Pt, and as a consequence reduces the formation of the undesired products

Acknowledgements

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References

1. See e.g. E.A. Mamedov and V. Cortés Corberán, *Appl. Catal. A*, 127 (1995) 1.
2. C.P. Tagmolila, US Patent No. 5043500 (1991).
3. T. Lægroid, M. Rønnekleiv and Å. Solbakken, *Ber.-Deutsch. Wiss.Ges. Erdöl, Erdgas Kohle, Tagungsber.* 9305 (1993) 147.
4. P.A. Agaskar, R.K. Grasselli, J.N. Michaels, P.T. Reischman, D.L. Stern and J.G. Tsikoyannis, US Patent No. 5430209 (1995).
5. J.G. Tsikoyannis, D.L. Stern and R.K. Grasselli, *J. Catal.*, 184 (1999) 77.
6. R.K. Grasselli, D.L. Stern and J.G. Tsikoyannis, *Appl. Catal. A*, 189 (1999) 1
7. R.K. Grasselli, D.L. Stern and J.G. Tsikoyannis, *Appl. Catal. A*, 189 (1999) 9
8. A. Beretta, L. Piovesan and P. Forzatti, *J. Catal.*, 184 (1999) 455.
9. A. Beretta, M.E. Gasperini, G. Treopiedi, L. Piovesan and P. Forzatti, *Stud. Surf. Sci. Catal.*, 119 (1998) 659.
10. R. Burch and E.M. Crabb, *Appl. Catal. A: General*, 100 (1997) 111.
11. O.A. Bariás, E.A. Blekkan and A. Holmen, *J. Catal.*, 956, 1 (1995)

12. W. Yang, L. Lin, Y. Fan and J. Zang, *Catal. Letters*, 12(1992) 267
13. A. Holmen, "Heterogen Katalyse", Laboratory of Industrial Chemistry, NTNU, Trondheim, Norway, (1996)
14. D. A. King and D. P. Woodruff, "The Chemical physics of solid surfaces and heterogeneous catalysis", Volume 4, Elsevier scientific publishing company, (1982)

Paper IV

Selective combustion of hydrogen in the presence of hydrocarbons

2. Metal oxide based catalysts

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Abbreviated title: SHC over oxide based catalysts

Keywords: In, Bi, Pb, propane, propene, dehydrogenation, selective hydrogen combustion

Abstract

The selective hydrogen combustion properties of some metal-oxide catalysts have been investigated at 500 and 550°C and atmospheric pressure. This reaction is of importance in the development of new dehydrogenation technology based on partial combustion of hydrogen to provide *in situ* heat generation to the endothermic dehydrogenation processes. Selective hydrogen combustion in the presence of light hydrocarbons is possible under certain reaction conditions for some catalysts. $\text{In}_2\text{O}_3/\text{SiO}_2$ and unsupported Bi_2O_3 is able to selectively combust hydrogen in a gas mixture with propane and oxygen, whereas $\text{Bi}_2\text{O}_3/\text{SiO}_2$ and $\text{PbO}_x/\text{SiO}_2$ show moderate properties as selective hydrogen combustion catalysts, and $\text{Cr}_2\text{O}_3/\text{SiO}_2$ and VMgO are rather ineffective as SHC catalysts. When propene is added to the gas mixture, $\text{Bi}_2\text{O}_3/\text{SiO}_2$ and $\text{PbO}_x/\text{SiO}_2$ are no longer able to selectively combust hydrogen. $\text{In}_2\text{O}_3/\text{SiO}_2$, on the other hand, combust hydrogen with 90% selectivity at low oxygen flows, and with 80% selectivity at stoichiometric amounts (to water) of oxygen. Unsupported Bi_2O_3 combusts hydrogen with 60% selectivity independent of the oxygen flow. $\text{In}_2\text{O}_3/\text{SiO}_2$ and $\text{Bi}_2\text{O}_3/\text{SiO}_2$ are found to be the most active catalysts for the conversion of oxygen.

Introduction

The catalytic dehydrogenation of light alkanes like propane and butane is growing in importance, in the case of propane due to an imbalance between the growth in demand for propene and ethene. The selective production of propene via catalytic dehydrogenation, reaction (1), is difficult to do economically using the existing process technology.



The strong endothermic character of the equilibrium limited reaction (1) ($\Delta H_{873K}^0 = 124$ kJ/mole) demands a high reaction temperature, low pressure or strong dilution (often with steam) to achieve high conversions. In addition is the propane - propene separation difficult and energy consuming due to a small boiling-point difference, thus making the recycling of unconverted reactant more expensive. Oxidative dehydrogenation (ODH) according to reaction (2), which is exothermic and without equilibrium limitations at normal conditions has been studied as an alternative, but so far there has been no breakthrough in the search for catalysts providing the necessary yield of propene [1].



