NTNU – Trondheim
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Catalytic Dehydrogenation of Propane

Oxidative and Non-Oxidative Dehydrogenation
of Propane

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PREFACE

This rapport is about the catalytic dehydrogenation of propane. It was done at the Norwegian University of Science and Technology (NTNU) in Trondheim, in the catalytic group, during the spring 2012. This work is the second part of a more complete study. During the fall 2011, a specialization project was done on the same topic, with the comparison of three kinds of catalytic supports. One of these catalysts was chosen for this work. Some results established during the project were used in this report. The main topic of this work was to compare the catalytic dehydrogenation of propane with different feed gas in a system, and to compare oxidative and non-oxidative propane dehydrogenation.

I want to thank my supervisor Professor Edd Anders Blekkan for his guidance and his availability during all this year. He has been a great support for this work, and his encouragements were very important for me.

I also want to thank my two co-supervisors, Andrey Sergeevich Volynkin and Ilya Viktorovich Gorelkin for helping me during my experiments, answering my questions and for their availability during this master thesis.

I want to thank Julian Tolchard, from Material Department, for helping me with XRD and BET analysis, and Harry Brun for his help with laboratory or material question. PhD students from catalysis group helped me with apparatus and answered my questions when I needed it, and I want to thank them.

I spent good time with the students from my office, and all the international students met during the year in Trondheim. I want to thank all of them for making this year in Norway so nice.

Finally, my family and friends in France are really important for me, and I want to thank them for their support.

ABSTRACT

The dehydrogenation of propane has a great interest, due to a global growing demand in propene. This reaction needs a catalyst, high temperature and low propane partial pressure.

During this work, platinum hydrotalcite-supported was used as catalyst. First, three different kinds of support were tested: the hydrotalcite 30 (30% MgO, 70% Al_2O_3), the hydrotalcite 63 and the hydrotalcite 70. The catalysts were prepared with 1 or 2 % mass platinum, by a kind of colloid method. They were characterized by BET, XRD, and chemisorption, and activity tests were performed. The catalytic tests were performed in a fix bed reactor in a temperature range from 350 °C to 650 °C. The propane conversion and selectivity were not really different between the three supports. For example, the selectivity to propene reached a maximum between 50 % and of 55 % at 550 °C for all the catalysts.

Then, the catalyst HT 63 with 1 % Pt was selected for further experiments. The feed gas composition was varied, to see the influence of the ratio Propane/Oxygen/Hydrogen. Some experiments involved oxidative dehydrogenation of propane, whereas some others were non-oxidative dehydrogenation of propane. The propane conversion was better when the reaction took place simultaneous with oxidative reactions. The system is complex, but some feed gas compositions favor the conversion of propane and the selectivity of propane to propylene.

The influence of pressure on the reaction was also investigated. Oxidative dehydrogenation of propane was studied at low (1.1 bar) and high pressure (above 3 bar). When the pressure in the reactor during the experiment was above 2 bar, the propane conversion, the propane selectivity to propene and the propene yield are improved.

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LIST OF ABREVIATIONS AND SYMBOLS

ADH	Autothermal dehydrogenation
A. U.	Arbitrary unit
BET	Brunaer-Emmett-Teller
DH	Dehydrogenation
FCC	Fluid catalytic cracking
GC	Gas chromatography
H	H_2/C_3H_8 ratio
HC	Hydrocarbon
HT	Hydrotalcite
Keq	Equilibrium constant
n	Amount of component
ODH	Oxidative dehydrogenation
P	Pressure
R	Ideal gas constant ($J.mol^{-1}.K^{-1}$)
SHC	Selective combustion of hydrogen
SMR	Steam Methane Reforming
SR	Steam Reforming
T	Temperature
V	Volume
WGS	Water Gas Shift reaction
x	Propane conversion
XRD	X-ray diffraction
$\Delta H°$	Heat of reaction (kJ/mol)
$\Delta H°_f$	Heat formation (kJ/mol)

1   INTRODUCTION

The propylene is an important chemical intermediate. It can be used to produce polymers. The propene is mainly consumed to produce polypropylene, around two thirds of the global demand. The polypropylene is used for making plastic films, packing or used in electrical or automobile industries. The second-largest propylene market consists on producing acrylonitrile, and then propylene oxide. The industrial demand in propylene is increasing, so producing propylene has a great commercial interest. Sales of propene are supposed to represent more than 90 billion $ in 2012 [1].

The most important way to produce propene is the steam cracking of alkanes, naphtha or oil gas, where propene is produced as a by-product. This process requires considerable amount of energy. Another way to obtain this component is the fluid catalytic cracking (FCC). The main function of FCC units is to produce gasoline, and propylene is formed as a by-product. Propylene is not the most important product for FCC units, and thus the propene yield is not always good. However, as the demand for propylene increases, maximizing yield propylene with FCC is currently studied [2]. Finally, it is also possible to produce propene by catalytic dehydrogenation of propane, according to the following reaction:

$$C_3H_8 \longrightarrow C_3H_6 + H_2$$
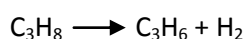
However, this reaction cannot be carried out easily, due to its strong endothermicity ($\Delta H° = 124$ kJ.mol^{-1}), and the necessity to heat at around 600 °C [3]. Noble metals have been used as catalyst since the beginning of the 20th century to carry out alkane dehydrogenation [4]. Particularly, Pt-based catalysts can be used for propane dehydrogenation, because the Pt-based catalysts are very active. Many catalytic processes, for dehydrogenation of propane, already exist. Indeed, a conventional catalytic dehydrogenation of propane, and more generally light alkanes, is well-established and used industrially all around the world. But all the current processes suffer from plenty of problems. One of the most important is that the catalyst is quickly deactivated, due to coke formation. So it is necessary to find a catalyst with both high activity and slow deactivation. Moreover, as the reaction is endothermic, it needs an external source of heating. Nowadays, the global energy demand is increasing, and some sources are limited, such as the fossil energies. The energy cost is increasing. So, finding a process using less energy is a major challenge. Some catalysts have a high potential for performing this reaction. The oxidative catalytic dehydrogenation of propane for the production of propene is a novel route currently studied. The mechanisms of the catalytic reaction are not well-known. Few aspects are explained by scientists, but a general theory was not found. Why some catalysts are very good under some conditions and very poor with other reactants is still a question for researchers. Consequently, it is not easy to find an efficient catalyst for the propane dehydrogenation, and finding a new way to produce propene is still a challenge. Trying to compare different catalysts to produce this molecule is a very interesting study. A lot of parameters can change the result of the reaction (propane conversion, selectivity…). Optimizing the various parameters, such as temperature, feed composition, pressure inside the reactor, is a long but thrilling research. Indeed, even if it is not easy to find the appropriate catalyst, the catalysis is a key technology at the moment. It is a vast and exciting field. The applications of catalytic research are very useful and a current industrial challenge.

The purpose of this work was to study the effects of few parameters on the dehydrogenation of propane. Different catalytic supports were used and compared, with platinum as active component: three different kinds of hydrotalcite, and a zeolite. The influence of the load of platinum was also investigated.

Both oxidative and non-oxidative propane dehydrogenation experiments were done during the semester, which means some experiments were performed with oxygen, whereas some other focused on propane and hydrogen only in the feed gas. One experiment was done with only propane in the feed gas, to notice the influence of additional active components on the reaction.

Different feed gases were used, both with different composition and rate of flow, to compare the effects of the propane/hydrogen/oxygen ratio. The activity tests were performed in a temperature range from 350 °C to 650 °C. Finally, different pressures into the reactor were used, between 1.1 bar and 2.8 bar. The experiments were repeated without catalyst, to emphasize the effect of the catalyst on the reaction.

2 THEORY ASPECTS

2.1 Reaction

The reaction of dehydrogenation of propane is the following:

$C_3H_8 = C_3H_6 + H_2$.
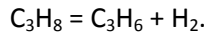
It is strongly endothermic ($\Delta H° = 124$ kJ.mol^{-1}). This reaction is also equilibrium limited; therefore not only a catalyst is necessary to carry out this experiment, but also high temperature, low pressure and dilution of propane in a gas mixture [3]. In the case where the feed gas is only propane, the equilibrium propane conversion is given by the formula: $K_p = P.x^2/(1-x^2)$ with K_p the equilibrium constant, x the equilibrium conversion and P the total pressure. Thanks to this formula, the plots given equilibrium conversion as a function of temperature and total pressure can be found (figure 1 and 2) [5].
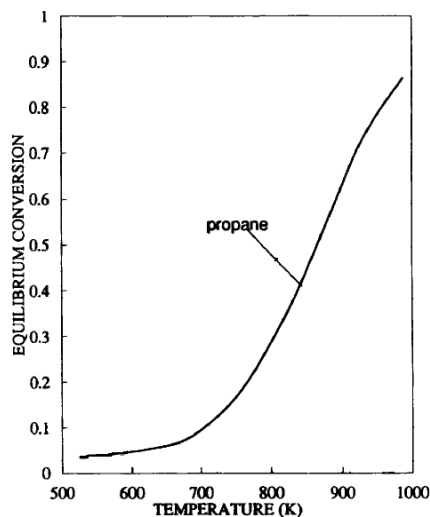

Figure 1: Dehydrogenation equilibrium conversion of propane as a function of temperature at a constant total pressure of 1 atm
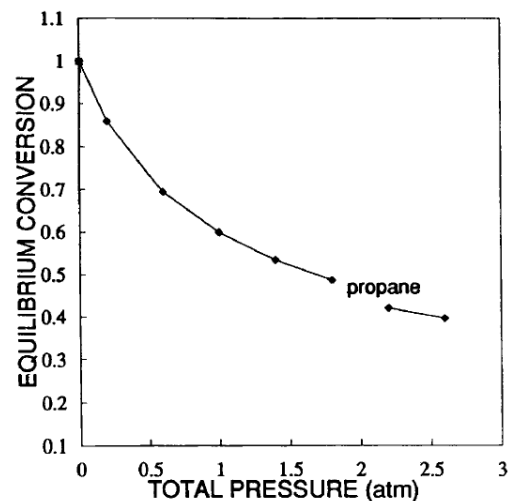
Figure 2: Dehydrogenation equilibrium conversion of propane as a function of total pressure at 873K

If the propane is not the only component of the feed gas, the equilibrium constant is modified. For example, if hydrogen is present in addition in the feed gas, the equilibrium conversion depends on the H_2/HC ratio. The constant equilibrium becomes: $K_P = (x^2 + H.x).P / (1 + H - H.x - x^2)$, where H is the feed molar ratio between hydrogen and propane [5].

Industrially, a temperature of about 600 °C is often chosen to obtain a satisfactory conversion rate. Two different ways are possible to carry out the reaction. The reaction can be oxidative or not, depending on the use of O_2 in the feed flow.

The most common way in industrial plants is a normal dehydrogenation, without O_2, but this reaction suffers from some problems. The main problems are a limitation in equilibrium conversion, a high heat requirement, a rapid deactivation of the catalyst (and so the necessity to regenerate it) and the formation of by-products due to cracking of propane molecule.

Without oxygen in the reactor, the main reactions are the following:

The propane dehydrogenation: $C_3H_8 \longrightarrow C_3H_6 + H_2$
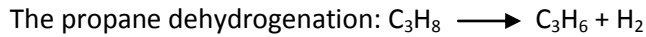
There is also cracking and hydrogenolysis of the molecules: $C_3H_8 \longrightarrow C_2H_4 + CH_4$

$C_3H_8 + H_2 \longrightarrow C_2H_6 + CH_4$

$C_3H_8\ 2\ H_2 \longrightarrow 3\ CH_4$
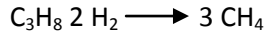
And finally, coke formation happens according to: $CH_4 \longrightarrow C + H_2$

An oxidative dehydrogenation of propane is interesting because the reaction of hydrogen oxidation is exothermic ($\Delta H° = -117$ kJ.mol^{-1}). The following reaction takes place into the reactor:

$C_3H_8 + ½\ O_2 \longrightarrow C_3H_6 + H_2O$
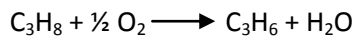
Consequently, with a selective oxidation of hydrogen, the dehydrogenation of propane can be carried out at lower temperature. Some problems are removed by this way. However, when the dehydrogenation of propane takes place, a lot of by-products can be formed, mainly due to non selective oxidation [6].
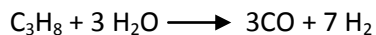
It is possible to have propane or propene combustion:

$C_3H_8 + 5\ O_2 \longrightarrow 3\ CO_2 + 4\ H_2O$

$C_3H_6 + 9/2\ O_2 \longrightarrow 3\ CO_2 + 3\ H_2O$
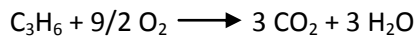
Cracking and hydrogenolysis form ethane, ethene and methane. And there is also coke and CO formation, with the following reaction:

$CH_4 \longrightarrow C + 2\ H_2$

$2\ CO \longrightarrow C + CO_2$

$C + ½\ O_2 \longrightarrow CO$

$C + H_2O \longrightarrow CO + H_2$
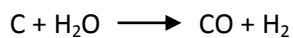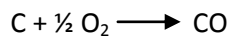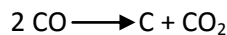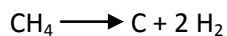
A steam reforming of propane can also be noticed:

$C_3H_8 + 3\ H_2O \longrightarrow 3CO + 7\ H_2$

The main problem of the reaction of dehydrogenation is the coking of the catalyst, which induces a loss of activity and selectivity.