The main problem is the lack of selectivity due to complete combustion, especially of the more reactive alkene.

A recently adapted idea as an alternative to the ODH for obtaining olefin yields higher than equilibrium and for making the total process heat balanced or exothermic is the selective hydrogen combustion (SHC) [2-7]. If the heat consumed in the endothermic dehydrogenation is balanced with the heat provided by selective hydrogen combustion it can be termed autothermal dehydrogenation (ADH) [3]. It turns out that ADH can be achieved by combustion of about half of the hydrogen formed in the dehydrogenation reaction in the reactor itself.

In the ADH process as published by Statoil [3], alternating zones of dehydrogenation (DH) and selective hydrogen combustion (SHC) was suggested. Over a Sn-Pt-Cs/ZnAl₂O₄ catalyst at 600°C and atmospheric pressure, 95% selectivity to propene at a 38% conversion of propane was reported. They also developed a new catalyst system with high surface area and with Pt as the active metal and produced a stable catalyst that achieved 96% selectivity to propene at 59% conversion of propane.

Grasselli et al. [5-7] have in several papers investigated catalysts for SHC. Several catalyst candidates (metal oxides and mixed metal oxides) were compared using a gravimetric investigation of reduction rates in hydrogen and hydrocarbon gases respectively [5]. From these experiments they proposed that materials that were more reactive towards hydrogen compared to propane or propene were suitable SHC catalysts, and they identified materials like Bi₂O₃, Bi₂Mo₃O₁₂, In₂O₃, In₂Mo₃O₁₂, Sb₂O₄ and WO₃ (all supported on SiO₂) as candidates. In a catalytic experiment Bi₂O₃/SiO₂ was exposed to alternate pulses of hydrogen/propane followed by oxygen. In this red-ox mode a high conversion of hydrogen and virtually no conversion of propane was observed, the hydrogen reacting with lattice oxygen to form water. This catalyst was also tested successfully in co-feed experiments, both with propane and propene as the hydrocarbon compound in the gas phase. In separate papers this and other catalysts were tested in co-feed mode in a reactor set-up arranged in series (DH-SHC-DH) [6], and in the red-ox mode a mixed catalyst phase [7], both with very promising results.

In a recent study [8,14], using a continuous reactor set-up, we have shown that it is possible to combust hydrogen in a gas mixture with propane and propene with a 90% selectivity to water when a Pt-Sn/SiO₂ catalyst is used at 500°C. If propane is the only hydrocarbon in the feed, the selectivity to water is close to 100% as long as there is excess hydrogen available in the system. The same selective hydrogen combustion as for Pt-Sn was also shown for Sn, while the pure Pt/SiO₂ catalyst was less selective.

In this paper we will show results of experiments performed with the aim of exploring the selective hydrogen combustion (SHC) properties for some metal oxide systems in a similar setup. We have been studying the SHC properties using a gas mixture of propane, oxygen and

hydrogen but we have also been interested in the selectivity in the presence of large amounts of propene (simulating high conversions). Experiments have been performed at 500°C and 550°C.

Experimental

Several different catalytic systems were prepared and tested. The VMgO catalyst, a system optimized for ODH, was prepared by impregnating $Mg(OH)_2$ with an aqueous solution of NH_4VO_3 . The solution was refluxed using a rotavapor for 16 hours at 70°C before the water was removed by distillation. The vanadium: magnesium atomic ratio was chosen to be 0.32, an optimum ratio for ODH [9]. The catalyst was dried for 12 hours at 120°C before it was calcined at 550°C for 9 hours with a ramp rate of 5°C/min from room temperature using an airflow of 50 ml/min (GHSV = 0.35). The preparation procedure is in accordance with the procedure given by Pantazidis and Mirodatos [9].

Bi_2O_3/SiO_2 , In_2O_3/SiO_2 , Cr_2O_3/SiO_2 and PbO_x/SiO_2 were prepared by refluxing aqueous solutions of the appropriate metal nitrates in the presence of silica (Merck Kieselgel 60, $S_{BET} = 483 \text{ m}^2/\text{g}$, particle size 0.063 - 0.2 mm). 50 wt% of the salts and 50 wt% of silica were used for both cases. In the preparation of Bi_2O_3/SiO_2 , HNO_3 was added to the solution in order to aid the solubility of bismuth-nitrate. An unsupported bismuth catalyst was prepared in the same way as the other catalysts, but in the absence of silica and HNO_3 . The resulting slurries were refluxed for 16 hours at 70°C, and dried at 120°C for 12 hours. The catalysts were then calcined at 600°C for 12 hours with a ramp rate of 5°C/min from room temperature using an airflow of 50 ml/min (GHSV=0.35 l/g h).

The oxide catalysts were characterized by XRD (Phillips 1710 spectrometer equipped with a graphite crystal monochromator, using $Cu \text{ K}\alpha$ radiation).

The BET surface area measurements were performed using a Carbo Erba Multisampler 1900 apparatus using liquid nitrogen at its boiling point. The samples were evacuated and dried at 150°C prior to the surface area measurements.

Catalytic test

The reactions were studied in a fixed bed quartz micro-reactor (U-shaped) with an inner diameter of 3.5 mm. The reactions were carried out at atmospheric pressure using air as the oxidant. The catalyst loading was varied between 0.11 and 0.25g in the experiments. The reactor was placed in an electrical furnace, and the temperature was controlled using external and internal thermocouples. The temperature used in the experiments was 500°C or 550°C. The total flow rate was 100 ml/min with varying compositions of propane, air, propene, hydrogen, the balance being helium. Gases were premixed and fed to the reactor using electronic mass flow controllers (Bronkurst). The product gas was analysed for hydrocarbons ($C_1 - C_4$) and for permanent gases (O_2 , N_2 , CO , CO_2) by GC. The chromatograph used was a Perkin Elmer autosystem XL equipped with a TCD (Carbosieve SII, 10ft, mesh 80) and a FID (PorapLOT Q, 27.5 m, i.d. 0.53mm). Water and hydrogen produced are not analysed by the GC, but were calculated through mass balances. In some of the experiments the catalyst was pre-reduced for 2 hours at reaction temperature with a hydrogen flow of 15 ml/min.

Results and discussion

Catalysts

Table 1 shows some characterization data for the catalysts used.

Table 1
Surface area (BET) and crystal structure (XRD) data for the catalysts.

Catalyst	Support	Surface area (BET) (m ² /g _{cat})	Crystal structure (XRD)
SiO ₂	-	483	n.d.
Bismuth-oxide	SiO ₂	242	Bi ₂ O ₃ (rombic)
Bismuth-oxide	none	n.d.	n.d.
Indium-oxide	SiO ₂	278	In ₂ O ₃ (cubic)
MgVO	none	38	MgO/Mg ₃ V ₂ O ₈
PbO _x	SiO ₂	120	amorphous
Chromium-oxide	SiO ₂	330	Cr ₂ O ₃ (rombohedral)

The XRD results for bismuth oxide and indium oxide are the same as observed by Grasselli et al. [6], but the result from the XRD on PbO_x are not the same. They found a crystalline phase of Pb₃O₄ to be the active phase in the catalyst, while an amorphous was observed in this study. The preparation procedure used in this work was as close as possible the procedure Grasselli et al. [6] used in their work. The XRD-lines found for the MgVO catalyst were the same as those observed by Creaser and Andersson [10], but in our study there are also indications of magnesium pyrovanadate crystallites in the catalyst.

Empty reactor

The possibility of gas-phase reactions was investigated using a gas flow consisting of 10 ml/min C₃H₈, 2 ml/min H₂, 2 ml/min O₂, balanced by He to total flow of 100 ml/min. There was no significant conversion of propane at temperatures below 600°C in the empty reactor. The oxygen conversion gradually increased as the temperature was increased from ambient, and at about 550°C the conversion was 10%. The results are in good agreement with the work of Beretta et al. [11, 12], whereas Burch and Crabb [13] observed propane conversion in the empty reactor already at 550°C. The main difference between our experiments compared to the results of the other groups, is that we had a co-injection of hydrogen in the feed.

Experiments with propane, hydrogen and air

The results using the silica support as catalyst was about the same as observed for the empty reactor at 500°C, 3-7 % conversion of oxygen and total conversion to water.

50 wt%-In₂O₃/SiO₂ was found to be the most active and selective catalysts for the SHC under these conditions. In Fig. 1 the activity and selectivity data for the indium catalyst are shown as a function of oxygen flow for two temperatures.