Concerning the kinetic of the propane dehydrogenation reaction, a lot of various theories were proposed by researchers, but they are still controversy. The details of the kinetic theory will not be given here. However, four different possible mechanisms can be quoted. The first one is a simultaneous adsorption of hydrogen and oxygen molecules on the catalyst, following by the reaction and finally desorption of water molecules. The kinetic constant in this case is proportional to $[O_2]^{0-1}*[H_2]^{0-1}$. Other mechanisms can be taken into consideration. If there is a reaction between

adsorbed oxygen and hydrogen, the kinetic constant, following a Van der Walls law, is proportional to $[O_2]^{0-1}*[H_2]^1$. Conversely, if the reaction takes place between adsorbed hydrogen and oxygen, and with a Van der Walls law again, it is to $[O_2]^1*[H_2]^{0-1}$. And finally, a complex two sites mechanism and alternate reaction mechanism is considered, with the kinetic constant proportional to $[O_2]^{x}*[H_2]^{y}$, where x and y are number between -1 and +1. The mechanism is difficult to establish because it depends on a lot of parameters. For example the temperature or the ratio between O_2/H_2 in the feed flow change the adsorption mechanism, and so the kinetic law [6].

The reaction of propane dehydrogenation is a heterogeneous catalytic reaction. The catalyst allows to increase the reaction rate and to decrease the activation energy. The gases are adsorbed on the catalyst prior to react.

Concerning the hydrogen, it seems that a dissociative chemisorption takes place on the catalyst surface. During the oxidative dehydrogenation of propane, water molecules are produced. Oxygen is also adsorbed dissociatively on the catalyst. Some studies showed that firstly there is a formation of $OH_{adsobed}$, and then a formation of H_2O molecules. The three molecules H, OH and H_2O seem to be adsorbed during the same time on the catalyst, in different areas [7].

2.2   Hydrotalcite support

The hydrotalcite (or Aluminum Magnesium Hydroxy Carbonate) supports were very used as catalytic support. In 1970, hydrotalcite was already considered as a good catalytic support for hydrogenation catalyst [8]. In 1991, F. Cavani *et al* .described many uses of hydrotalcite-like compounds use in a variety of application [9]. The general formula of hydrotalcite-like compounds is the following:

$[M^{(II)}_{1-x}M^{(IIi)}_{x}(OH)_2]^{x+}(A^{n-}_{x/n}).mH_2O$, where $M^{(II)}$ and $M^{(III)}$ are cations, and A^{n-} are anions. Most of the time, the cations are Mg^{2+} and Al^{3+}. The net positive charge of the brucite-like octahedral layers is balanced by an equal negative charge from the interlayer anions, most of the time CO_3^{2-}. The most popular hydrotalcite is $Mg_6Al_2(OH)_{16}CO_3,4H_2O$. The structure of the hydrotalcite-compounds is the same than brucite ($Mg(OH)_2$), where octahedral of Mg^{2+} share edge to form infinite sheets, which are stacked on the top of each other and are held together by hydrogen bonding [10, 11].

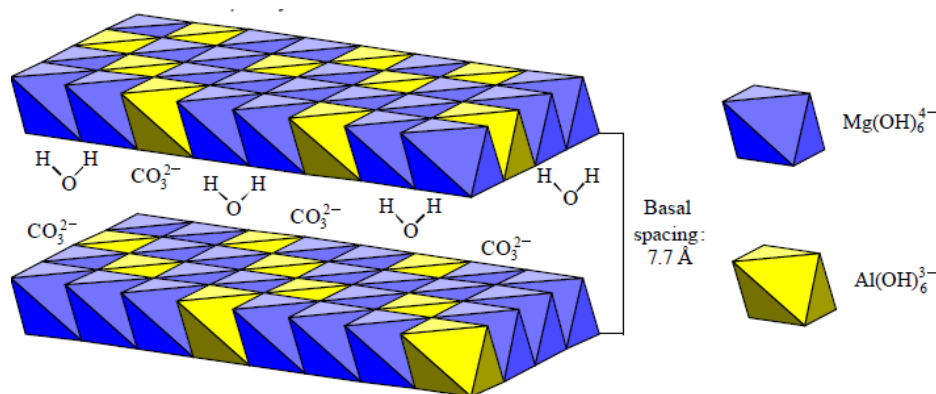A schematic presentation of hydrotalcite-like materials is given:

Figure 3 : Schematic presentation of hydrotalcite-like materials [41]

The calcined hydrotalcite has several interesting properties. Indeed, W.T. Reichle *et al.* show that during calcinations, interstitial water and carbon dioxide are lost. Moreover, numerous fine pores are formed [12]. Consequently the surface area of hydrotalcite increases after calcination.

After calcination, this material has moderate basic properties. The number of basic sites and their strength distribution depend on the ratio of Al and Mg in the hydrotalcite [13].

Finally, hydrotalcite has a particularity: the "memory effect". J. A. van Bokhoven *et al* studied the changes in the structure of hydrotalcite-components with the temperature [14]. This equip is one of the various group which showed the reversibility of changes after hydrotalcite heat treatment, that is to say the possibility, after heating the material, to obtain the initial hydrotalcite structure when it comes back at room temperature.

Consequently, hydrotalcite is an interesting material. It can be used in various yields. In addition to the catalyst support uses, it is also reported that calcined hydrotalcite can be used as recyclable sorbents [15], ion-exchanger [16] or thermal stabilizers [17].

3   LITERATURE REVIEW

The catalytic dehydrogenation of propane has an important commercial interest for industry. Consequently, this reaction has been studied by a lot of scientists for 50 years.

2.1   Choice of catalyst

- Metal

Concerning the choice of the catalyst, noble metals are known to be efficient for dehydrogenation of light alkanes. Indeed, the first catalysts were discovered at the beginning of the 19th century. Döbereiner noticed the interest of using platinum to catalyze ignition of H_2 in oxygen at ambient temperature [18]. Sabatier and Senderens found some catalytic dehydrogenation processes in 1907. They studied various oxides which were able to catalyze this reaction [19]. And finally, in the early 1940's, Vladimir Haensel found a reforming process with platinum as catalyst to produce a high octane gasoline from naphtha (for Universal Oil Product Company) [6]. Platinum was particularly studied, because it has a high activity for activating C-H bonds, and a relatively low activity for the rupture of C-C bounds. Chromium is also a really good metal for catalytic dehydrogenation of propane [20]. For example, S. Thapliyal *et al.* studied the catalytic dehydrogenation of propane over alumina supported chromium catalyst, both oxidative and non oxidative dehydrogenation [21]. Chromia oxide was the first catalyst used industrially for the dehydrogenation of alkane, and some of them had interesting proprieties (prolonged operation without regeneration, durability, mechanical strength), but suffer from problem such as poor selectivity and alkene yield. With some chromia-oxide catalyst, the selectivity was quite good but the catalyst was quickly poisoning by cocking [22].

The real mechanism for the effect of Pt as catalyst is not well-known. A lot of parameters seem influenced the catalytic reaction. For example, *S.* Sahebdelfar *et al.* showed that the propene selectivity to propane depends on the operating conditions, (temperature, ratio of H_2 and propane…) [23].

However, Pt-supported catalysts need to be improved because they suffer from rapid deactivation, or poor selectivity, depending on experimental conditions. A lot of studies showed that the performance of Pt can be enhanced if another metal is added. In the literature, studies about alloys Pt-Sn, Pt-K, Pt-Zn are available [24]. G. J. Siri *et al.* demonstrated the existence of a Pt-Sn alloy for both PtSn/γ-Al_2O_3 and PtSn/SiO_2 when Sn is added during the preparation of the catalyst. Indeed, they compared two kinds of catalysts: Pt/γ-Al_2O_3 and PtSn/γ-Al_2O_3 on one hand, Pt/SiO_2 and PtSn/SiO_2 on the other hand. They prepared the first catalysts by surface organometallic reactions, and they made the seconds by addition of $SnBu_4$ in solvent on the monometallic catalyst. The presence of PtSn alloy was noticed thanks to an EXAFS experiments. This alloy seems to be very important for selectivity and stability during dehydrogenation reaction, inhibiting cracking and coke formation reactions. They also found a maximum of reaction rate when the ratio Sn/Pt was between 0.4 and 0.8. However, they thought that PtSn has not influence on the activity of the reaction [25]. The molecules of Pt seem much more active than PtSn in the reaction. Another equip, V. Galvita et al. studied the effect of the addition of Sn to a Pt/Mg(Al)O catalyst. They found a higher activity of the

PtSn/Mg(Al)O catalyst than Pt/Mg(Al)O, and also a better selectivity for the reaction of ethane dehydrogenation [26].

The catalytic dehydrogenation of propane has also been studied without noble metals. Two examples of catalysts without noble metals will be given. The first one, developed by J. Schäferhans *et al.,* is an oxidized porous Cu-Al alloy. They succeed to find an interesting propane rate consumption at 350°C, so a low temperature. However, the propene selectivity is not mentioned with this catalyst [27]. Another kind of catalysts, developed by C. Mazzocchia *et al.*, is the mass catalyst $NiMoO_4$ or NiO, MoO_3, nH_2O, mNH_3. They used an oxidative dehydrogenation of propane process. They analyzed the products of the reaction thanks to a gas chromatogram and found good propane conversion, propene selectivity and yield with their catalyst [28].

- Dispersion

The dispersion of platinum on the support has an impact on the reaction. For example, Santhosh Kumar *et al.* compared the dispersion of Pt and Pt-Sn SBA-15 supported, and their efficiency for the dehydrogenation of propane. When alloys were considered, the dispersion of platinum was affected. Indeed, the dispersion was increased when Sn was added. Consequently, the catalyst with Sn presented smaller bimetallic Pt-Sn particles than the monoparticles of Pt in the monometallic catalyst. They practiced some activity tests, and found a better activity for the Pt-Sn-SBA-15 catalyst. They supposed that the dispersion of Pt, and so the average size of particle, is responsible for the activity of the reaction [29]. S. Vajda *et al.* compared nanoparticles of Pt alumina supported catalyst for the oxidative dehydrogenation of propane, and taller Pt alumina catalyst. They found a higher activity than for the same catalyst (Pt alumina supported) with taller particle sizes. The selectivity was the same between these two catalysts. They tried to explain this result by the presence of under-coordinated Pt sites in small Pt clusters, which are more active than Pt surface for the oxidative dehydrogenation of propane, due to an attractive interaction between the clusters and propane [30].

- Support

The support plays an important role in the catalyst behavior. Particularly, the surface acidic sites and its stability during the reaction and the regeneration phases are significant. This work is mainly focus on hydrotalcite support. However, catalyst Pt hydrotalcite supported is not the only kind of catalyst used for propane dehydrogenation. It is common to use a catalyst alumina supported. In the literature, SiO_2 or zeolite (ZSM 5, SAPO 34) were also noted as supports. Z. Nawaz *et al.* chose to use a support composed by zeolite SAPO 34 and additional aluminum as support for their catalyst. Thanks to this support, they found high propene selectivity during the dehydrogenation of propane [31]. Some equips tried to compare different Pt support. The Bariå *et al.*'s study can be quoted. Both SiO_2 and Al_2O_3 were used as support. They did not seem really different for the initial specific activity of the catalyst. They found that the addition of Sn was more influent on the reaction than the support [32].

2.2   DH/ODH/ADH/SHC

The catalytic dehydrogenation of propane can be done with or without oxygen.

- Without oxygen, non-oxidative reaction (DH)

Performing the experiment without O_2 is a well-known technology. Houdry found and used a process for producing butadiene during the Second World War. He used a chromium oxide-alumina catalyst [33]. Currently, the catalytic dehydrogenation of propane is commercially available. In this case, the feed gas is composed by propane, hydrogen and an inert gas. Some processes used for this reaction can be quoted, such as UOP Oleflex, ABB/Catofin, Snamprogetti, Phillips STAR, PDH (Linde). For example, one of these processes, using Pt as catalyst is described in the following paragraph.

The PHD (Propane DeHydrogenation process), by Linde-BASF-Statoil, is based on a steam-reformer type dehydrogenation reactor. Three reactors compose the reaction section. Two of them operate under dehydrogenation conditions, while the third reactor is used to regenerate the catalyst by coke combustion in a steam-air mixture. The main advantage of the process, compared to other processes, is the absence of reactant dilution. This allows to reduce the size of the reactor, and to make easier the purification of the product. The reaction temperature is controlled very carefully in this case [34].
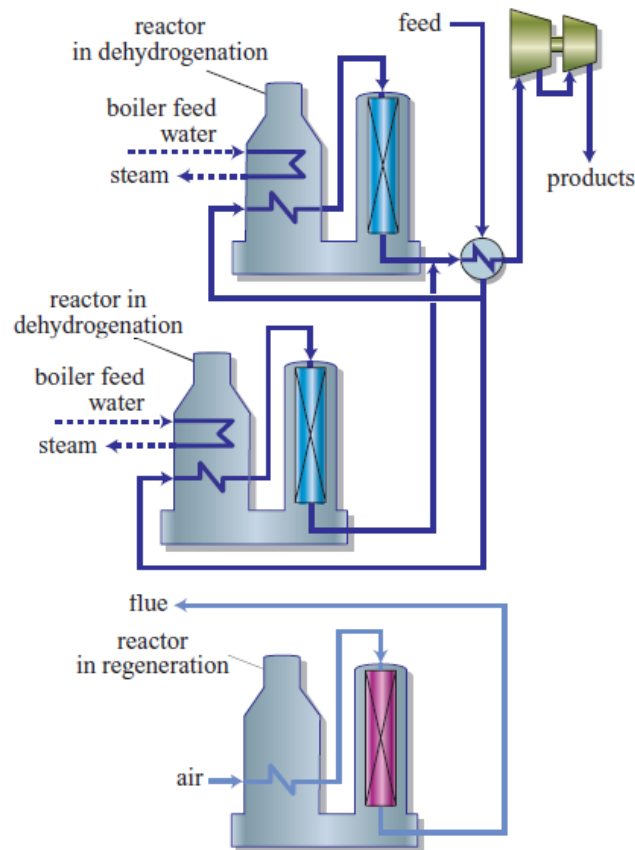

Figure 4: Scheme of the reactors

However, even if these processes are well-developed, some major problems are still present. One of them is the high cost, induced by the equipment and the heat necessary to perform the dehydrogenation. As the reaction has to be carried out at high temperature, energy must be furnished to the system. Consequently, as the demand for propene is increasing, new technologies must be found to improve the dehydrogenation of propane.

- Oxidative reaction (ODH)

Producing propene is possible by using oxygen during the dehydrogenation. In this case, an oxidative dehydrogenation takes place according to the following equation:

$$C_3H_8 + \frac{1}{2} O_2 \longrightarrow C_3H_6 + H_2O$$
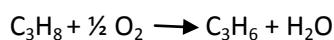
This reaction is strongly exothermic, so it is an interesting alternative to simple dehydrogenation. The problem with this reaction is the consecutive reaction to the alkane combustion. For example, it may have a complete oxidation of propane, or a thermal cracking (so a production of CO_2), that is to say a lack of selectivity. As the reaction is strongly exothermic, a heat excess has to be taken away thanks to heat exchangers. A. Beretta *et al.* studied the effect of Pt/Al_2O_3 catalyst on the oxidative dehydrogenation of propane. They used an annular reactor in order to obtain high space velocity and very controlled temperature, and load a very small amount of catalyst in the reactor. They found that catalyst was very active at all the temperatures. Besides, they compared this kind of dehydrogenation at high temperature with or without catalyst. At low and medium temperature, the oxidative dehydrogenation of propane took place only with the catalyst. They did not find a significant difference between using or not the catalyst at high temperature (the same products were formed, almost the same quantity). They conclude that gas-phase reactions were both active and selective to produce olefins at high temperature [35].

- Autothermal dehydrogenation (ADH)

During normal dehydrogenation, an external heat supply is required. The autothermal dehydrogenation process is a method used to free from this problem. The propane dehydrogenation is effected in combination with hydrogen combustion. Produced hydrogen reacts with oxygen from the feed-gas to form water. At typical dehydrogenation conditions, the combustion of half of the formed hydrogen provides necessary heat to compensate the loss due to the endothermic dehydrogenation. Various processes are used for ADH. A method can be described. The propane containing feed gas can be mixed with steam or hydrogen, before being preheated. The mixture is led into the reactor, which contains a catalytic bed. Oxygen flow is passed through the reactor. It is added in an inert bed before the catalytic bed, or directly inside. E. Rytter *et al.* developed a reactor for autothermal dehydrogenation, with an oxygen containing gas passed directly through the catalytic bed. Feeding oxygen directly into the dehydrogenation catalytic bed reduces the temperature gradient inside the bed. In this process, selective oxidation of hydrogen is favored over propane oxidation, so oxygen is mainly consumed by the following reaction: $2 H_2 + O_2 = 2 H_2O$. E. Rytter and his team found a high propene yield and high catalyst stability with their method [36].

- Selective combustion of hydrogen (SCH)

A Selective Combustion of Hydrogen was also studied by some equips. This combustion allows to furnish the necessary reaction heat with the combustion of a part of the hydrogen produced in situ. Burning H_2 is also supposed to drive the equilibrium of the dehydrogenation reaction towards products. Another advantage is that O_2 or steam atmosphere reduces the coking of the catalyst.

It is possible to combine a traditional unit of dehydrogenation of propane and a unit of SCH. R. Grasselli *et al.* tried to combine these two processes, with three reactors in series. A scheme of the experimental set-up can be given:
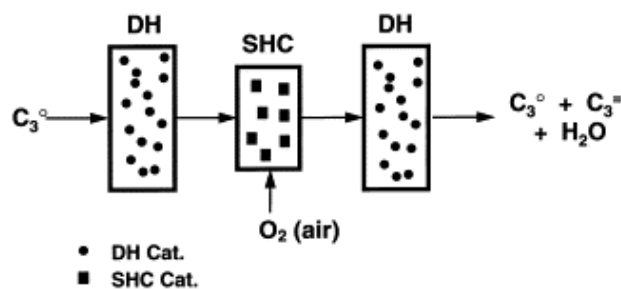
They worked with some kinds of catalysts, to find the best for each part of the process. Finally, they selected In_2O_3–ZrO_2 for the SCH part and Pt-Sn-ZSM5 for the dehydrogenation part. They found a good selectivity and activity for the combustion of H_2 thanks to this catalyst, if they used an appropriate air/propane ratio in the SCH reactor. With this process, the propane yield was really better than with a simple propane catalytic dehydrogenation unit [37].

S. Kaneko *et al.* studied also the catalytic dehydrogenation of propane with selective hydrogen combustion. They focused on Pt-Sn alumina supported catalysts. They used only two different isothermal reactors, one for the normal dehydrogenation of propane, and the other one for the selective combustion of hydrogen. Some air was added between the two steps, to furnish the necessary oxidant for the combustion of hydrogen in the second reactor. They found that Pt-Sn catalyst was really efficient for selective combustion of hydrogen. They also found that the association of a normal dehydrogenation and a selective combustion led to a high propane conversion rate, and reduced dramatically the heat required for the dehydrogenation of propane during the entire process [38].

2.3 Membranes

A technology using membranes for the oxidative dehydrogenation of propane was also tried by some teams. A. Pantazidis *et al.* They tested three kinds of membranes (V-Mg-0 or Ni on porous alumina membranes, or a V-Mg-0 catalyst bed enclosed in a zeolite membrane). During the oxidative dehydrogenation of propane, a total combustion of all the products might happen. So, it is interesting to limit the combustion. A membrane reactor with separate feed of propane and oxygen might be efficient. The micro porous zeolite membrane acts as a gas barrier, and gave quite good results, provided the oxygen partial pressure was high [39]. Other kinds of membranes were also studied for oxidative dehydrogenation of propane. A. Julbe *et al.* focused on zeolite membranes, MFI and V-MFI. They performed an oxidative dehydrogenation of propane, and succeed to form propene with about 40 % selectivity but a low conversion rate. The membrane behavior seems to depend on the ratio of O_2 in the feed flow [40]. Finally, the work of Y. Yildirim *et al.* can be quoted. They used porous and dense membranes, composed by Pd/Ag, silica or Pd-dispersed porous. The feed gas contained C_3H_8, CO, N_2 and O_2. They found a high propane conversion at high temperature, depending on the composition of the feed gas [41].

2.4 Non catalytic reaction

The oxidative dehydrogenation of propane was also studied without catalyst. M. Xu and J. H. Lunsford tried to compare ethane and propane dehydrogenation with two catalysts (LiCl/TiO$_2$ or LiCl/MnO$_2$) or without catalyst. They used a non isothermal reactor to carry out their experiments, and a high temperature (650 °C). For their system, they did not find a huge difference between the reaction with catalysts and without catalyst. The catalyst increases the reaction rate, but had not major impact on the conversion rate or the selectivity at this temperature. In their case, they noticed that O$_2$ was mainly consumed to produce CO$_2$ instead of CO [42]. The dehydrogenation of other light alkane (mainly ethane) without catalyst was also studied. R. Bruch *et al.* concluded after their work that MgO based catalyst did not always improve the ethane conversion or yield of ethene during the dehydrogenation of ethane. Indeed, they succeed to find a temperature and oxygen ratio for which the dehydrogenation of ethane was efficient to produce ethene – without catalyst [43]. However, for S.A.R. Mulla *et al.*, with a catalyst, the maximum ethene yield is reached at lower temperature than without. They worked with Sr$_1$La$_1$Ld$_1$O$_x$ as catalyst. They did not notice any yield improvement or better ethane conversion with the catalyst [44].

4 EXPERIMENTAL PART

4.1 Preparation of the catalysts

The catalysts are platinum hydrotalcite supported. They were prepared by a method based on polyol process [45]. This method makes possible to get both advantages of colloid method (well-homogenized ultrafine Pt particles, [46]) and impregnation method (easy preparation method, [47]). The hydrotalcite are commercial product from SASOL, and three different kinds of support were used. The characterizations of each hydrotalcite, which formula are $Mg_{2x}Al_2(OH)_{4x+4} CO_3 \cdot n H_2O$, are the following:

	HT 30	HT 63	HT 70
MgO / Al₂O₃	30 / 70	63 / 37	70 / 30

Table 1: Hydrotalcite characterizations

To prepare the catalysts, the precursor chloroplatinic acid hexahydrate ($H_2PtCl_6,6H_2O$; SIGMA-ALDRICH) was dissolved into ethylene glycol. The chloroplatinic acid hexahydrate crystals were stirred for 30 minutes with 50 mL of ethylene glycol under argon flow, at room temperature.

The amount of precursor varies between the catalysts at 1% weight platinum and 2% weight platinum (Appendix 1). Then, 2 grams of support and 50 mL of water were added. The solution is heated around 110 °C, thanks to an oil bath. When the steady state is reached, the solution is left under argon flow with reflux during 3 hours, in order to ensure the full reduction of the platinum. After, the catalysts were filtered under vacuum (thanks to a water pump) and washed with around 700 mL distilled water. They were dried at 70 °C overnight in air flow. Finally, the catalysts were calcined for 4 hours, with a heating rate of 4 °C/min until 600 °C. (The oven used was a controller P320 by Nabertherm,). The calcination took place in air.

For the second part of this work, a bigger amount of catalyst with the support HT 63 and 1 % Pt was made. The catalyst was prepared with the same process than previously explaining. Three different batches, with the same composition, were prepared. They were mixed together to homogenize the catalyst. Then, it was sieved. The particle diameters used during the dehydrogenation process were inferior to 106 µm. 6 g of catalyst were prepared during the spring semester.

Concerning the supports without Pt, the same treatments than for the catalysts was made; the supports were treated with the same amount of ethylene glycol and water, heated and stirred, filtrated, dried and calcined under the same conditions. It allows to compare accurately the results with or without the metal.

4.2 Apparatus used for the catalytic test

The reaction of dehydrogenation of propane took place in a tubular fixed bed reactor placed into an oven. The temperature inside the oven reached 650 °C at the end of the experiment. The output products were analyzed by gas chromatography.

Thanks to the GC, for each component, the following data are available: the retention time, the width of each peak, the area and the height of the peak. These data were used to find the conversion rate, the selectivity or the yield of the dehydrogenation of propane.

Four columns are present in the GC. In this case, the first one allows to know the quantities of He, H_2, O_2, N_2, CH_4 and CO. With the second one, the amounts of CO_2, C_2H_4 and C_2H_6 are open. Finally, the 3rd one is necessary to know data about C_3H_8 and C_3H_6.

Concerning the treatment of these data, the height of the peak for helium and hydrogen was used, whereas the area of the peak was used for the other components. Indeed, for He and H_2, the concentration is proportional to the height of the peak with a GC analysis. As this is not true for other species, the surface area has to be taken into consideration. Some calibration formulae allow to find an equation between the GC peak and the concentration of the products, both with height and with surface area of the different peak.