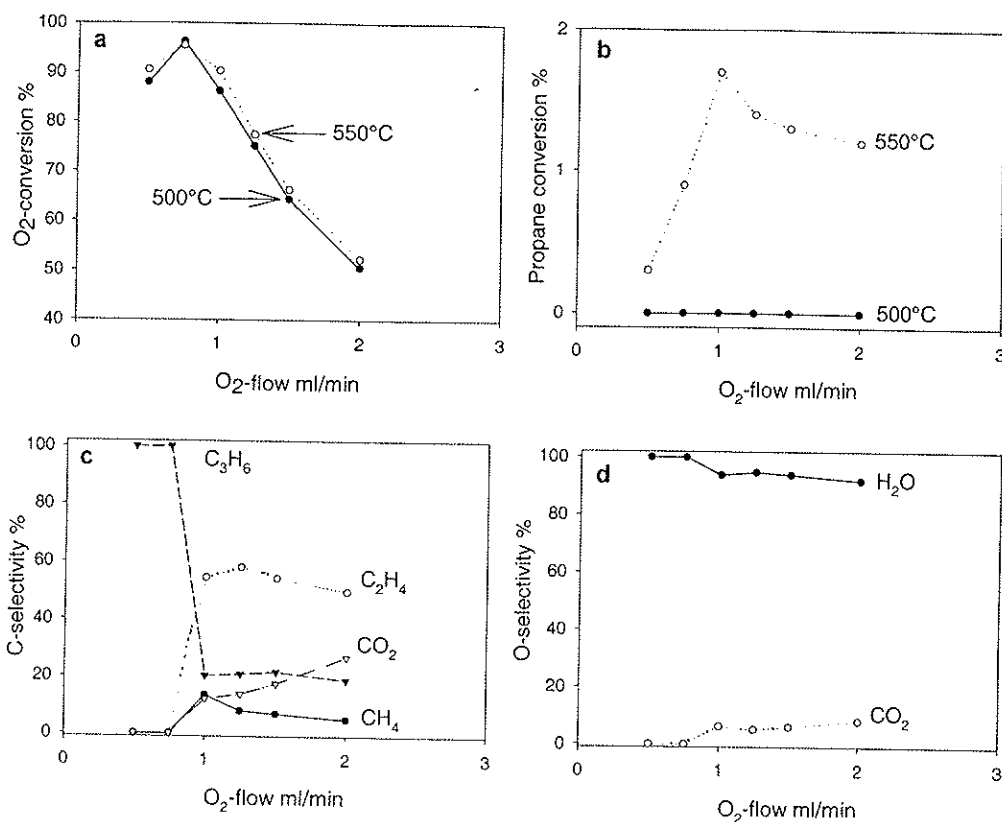


Figure 1. Catalytic combustion over $\text{In}_2\text{O}_3/\text{SiO}_2$. a) O_2 conversion b) propane conversion c) C-selectivity d) O-selectivity. Conditions: 500°C (●), 550°C (○), 1 atm, 0.11g catalyst, Feed gas: 2 ml/min H_2 , 10 ml/min C_3H_8 , O_2 as shown in the figure, total flow 100 ml/min, balance is He.

The oxygen conversion is above 90% until all the hydrogen is combusted, water (and propene) being the only products. It can be noted that an oxygen flow of 1 ml/min corresponds to the stoichiometry of the $\text{H}_2 - \text{O}_2$ reaction with the co-fed H_2 . If the oxygen flow was further increased (above the stoichiometry to water), some CO_2 was formed at 550°C. No CO was observed over this catalyst. The selectivity to water was 100% at 500°C, and above 90% for all oxygen flows at 550°C. The conversions of propane over the indium catalyst are also shown in the plot, and one can see that there was no conversion of propane at 500°C. There was some conversion in the range 1-2% at 550°C, giving ethene, propene, CO_2 and methane as the main products. The cracking of propane to ethene and methane seems to be the main products from the propane conversion at high O_2 -flows.

In Fig. 2 are shown the data for the Bi_2O_3 catalysts (unsupported Bi_2O_3 and 50wt% $\text{Bi}_2\text{O}_3/\text{SiO}_2$) at 500°C and 550°C. The unsupported Bi_2O_3 shows an excellent ability to preferentially attack hydrogen in the presence of propane, but its activity is not as high as the case is for the indium catalyst. From Fig. 2a one can see that the drop in oxygen conversion is extensive with an increase in the oxygen flow for both temperatures. Water is the only product formed over the unsupported bismuth at both temperatures, which means there is no conversion of propane over this catalyst. An experiment with 50wt% $\text{Bi}_2\text{O}_3/\text{SiO}_2$ at 500°C was also performed. About 80% selectivity to water was obtained throughout the experiment (the rest being CO_2), compared to a 100% selectivity to water over the unsupported Bi_2O_3 .