4.3   Experimental set-up

To carry out the experiments, a fixed-bed quartz reactor was used (U-shaped). The catalysts were placed in one arm of the reactor, between two small amounts of quartz wool. The reactor was heated by an electrical furnace. The temperature was controlled thanks to two thermocouples, one in the furnace, close to the reactor and the other outside the furnace. The temperature given by the thermometer next to the reactor is supposed to be the same than the temperature inside the reactor. Some previous experiments were carried out to check this assumption. The temperatures used for the reaction were between 350 °C and 650 °C. The temperature is increased step by step, from 350 °C to 650 °C, so the increasing in temperature is also the chronological order. The pressure drop in the reactor could be monitored thanks to a manometer. A schematic drawing of the set-up is given:
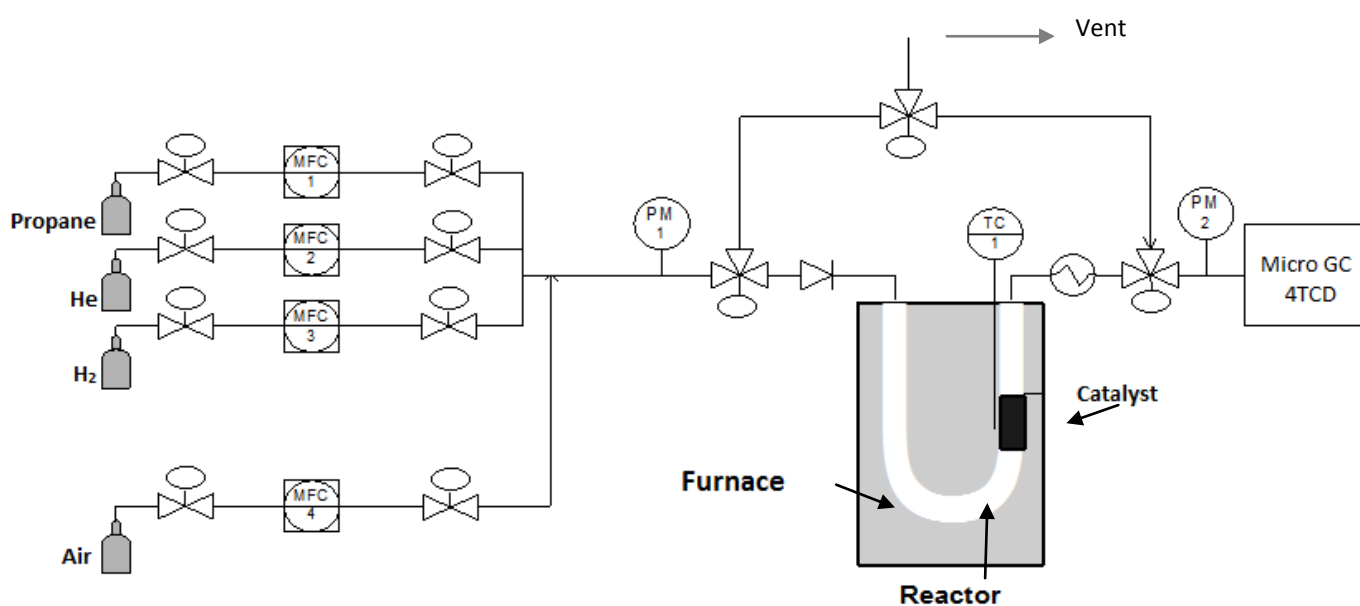

Figure 6: schematic set-up

Various kinds of catalyst were tested during this work. For the hydrotalcite-supported catalysts, prior to the activity test, they were reduced in hydrogen flow *in situ*. The composition of the gas flow was 10 mol.min^{-1} of H_2 and 30 mol.min^{-1} of He. The temperature was slowly increased until 500 °C, and the reduction happened for 2 hours. Then, the experiences were done.

For the zeolite catalysts, the catalysts were reduced during the preparation. They were put into the reactor, and the temperature was increased to 350°C, with the same gas mixture than for the hydrotalcite catalyst (10 mol.min^{-1} of H_2 and 30 mol.min^{-1} of He). The experiment was performed as soon as the temperature reached 350 °C.

For the first series of experiments, with the various hydrotalcite supports and Pt loading, the composition of the gas mixture send in the reactor was the same for each experiment. It is done in the following table. The total gas flow was 50 mL/min.

	C_3H_8	H_2	Air	He	Total
Flow (ml/min)	10	5,7	15	19,3	50

Table 2 : Composition of the gas mixture sent in the reactor

For the catalysts with 1 % Pt, the loading used were 0,150 g. For the catalysts with 2 % Pt, the loading used were 0,075 g.

Concerning the zeolite catalysts, the same feed gas was used.

For the second series of experiments, a first activity test was performed, but the pressure drop inside the reactor was significant. Indeed, 1.5 bar overpressure was measured inside the reactor. The size of the particle (inferior to 106 µm) and the amount of the catalyst (150 mg) can explain this difference with the first series of experiments. In order to decrease the drop pressure, the preparation of the reactor was a bit changed. Some amount of quartz was added in the reactor, between two layers of catalyst. Thus, three or four layers of catalyst were in the reactor. The catalyst and the quartz were not compacted during the loading of the reactor. The catalyst was dried before using, thanks to a desiccator. A silica drying agent was used (BASF Sorbead Orange Chameleon®). This agent is not supposed to react with the catalyst, neither to poison it. Firstly, the gas was send slowly through the reactor. For this part of the work, 12 different feed gas containing O_2 were tested. The pressure was not the same for all the experiments. Indeed, in some experiments, the overpressure was only 0.1 bar, but reached 2.3 bar overpressure for some tests, i. e. 3.3 bara. For three experiments, the pressure drop was so high that the tests were performed again, at lower pressure. As during the previous experiments, the gas total amount passed through the reactor was 50 mL/min. In addition, the quartz wool without catalyst was also tested, at low pressure drop (inferior to 0.1 bar) and high pressure drop (above 1.5 bar).

After the reactor, a cooling down system was used to condense water, before analyzing the composition of the gas mixture. Indeed, the composition of the products was determinate thanks to a micro GC (Agilent 3000A), and micro GC are sensitive to water.

The initial composition of the gas mixture was checked at the beginning of each experiment. The gas mixture went directly through the GC for analysis to check its composition. Then, the gases were passed through the reactor, where the initial temperature was 350 °C. For each temperature, five measurements were done by GC, to be sure that the results were correct. The composition of

the gas mixture should be the same for the three last measurements. After the fifth measurement, the temperature was increased into the reactor. Few minutes were necessary to reach the steady state. Ten different temperatures were tested between 350 °C and 650 °C.

The feed gas compositions were chosen according to an experiment plan. The theory about experimental plan was described by S.L. Akhnazarova *et al.* for example [48]. This theory will not be explained in this report.

4.4 Characterization

- **XRD**

The XRD analyses were performed with a Dfocus 8 using CuKα radiation, and a Lynxeye detector. The wavelength was 1,5406 nm. For each samples, the scan were performed with an angle 2Ө in the range from 5° to 70°, a step of 0,02° and a step time of 0,5 s. The powders were analyzed without rotation. The software EVA was used for phase identification.

- **BET**

For the BET analysis, about 100 mg of catalysis was used. Prior the analysis, the samples were degassed at least 8 hours in a sample degas system (VacPrep 061). The temperature used for degassing was 250 °C.

After degassing, the weight of the samples was measured again. The samples must lose little weight after degassing, or keep the same weight.

The BET measurements were done with the device TriStar 3000. The nitrogen adsorption isotherms at 77.3 K were used for calculating the various surface areas. The cross-section of the nitrogen molecule was 0.162 nm².

- **Chemisorption**

Volumetric chemisorption of hydrogen was performed on a Micrometric ASAP 2020. The main purpose of chemisorption analysis is to determine the number of active sites on the catalyst. Only one catalyst was analyzed: the catalyst with 1 % Pt HT 63. Prior to the experiment, the catalyst was reduced in situ in a H_2 flow, with a heating rate of 10 °C/min up to 500 °C. Then, the sample was evacuated during 30 min in He flow at 120 °C. A leak test was performed. Finally, the temperature was decreased to 34 °C before the analysis. The weight of the catalyst used for the experiment was 0.148 g. The pressure range for the measurements was 81-207 mmHg. The assumption that the H/Pt ratio is 1:1 was done. Consequently, the spillover is neglected. Temperature, equilibrium time, pressure and flow rate, that is to say operative conditions, have to be chosen carefully to obtain accurate results.

During the chemisorption analysis, the reactive gas interacts with the catalytic surface to form some gas-solid interactions. All this interactions are not equal, as bounding energies are not the same for interactions. Two different isotherms were found during the analysis. The first one is supposed to contain both strong and weak adsorption. Then, the gas molecules weakly bounded are

removed during the evacuation of the sample. The strong bounded molecules can be removed only at high temperature and very low pressure, so they are not removed during the evacuation. A second isotherm is measured. It is supposed to be only the weak interactions. The difference between the two isotherms is supposed to be chemisorption [6]. Then, the amount of adsorbed molecules can be calculated. The calculations were done with two different methods: the difference method or the extrapolation method. The difference method consists on calculate the difference between the two isotherms. The second one is the extrapolation to zero pressure methods. It consists in identifying a linear part in the isotherm and extrapolating from this data a straight line to zero pressure [49]. Both calculations were done during the analysis, but only the second one will be reported and used for discussion in the following parts.

5 RESULTS

5.1 Characterization results

5.1.1. BET results

The surface area of each kind of catalyst was measured by BET analysis. The BET results were done for all supports and catalysts. A comparison between the supports only and the two kinds of catalysts is possible. The surface areas found by BET measurements are the following:

	HT30 (calcined)	HT30 1%w Pt	HT30 2%w Pt	HT30 (precursor)
Surface area ($m^2.g^{-1}$)	233	197	203	176

	HT63 (calcined)	HT63 1%w Pt	HT63 2%w Pt
Surface area ($m^2.g^{-1}$)	172	136	137

	HT70 (calcined)	HT70 1%w Pt	HT70 2%w Pt
Surface area ($m^2.g^{-1}$)	188	163	149

Table 3: Surface area of each support

For each result, the relative error is about 1 $m^2.g^{-1}$.

The surface area is between 100 $m^2.g^{-1}$ and 250 $m^2.g^{-1}$. These results are in accordance with the found literature results [50].

For the catalyst HT 30, the commercial support was analyzed, and the same support after treatment was also analyzed (after water and ethylene glycol treatment, and then calcination). The surface area increases after the calcination. This illustrates the modification of the hydrotalcite support after calcination [12-14].

The surface areas of catalysts with 1 % or 2 % of platinum were also measured. When there is some platinum, the surface area decreases (compared with the support only). However, for the supports HT30 and HT63, the surface area is higher when there is 2 % Pt and not only 1 %. For the hydrotalcite HT70 on the contrary, the surface area decreases when the amount of platinum increases.

The catalysts HT30-supported present the highest surface area both for 1 % and 2 % Pt. The results for the two supports HT30 and HT70, after calcination, are in accordance with the manufacturer data [51].

5.1.2 XRD results

The results from the XRD analysis are presented in this paragraph. First, the three different supports were analyzed. For each support, the XRD-diffractograms look quite similar.
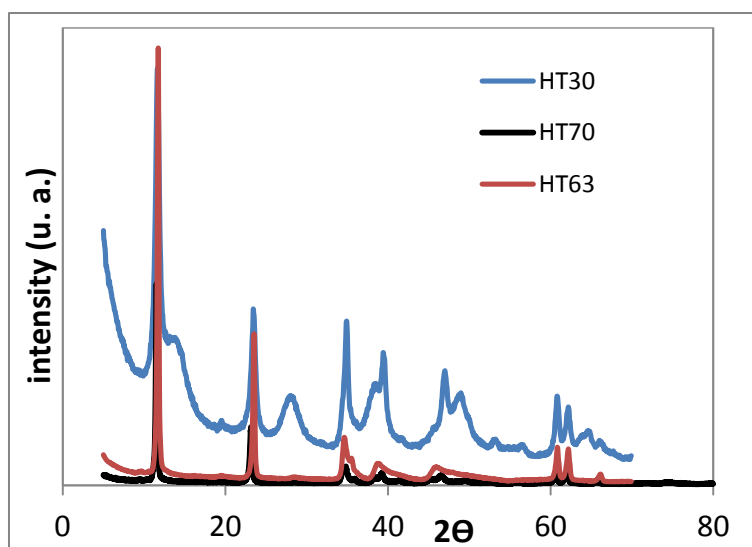
Figure 7: XRD-patterns for the three supports

Then, a comparison between the precursor and the same support after calcinations was done, for the hydrotalcite 30 and 63.
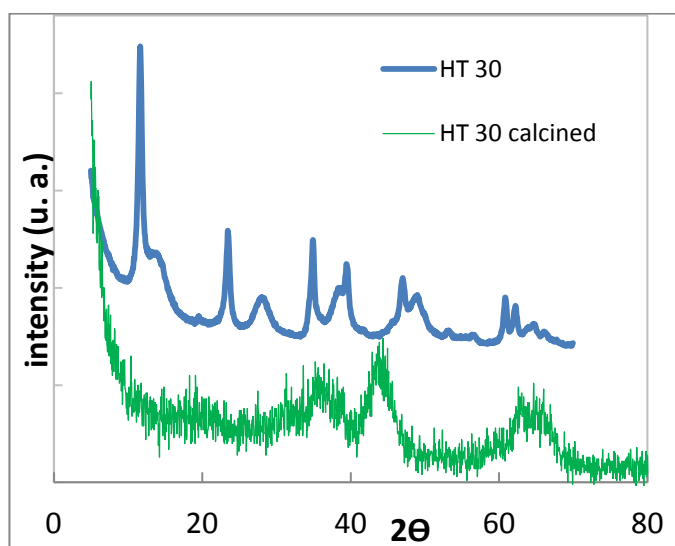
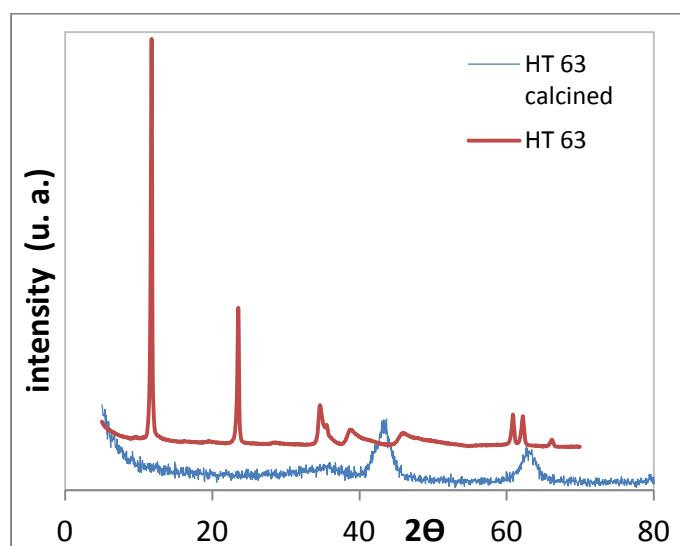Figure 8: XRD patterns for the hydrotalcite 30 prior and after the calcination

Figure 9: XRD patterns for the hydrotalcite 63 prior and after the calcination

The XRD patterns (figure 8) show that the structure is the same for each support. The most characteristic peaks of hydrotalcite are visible. Particularly, the following peaks can be noticed : d=7,6 Å , with a reflection angle 2Θ=11,6 °, d=3,8 Å with a reflection angle 2Θ=23,5 °, d=2,57 Å (2Θ=34,8 °), d=1,94 Å (2Θ=46,5 °) and d=1,52 Å (2Θ=60,7 °). The peaks were identified by comparing standards in a database.

The structure is dramatically modified after the calcination (figure 9). These results can be compared with results found in the literature. For example, theses plots are really similar to these established by V. Galvita *et al.* [26]. The difference between the two XRD patterns shows that the structure of hydrotalcite is changed due to heat treatment, and it is a confirmation that the coordination of Al and Mg are affected by heat. On the XRD pattern of the calcined catalyst, there are

two significant peaks. These peaks are characteristic of cubic MgO, which is a poorly crystalline phase. Indeed, this component MgO is formed after the heat treatment of hydrotalcite, provided that the temperature was above 450 °C [11].

Concerning the catalyst with Pt, the metal is not visible on the XRD patterns. To analyze the results, EVA software was used. This software is graphics software for data presentation and evaluation. During the analysis, the background was subtracted, the peaks were search and the main parameters found thanks to it (distance, reflection angle, intensity…). However, even with software, the Pt characteristic peak cannot be found. This may be due to the small size of the Pt particles. With other software or a better acknowledgement of this one, it may be possible to obtain some data about platinum particles.
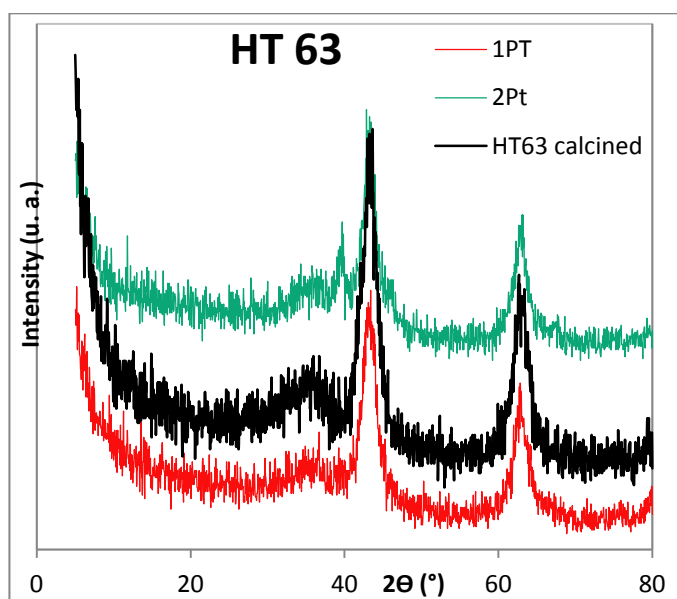
Figure 10: XRD patterns for the support HT 63
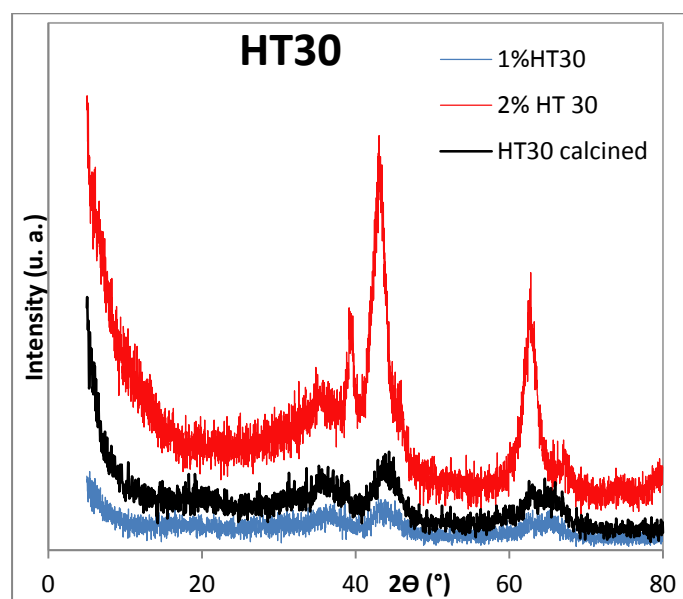
Figure 11: XRD patterns for the support HT 30

The calcined HT70 support and the two HT70-supported catalysts did not been analyzed by XRD. However, as the surface was similar to other supports before calcinations, the same structure evolution after calcination can be supposed.

5.1.3   Chemisorption test

The chemisorption test was done on the reduced catalyst. The metal dispersion could be determinate thanks to this volumetric hydrogen chemisorption. The dispersion is based on total adsorption of hydrogen. The metal dispersion is 55.1 %. The metallic surface area is 1.36 m²/g of sample, or 136.1 m²/g of metal. The crystallite size is 2.05 nm. These results are in accordance with thus fund in the literature, for a similar catalyst [6].

5.2   Activity test

For each component detected by GC, the retention time, the surface area and the high of the peak are available. Thanks to theses data, the concentration of each product at the output of the reactor can be known. An average was calculated between the different measurements, to be sure

that the results were quite good. At the beginning, the composition of the initial gas mixture was checked.

Two main series of experiments were performed. First, 3 different kinds of hydrotalcite with different Pt loading and a catalyst based on zeolite with platinum were tested. The feed gas was the same for all these experiments. Then, one of the catalysts hydrotalcite supported was selected, and different feed gases were used.

5.2.1 With O_2

5.2.1.1 Support test

During the experiments, the pressure drop increased slowly with the temperature. The maximum pressure drop was inferior to 1 bar for the hydrotalcite supported catalysts except the catalyst 2 % Pt HT 63, whom pressure reached 1.25 bar at 650 °C. For the catalyst with 1 % Pt and zeolite, the pressure drop at the final temperature was high (above 1.9 bar overpressure).

- Conversion

Thanks to the experiments, the C_3H_6 conversion is calculated (Appendix 2). The plot conversion as a function of the temperature can be draw. An activity test was done for all the catalyst, with the same conditions. The following results were obtained:
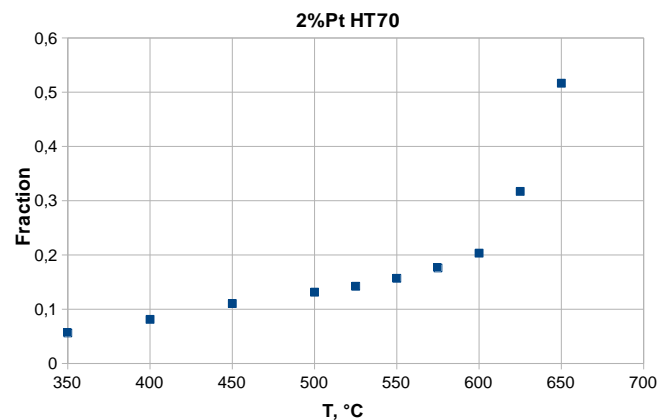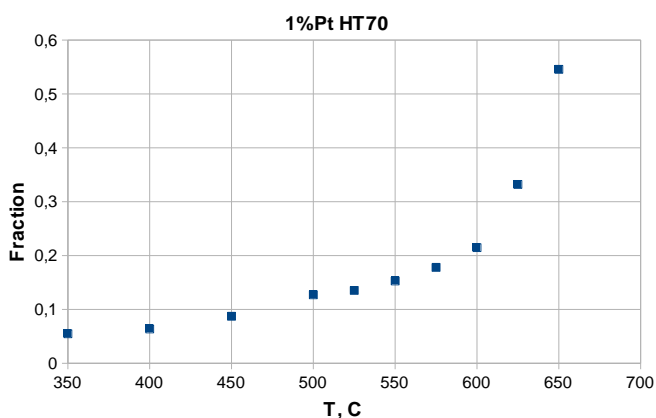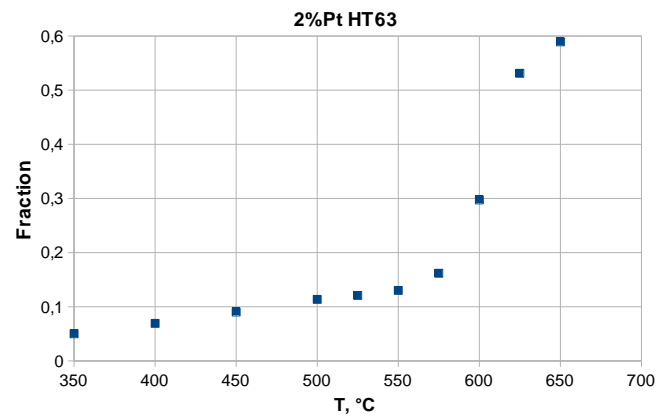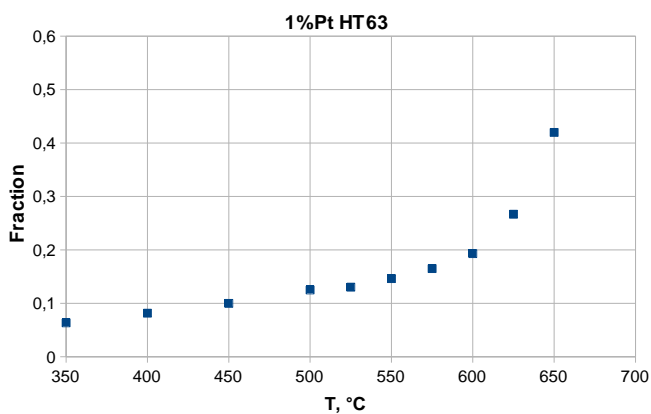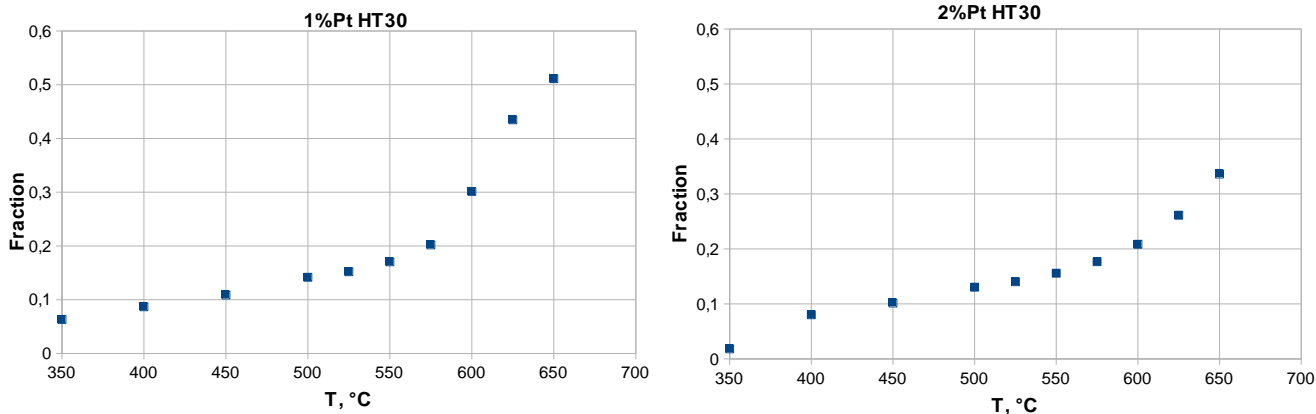
Figure 12: Conversion of propane as a function of temperature

As expected, the conversion rate increases when the temperature increases. However, the conversion increases very slowly until 600 °C in all the cases. The very low conversion rate for a temperature inferior to 575 °C can be noticed.

For the two supports HT 63 and HT 70, when the quantity of Platinum increased, the conversion rate increases. On the contrary, the conversion decreases when the weight percentage of platinum goes from 1 to 2 % for the support HT 30.