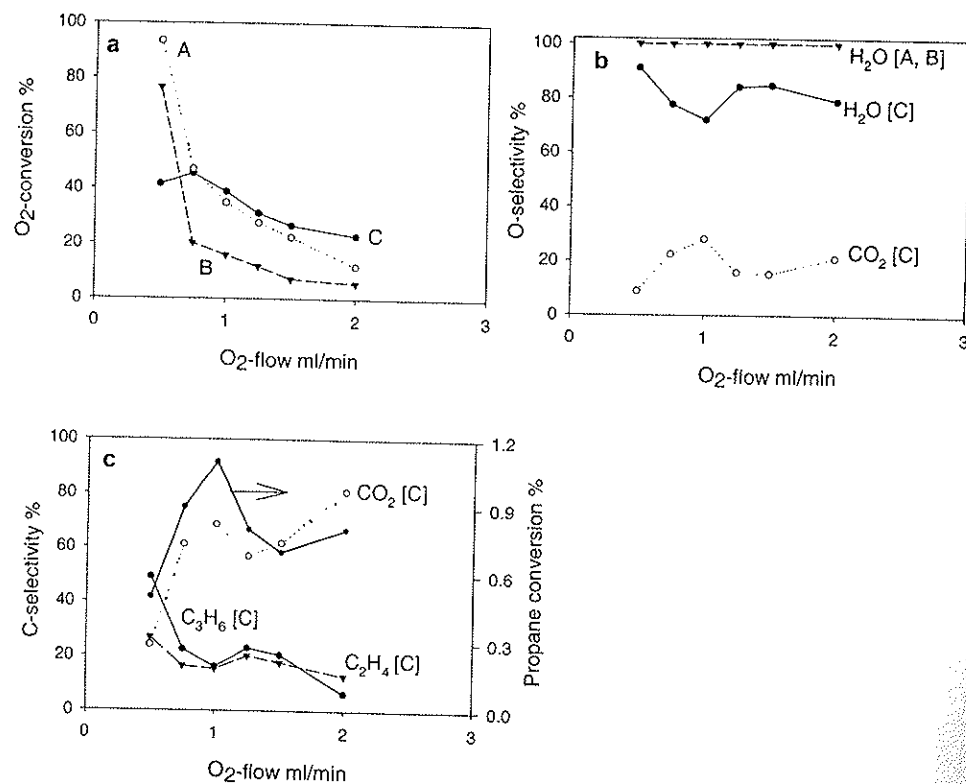


Figure 2. Catalytic combustion over bismuth-oxide. a) O₂ conversion b) O-selectivity c) C-selectivity/propane conversion. Conditions: 1 atm, 0.11g catalyst, Feed gas: 2 ml/min H₂, 10 ml/min C₃H₈, O₂ as shown in the figure, total flow 100 ml/min, balance is He.
 A: Bi_2O_3 (unsupported), 550°C
 B: Bi_2O_3 (unsupported), 500°C
 C: 50 wt-% $\text{Bi}_2\text{O}_3/\text{SiO}_2$, 500°C

The oxygen flow was increased throughout the experiment, which means that the x-axis also indicates the oxygen conversion as a function of time on stream. It is thus possible that the different response to increased O₂ flow also reflects a difference in the deactivation of the supported/unsupported catalysts (Fig. 2a, curve B & C). Pre-reduction gave no significant changes in the behaviour of the catalyst.

The results for 50wt% PbO_x/SiO₂ at 500°C are shown in Fig 3. This catalyst showed a low activity for oxygen conversion, and at the same time a relatively low selectivity to water.

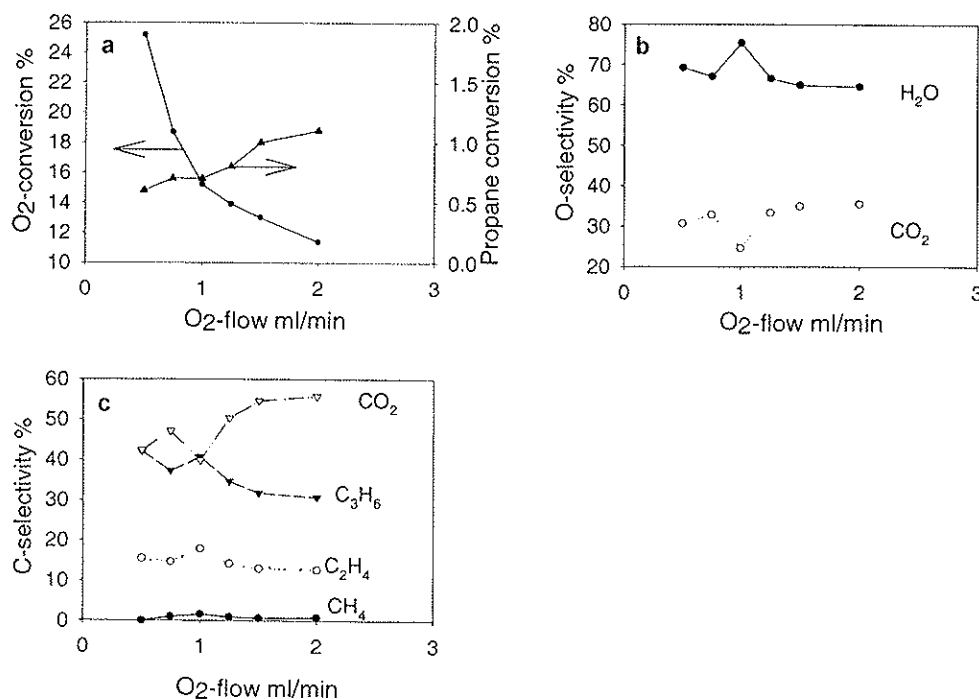


Figure 3. Catalytic combustion over 50 wt-% PbO_x/SiO₂. a) O₂ conversion/propane conversion b) O-selectivity c) C-selectivity. Conditions: 500°C, 1 atm, 0.11g catalyst, Feed gas: 2 ml/min H₂, 10 ml/min C₃H₈, O₂ as shown in the figure, total flow 100 ml/min, balance is He.

The selectivity to water is between 70 and 65%, the rest being CO₂. As the oxygen flow increased the conversion dropped from 25 to 11% with increasing oxygen pressure still giving a total increase in the reaction rate of oxygen. There was no effect from pre-reducing the catalyst.

Two catalysts showed very poor SHC properties. Both chromium- and magnesium-vanadium oxide catalysts gave close to pure combustion of the propane, resulting in about

55% selectivity to CO₂, 35% selectivity to water, and small amounts of CO (in the range 3-7%). The conversion of oxygen over the chromium catalyst was complete for all oxygen flows and the conversion of propane was increasing from about 5 to 15% as the oxygen flow increased. No changes were observed in the product distribution during the run. There was no effect of pre-reducing the chromium catalyst. The oxygen conversion over the VMgO catalyst was somewhat lower than for the chromium catalyst, decreasing from 70 to 50% as the oxygen flow was increased from 0.5 to 1.5 ml/min, corresponding to an increase in the rate of oxygen consumption. It is obvious that MgVO and Cr₂O₃ are rather ineffective as SHC catalysts and can not be used for such a purpose.

It could be observed for several of the catalysts that the selectivity to methane was lower than what would be expected if the C₂ products were formed by a simple C-C bond cleavage of propane/propene. A possible explanation is that the C₁-species is oxidised to carbon oxides, leaving a C₂-unit as a hydrocarbon product. In Table 2 are listed the product distribution of C₁ and C₂ products for the different catalysts. Since methane is the most stable hydrocarbon, it is clear that the C₁ species can not desorb as methane, but has to react directly (possibly from an adsorbed state) after the C-C bond cleavage of the propane/propene. A similar effect was also observed previously over Pt-based catalysts [8,14].

Table 2
Product distribution (% C-mole selectivity) to methane and ethene over Cr₂O₃, 50 wt% Bi₂O₃/SiO₂, ZSM-5 and PbO_x. Conditions: 500°C, 1 atm., 0.11 g catalyst, Feed gas: 2 ml/min H₂, 5 ml/min C₃H₈, O₂ as shown in the table, total flow 100 ml/min, balance is He. For conversions and other selectivities see Fig. 1- Fig. 4.

O ₂ - flow (ml/min)	In ₂ O ₃ (*)		Bi ₂ O ₃ /SiO ₂		PbO _x	
	CH ₄	C ₂ H ₄	CH ₄	C ₂ H ₄	CH ₄	C ₂ H ₄
0.5	0.0	0.0	0.0	26.8	0.0	15.5
0.75	0.0	0.0	0.0	16.3	1.0	14.7
1.0	13.4	54.4	0.0	15.3	1.6	17.9
1.25	7.9	58.0	0.0	20.1	0.9	14.2
1.5	6.9	54.2	0.0	17.7	0.7	13.0
2.0	4.9	49.6	0.0	12.8	0.8	12.7

(*) Experiment performed at 550°C

Simulated high conversion

Experiments with a mixture of propane, a high concentration of propene and hydrogen at 500°C over different catalysts have been performed to study the competitive reaction between hydrogen and propene towards oxygen.

The catalysts tested at these conditions include In₂O₃/SiO₂, unsupported Bi₂O₃, 50% Bi₂O₃/SiO₂ and PbO_x/SiO₂. The main results are shown for all the catalysts in Fig. 4. In₂O₃/SiO₂ and 50% Bi₂O₃/SiO₂ give close to total conversion of oxygen for all oxygen flows. There is, however, some unconverted oxygen in the range 3-5% of the oxygen fed to the reactor. This could indicate a by-pass of some of the reactant gas through the catalyst bed, or as indicated by Beretta et al.[11], that the oxygen conversion is limited by diffusion (although their results were obtained in an annular reactor with much higher flow-rates). In₂O₃ shows qualities of being a good SHC catalyst. 90% selectivity (based on oxygen) to water was

obtained at low oxygen flows (0.5 ml/min) and an oxygen selectivity of 80% is obtained at stoichiometric amounts (1 ml/min) of oxygen. Indium is the only catalyst in which the selectivities to the products change as a function of the oxygen flow. As the oxygen flow increases, the production of CO_x becomes more and more pronounced.