- Selectivity

The carbon selectivity is defined by the ratio of the molar amount of key reactant formed during the reaction on the total quantity of C_3H_8 converted by the reaction. The selectivity was calculated for different products: C_3H_6, which is the interesting product, but also CO, CO_2, CH_4, C_2H_4, and C_2H_6. Oxygen selectivity was also established for CO, CO_2 and H_2O according to the molar amount of O_2. All the details for calculation of selectivity are given in appendix 2. The various plot of carbon selectivity are the following:

28
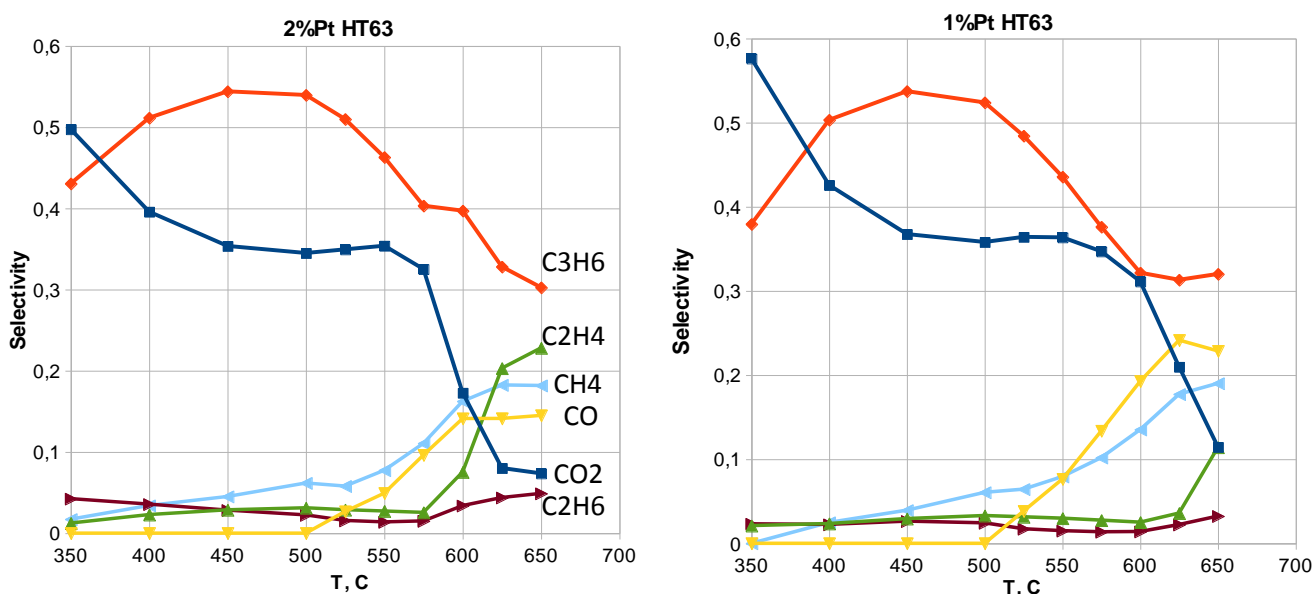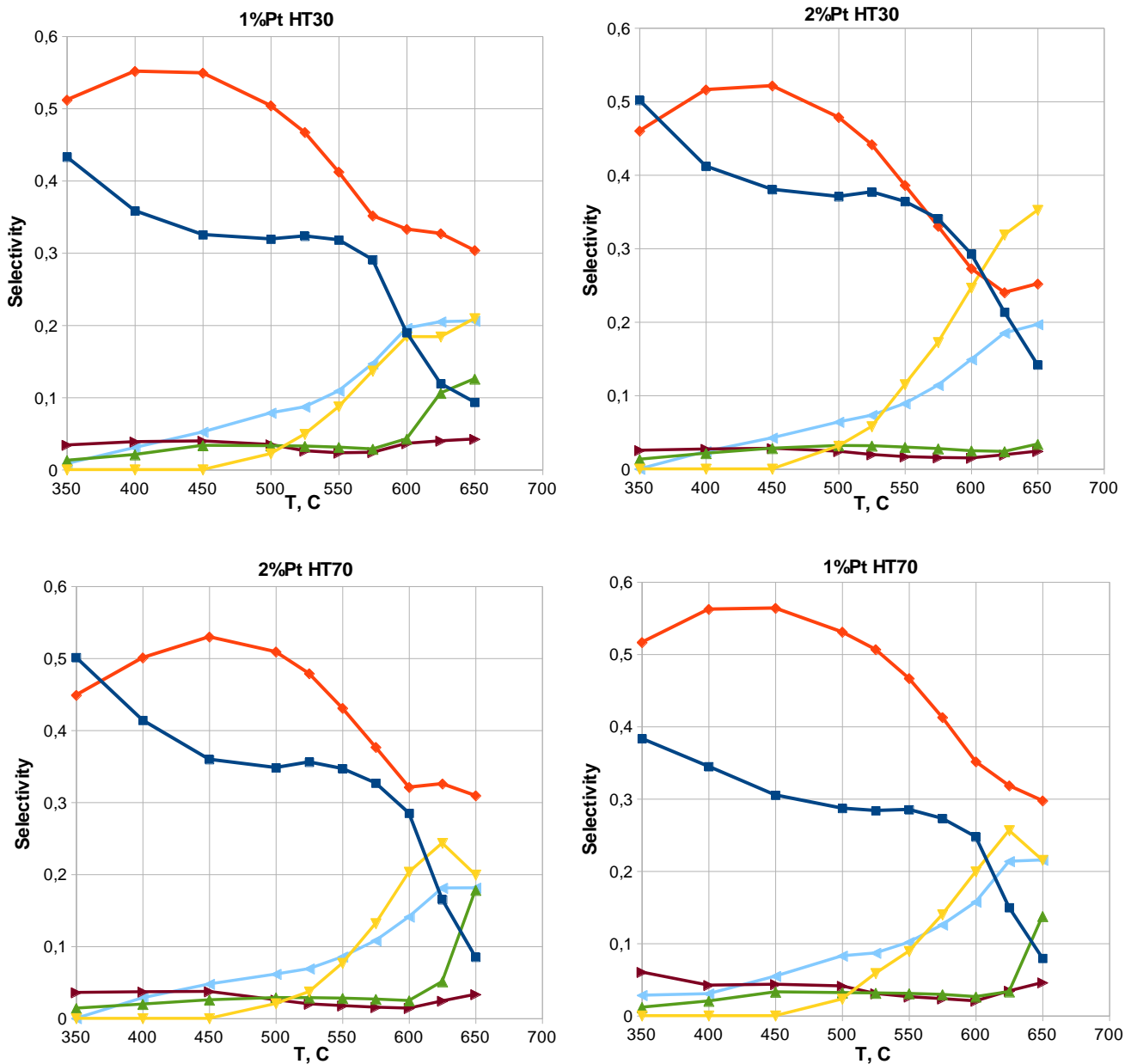
Figure 13: Carbon selectivity as a function of temperature, for all the catalysts

With all the catalysts, the selectivity reaches a maximum for a temperature around 500 °C. A significant amount of CO_2 is produced even at low temperature. For the catalysts 1 % Pt HT70, 1 % Pt HT63 and 2 % Pt HT30, the selectivity of the by-products C_2H_4 and C_2H_6 is very low at all the temperature. For the three other catalysts, the C_2H_4 selectivity increases for temperature above 600 °C until 0.23 for the catalysts 2 % Pt HT63.

The oxygen selectivity can also be determinate. In this case, the molar amount of O_2 is considered instead of C_3H_8. The calculations are given in appendix 2. All the oxygen was consumed during the reaction, whatever the catalyst. The main part of oxygen is used to produce water below 550 °C. The selectivity of H_2O is about 90 % at 350 °C. For temperatures above 550 °C, carbon dioxide and carbon monoxide consumed a significant amount of O_2. The oxidation is less selective at high temperature, since hydrogen is not the only molecule that is oxidized.
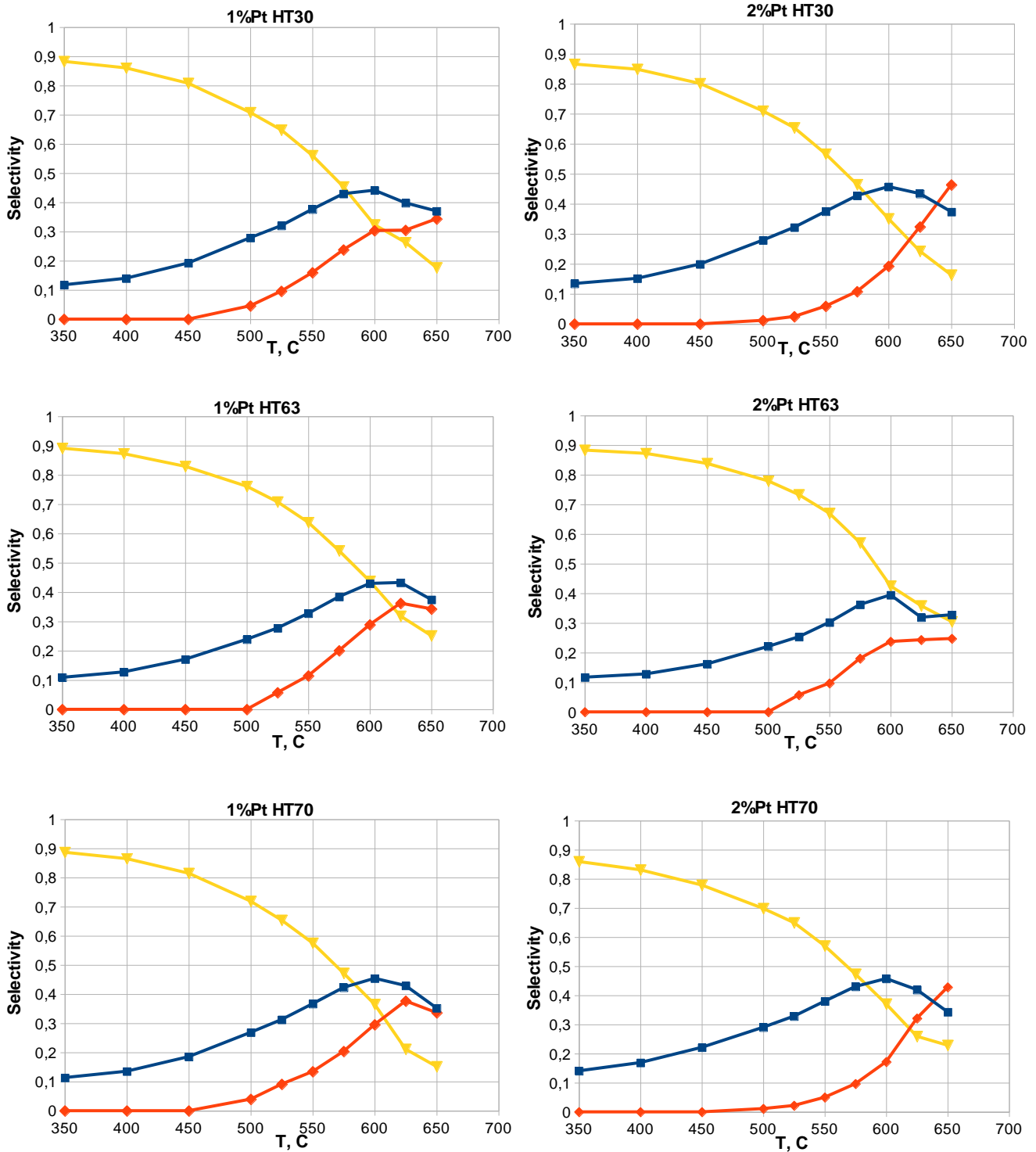
Figure 14 : O2 selectivity to H2O, CO and CO2 as a function of the temperature

Concerning the zeolite support, two different loading were used: 0.5 % and 1 % Pt. The pressure drop was higher for the catalyst with 1 % Pt.