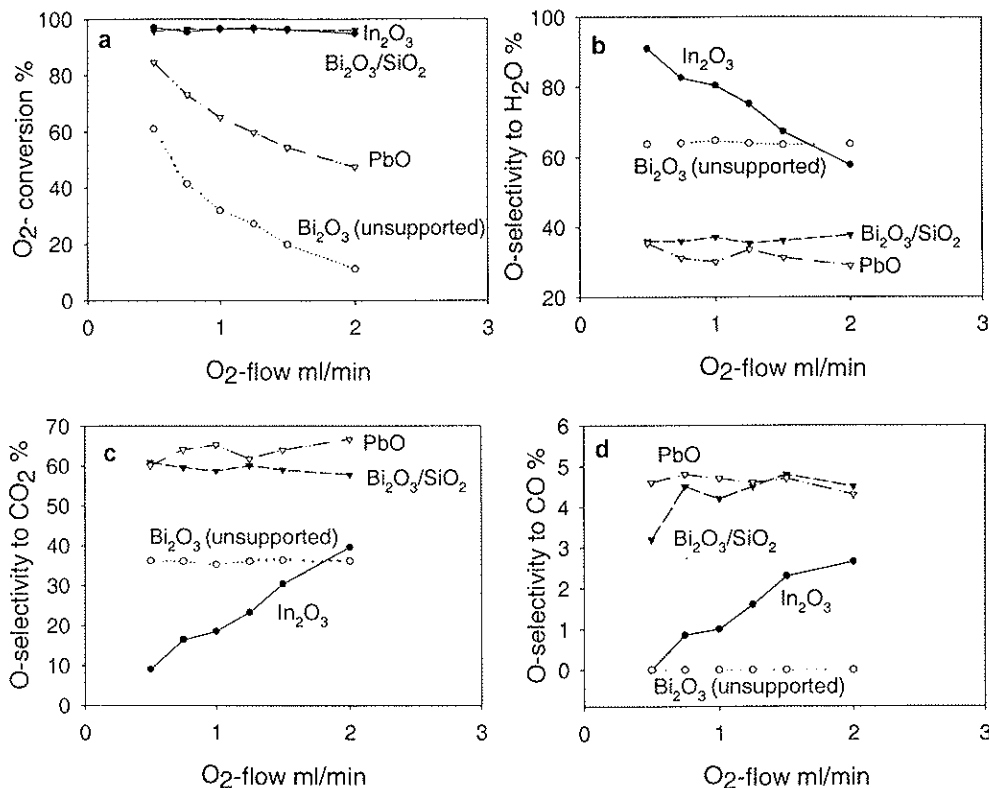


Figure 4. Catalytic combustion over $\text{In}_2\text{O}_3/\text{SiO}_2$, Bi_2O_3 (no support), 50 wt-% $\text{Bi}_2\text{O}_3/\text{SiO}_2$ and 50 wt-% $\text{PbO}_x/\text{SiO}_2$. a) O_2 conversion b) O-selectivity to H_2O c) O-selectivity to CO_2 d) O-selectivity to CO . Conditions: 500°C, 1 atm, 0.11g catalyst, Feed gas: 2 ml/min H_2 , 5 ml/min C_3H_8 , 8.4 ml/min C_3H_6 , O_2 as shown in the figure, total flow 100 ml/min, balance is He.

All the other catalyst reported in Fig. 4 show close to constant selectivities for all oxygen flows and can be said to be independent of the oxygen partial pressure. Unsupported Bi_2O_3 gives 65% selectivity to water and 35% selectivity to CO_2 for all oxygen flows for the equilibrium mixture of propane, propene and hydrogen. It follows that the rate of H_2 oxidation is higher than the rate of propene oxidation, and that the relative oxidation rates are constant throughout the experiment, irrespective of oxygen flows. 50% $\text{Bi}_2\text{O}_3/\text{SiO}_2$ and $\text{PbO}_x/\text{SiO}_2$ do not show any tendency towards the selective combustion of hydrogen preferentially to propene. About 60% selectivity to CO_2 is found for these catalysts, which indicates combustion of propene. A complete combustion of propene gives according to Eq. 3 a 66%

oxygen selectivity to CO₂ and 33% selectivity to H₂O. The corresponding partial oxidation to CO (Eq. 5) gives 50% CO and 50% H₂O from the oxygen balance. Since the selectivity to CO₂ is above 60% over the PbO_x and supported bismuth catalysts, and there also is some CO formed, the rate of hydrogen combustion must be close to zero over these catalysts. From Eq. 3- Eq. 5 and by using the product selectivities (Fig. 4) the contribution to the water production from each of the reactions was calculated. From Fig. 4b-Fig. 4d the selectivities of H₂O, CO₂ and CO over Bi₂O₃/SiO₂ at 1 ml/min oxygen are found to be 37%, 58% and 4, respectively.