Another kind of catalyst was also tested during this work. It was a platinum zeolite supported catalyst. This catalyst was prepared by impregnation. An activity test was performed. 150 mg of catalyst were used for the two first experiments. Prior to the activity test, the catalyst was reduced. Then, the catalyst was put in the oven, and the temperature increased until 350 °C. A mixture of

helium (30 mol/L) and H$_2$ (10 mol/l) went through the reactor during the increasing of temperature. From 350 °C to 650 °C, the outlet gas was analyzed thanks to the GC. Two different Pt loading were used, and the experiments were done at two different pressure. The first results given are for catalyst with a load of 0.5 % Pt, and the pressure was 1.6 bar.
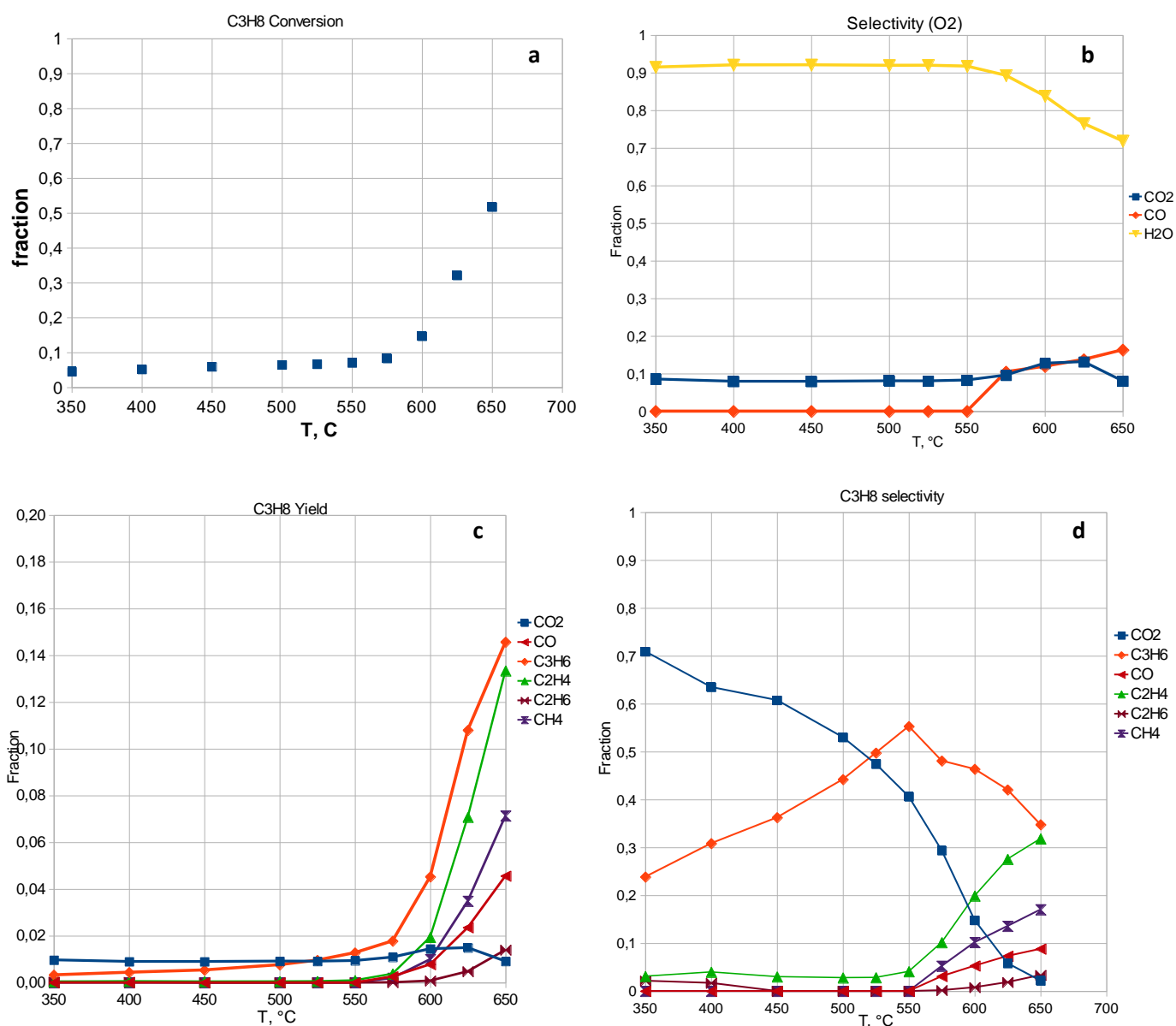
Figure 15: a) propane conversion, b) O2 selectivity, c) propane yield and d) propane selectivity as a function of the temperature, for a zeolite catalyst with 0.5 % Pt

For the second experiment, the load was 1 % weight Pt, and the maximum pressure was around 3 bar.
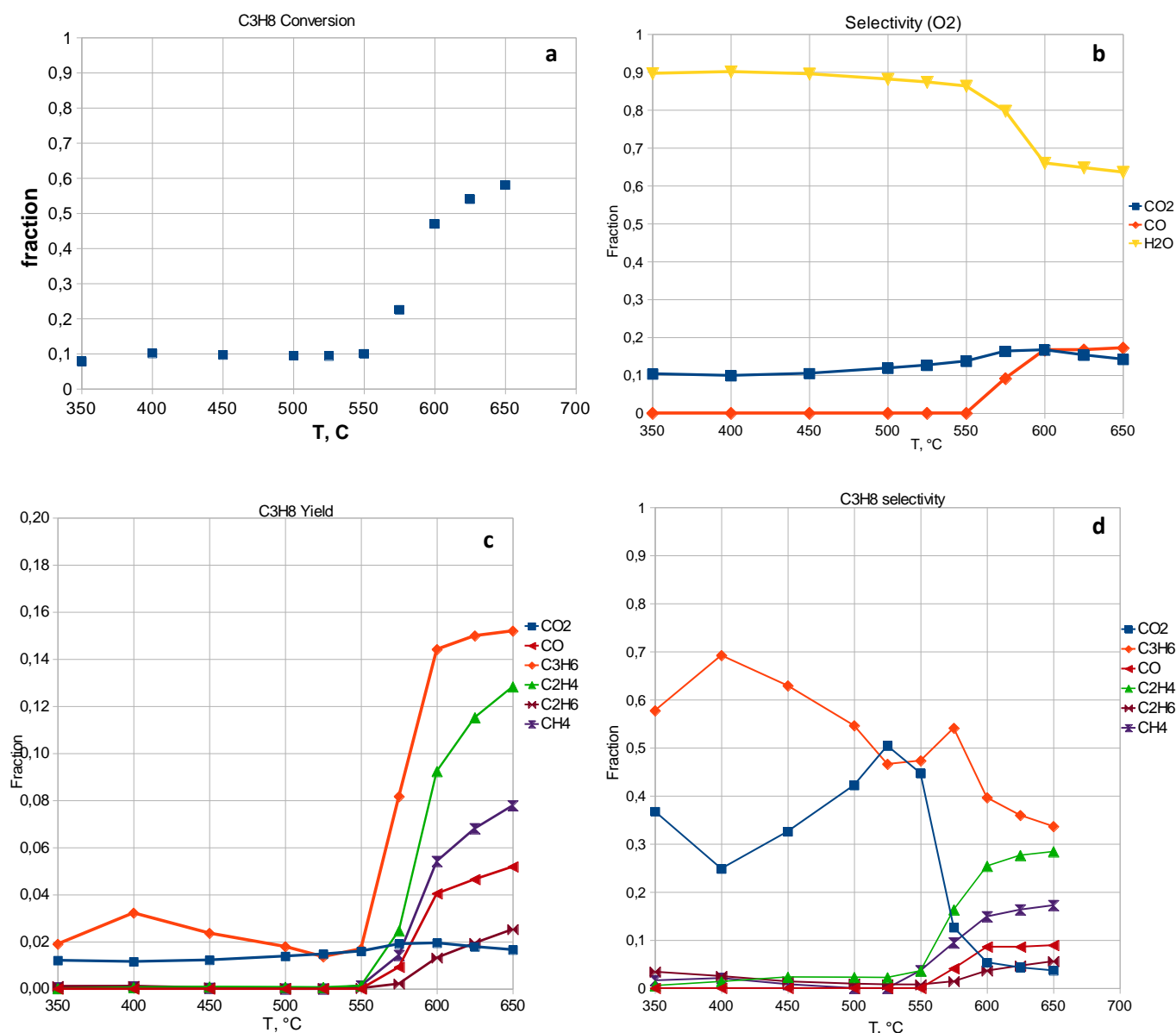
Figure 16: a) propane conversion, b) O2 selectivity, c) propane yield and d) propane selectivity as a function of the temperature, for a zeolite catalyst with 1 % Pt

The conversion is improved for the second catalyst, that is to say for the catalyst with a higher Pt-loading. However, as the pressure was higher, it could be this parameter which influences the results. As expected, the selectivity to propene decreases with the temperature. It is not possible to have on the same time a very high propane conversion and a good selectivity to propene. The behavior of the system is similar with the zeolite support and the hydrotalcite support.

5.2.1.2 Feed composition

The catalyst HT 63 with 1 % Pt was used for the following experiments. The following table sums up the more relevant points: the feed gas composition, the maximum overpressure, the presence or not of a jump in the propane conversion, and the jump temperature if there is one. The feed gas composition varies from 7 % of oxygen to 44 %, and 30 to 85 % of propane. To choose the feed gas composition, an experiment plan was done.

Four full examples of results are given in this part of the report. The other plots are put in appendix (appendix 3 for the propane conversion, 4 for carbon selectivity, 5 for yield and 6 for oxygen selectivity).

The propane conversion jump occurs when the pressure is high (above 2 bara), and for a temperature superior to 575°C. In this case, the final propane conversion is always superior to 52 % (up to 68 %) and the propene yield is around 15 %. The selectivity rank is between 26 and 61 %.

Difference between various feed mixtures can also be noticed, without taking into consideration the pressure difference. So, two series of measurements can be compared.

The darkest lines in the following table refer to experiments with low pressure.

N°	H_2	C_3H_8	O_2	Over pressure (bar)	Jump (conversion)	Max conversion	Max selectivity (C_3H_6)	Max yield (C_3H_6)	Selectivity max (CH_4/C_3H_8)	T° CO increases	Selectivity max (CO/O2)	Selectivity max (CO_2/O_2)
1	0	56	44	0.45	No	0.38	0.09	0.17	0.06	450	0.29	0.69
2	0	70	30	2.45	Yes (575 °C)	0.65	0.38	0.17	0.14	450	0.33	0.72
3	0	85	15	0.6	No	0.14	0.35	0.03	0.1	450	0.87	0.68
4	25	45	30	2.15	Yes (575 °C)	0.8	0.26	0.16	0.18	500	0.43	0.55
5	55	30	15	2.2	Yes (575 °C)	0.68	0.26	0.13	0.35	450	0.54	0.35
6	27	58	15	2	Yes (550 °C)	0.52	0.61	0.145	0.21	450	0.5	0.42
6	27	56	16	0.8	No	0.42	0.14	0.148	0.20	450	0.5	0.40
7	7	60	33	0.2	No	0.43	0.2	0.082	0.14	450	0.46	0.64
8	59	34	7	0.7	No	0.4	0.44	0.108	0.38	450	0.54	0.2
9	8	71	21	1.4	Yes (575 °C)	0.59	0.36	0.16	0.17	450	0.3	0.6
10	34	59	7	0.1	No	0.18	0.64	0.07	0.17	450	0.71	0.23
11	37	45	18	1.9	Yes	0.61	0.52	0.153	0.23	500	0.39	0.42
11	37	45	18	0.2	No	0.27	0.61	0.05	0.18	500	0.31	0.41
12	19	58	23	2.3	Yes (600 °C)	0.6	0.38	0.162	0.19	500	0.3	0.54
12	18	60	22	0.1	No	0.32	0.39	0.052	0.14	500	0.63	0.53
Without catalyst (12)	31	62	7	2	Yes (600 °C)	0.37	0.59	0.12	0.17	600	0.07	0.05
Without catalyst (12)	31	62	7	0.2	no	0.36	0.57	0.13	0.15	600	0.11	0.08

Table 4: Main parameters for the feed gas analysis, with 1 % Pt HT 63

Five full examples are given to illustrate the table of results. The four first experiments in this part were done at low pressure, the last one at high pressure.