From this it is calculated that 76% of the H₂O production can be related to Eq. 3, 13% related to Eq. 4 and the last 11% from Eq. 5. In other words, water production from total combustion of propene to CO₂ is about 6 times faster than the combustion of hydrogen over the Bi₂O₃/SiO₂ catalyst. A similar result was also found for the PbO_x/SiO₂ catalyst.

The reason for the different behaviour of the indium catalyst compared to the others is not yet understood. It has been suggested [6,7] that the SHC properties of the metal oxides are linked with a certain electron configuration. Our most selective catalyst, In₂O₃/SiO₂ does not have any free [s²] electron pairs in the outer shell (In has electron configuration [Kr 4d¹⁰ 5s² 5p¹]. Pb²⁺ and Bi³⁺, on the other hand have free [s²] electronpairs in their oxidized state (Pb has electron configuration [Xe 4f¹⁴ 5d¹⁰ 6s² 6p²] and Bi [Xe 4f¹⁴ 5d¹⁰ 6s² 6p³]). It is therefore possible that the two free [5s²] electrons in Pb²⁺ and Bi³⁺ may affect the catalytic properties of the metals in a way that favour the adsorption and total combustion of propene over the combustion of hydrogen. However, firm conclusions on these issues can only be drawn based on characterization of the oxidation state of these metals at reaction conditions.

Summary and conclusions

The results show that over some catalysts the selective combustion of hydrogen in the presence of light hydrocarbons is possible under certain reaction conditions. In₂O₃/SiO₂ and unsupported Bi₂O₃ show the ability to combust hydrogen in a gas mixture with propane and oxygen with good selectivity. Bi₂O₃/SiO₂ and PbO_x/SiO₂ show moderate properties as selective hydrogen combustion catalysts, and Cr₂O₃/SiO₂ and VMgO are ineffective as SHC catalysts. If propene is added to the gas mixture, Bi₂O₃/SiO₂ and PbO_x/SiO₂ are no longer able to selectively combust hydrogen. In₂O₃/SiO₂, on the other hand, combusts hydrogen with 90% selectivity at low oxygen flows, and with 80% selectivity at stoichiometric amounts (to water) of oxygen. Bi₂O₃ (no support) combusts hydrogen with 60% selectivity independent of the oxygen flow. In₂O₃/SiO₂ and Bi₂O₃/SiO₂ are found to be the most active catalysts for the conversion of oxygen.

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References

1. See e.g. Mamedov E.A. and Cortés Corberán V., *Appl. Catal. A*, 127 (1995) 1.
2. Tagmolila C.P., US Patent No. 5043500 (1991).
3. Læg Reid T., Rønnekleiv M. and Solbakken Å., *Ber.-Deutsch. Wiss.Ges. Erdöl, Erdgas Kohle, Tagungsber.* 9305 (1993) 147.
4. Agaskar P.A., Grasselli R.K., Michaels J.N., Reischman P.T., Stern D.L. and Tsikoyannis J.G., US Patent No. 5430209 (1995).
5. Tsikoyannis J.G., Stern D.L. and Grasselli R.K., *J. Catal.*, 184 (1999) 77.
6. Grasselli R.K., Stern D.L. and Tsikoyannis J.G., *Appl. Catal. A*, 189 (1999) 1
7. Grasselli R.K., Stern D.L. and Tsikoyannis J.G., *Appl. Catal. A*, 189 (1999) 9
8. Lâte L., Runderheim J.-I. and Blekkan E. A., *Stud. Surf. Sci. Cat.* 136(2001) 289
9. Pantazidis A. and Mirodatos C., 11th International Congress on Catalysis-40th Anniversary, *Studies in Surface Science and Catalysis*, 101, 1029 (1996)
10. Creaser D. and Andersson B., *Appl. Catal. A: General* 141 (1996) 131
11. Beretta A., Piovesan L. and Forzatti P., *J. Catal.*, 184 (1999) 455.
12. Beretta A., Gasperini M. E., Treopiedi G., Piovesan L. and Forzatti P., *Stud. Surf. Sci. Catal.*, 119 (1998) 659.
13. Burch R. and Crabb E. M., *Appl. Catal. A: General*, 100 (1997) 111.
14. Lâte L., Runderheim, J. I. and Blekkan E. A., in preparation