The first example is the experiment 12, with the feed gas composed by 18 % H_2, 60 % C_3H_8 and 22 % O_2.
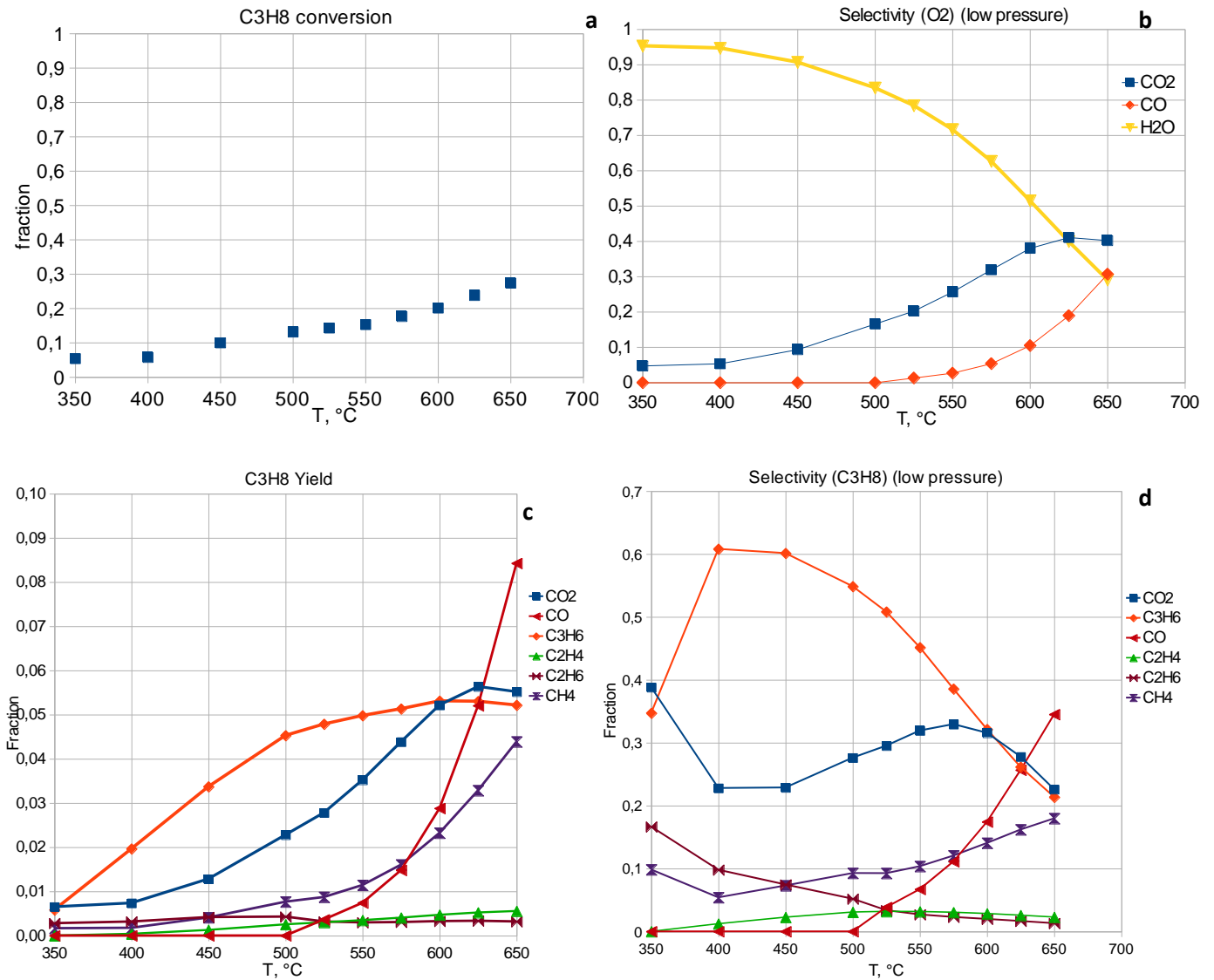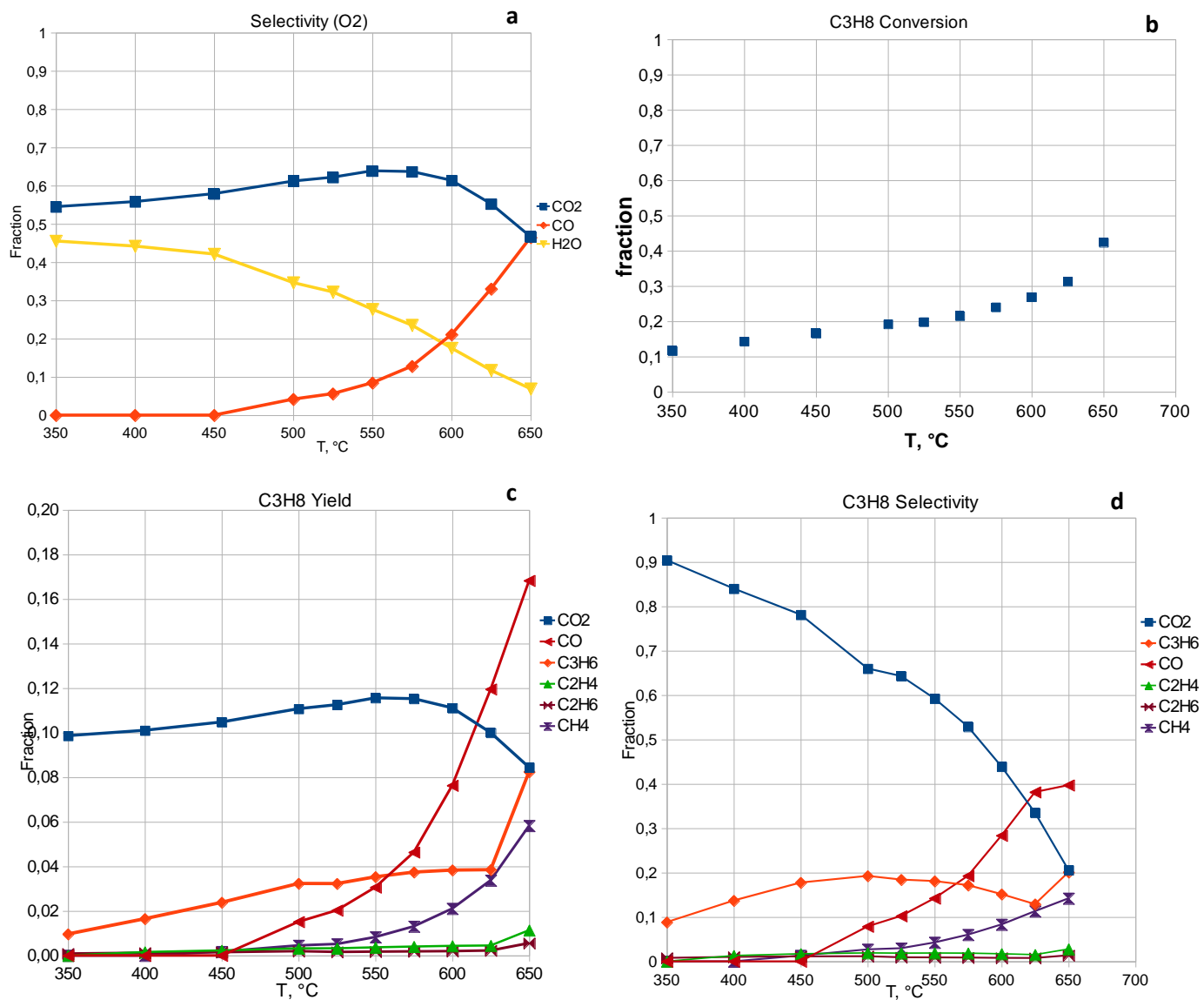

Figure 17: a) propane conversion, b) O2 selectivity, c) propane yield and d) propane selectivity as a function of temperature

The amount of oxygen was quite high in this example. The results are quite similar to the results with other feed gas composition including propane, hydrogen and oxygen.

A second example, with less oxygen but a lot of propane is also given. This second example is the experiment 7. In this case, the composition of the active species in the feed gas is 7 % H_2, 60 % C_3H_8 and 33 % O_2.

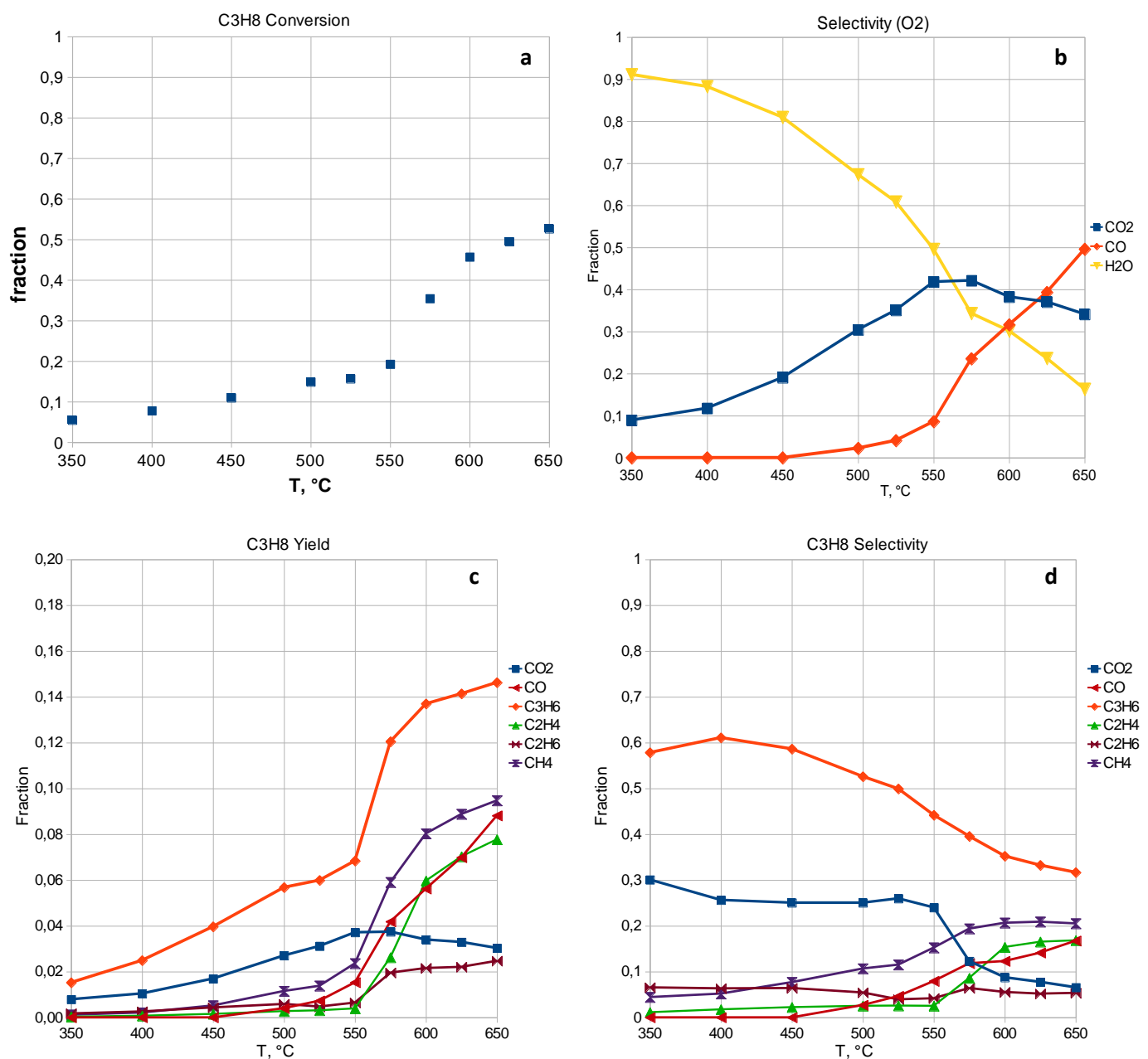**Figure 18: a) propane conversion, b) O2 selectivity, c) propane yield and d) propane selectivity as a function of temperature**

In this example, the propane conversion is a bit better than in the previous one, with around 41 % maximum conversion. The amount of H_2 in the feed gas was quite low (only 7 %, in comparison with 18 % for the other one). This may explain the selectivity of oxygen to CO_2 instead of H_2O. In this case, the selectivity to propene is not really good: only 20 % maximum selectivity.

Some experiments were performed without hydrogen in the feed gas. Two examples of this system are given.

The third example is the experiment 1, with the following feed gas composition: 56 % of C_3H_8 and 44 % of O_2.
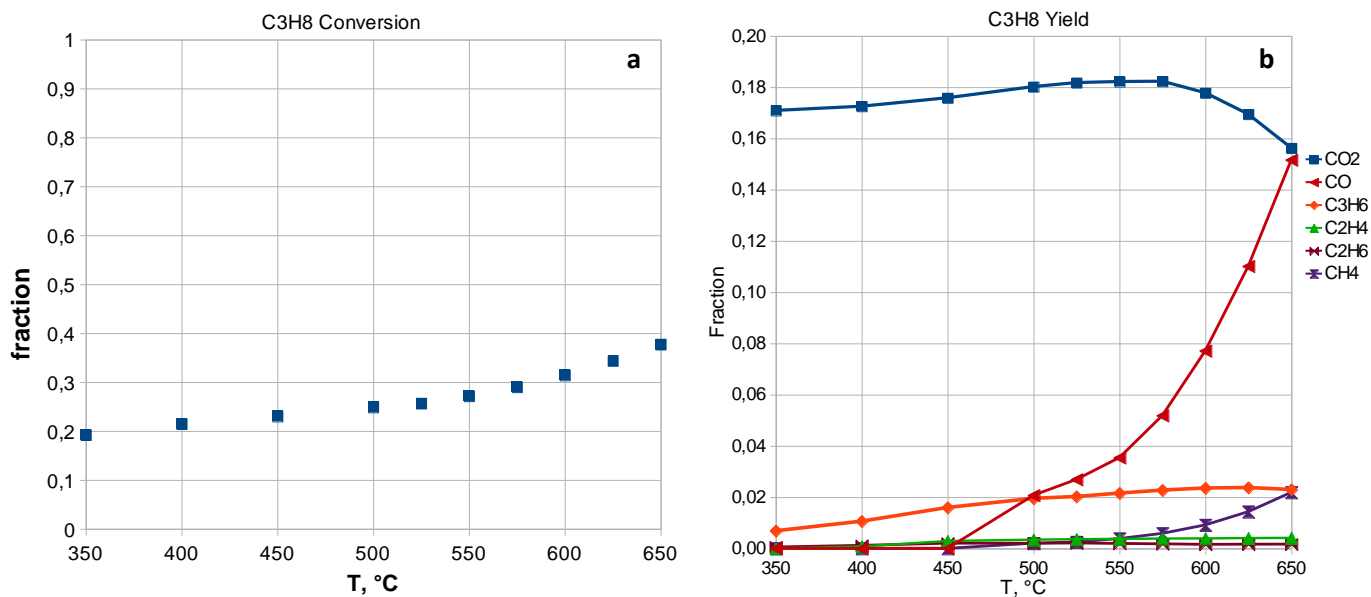
Figure 19: a) propane conversion, b) propane yield as a function of temperature

The fourth example is the experiment, whose feed gas composition was 85 % of C_3H_8 and 15 % of O_2.
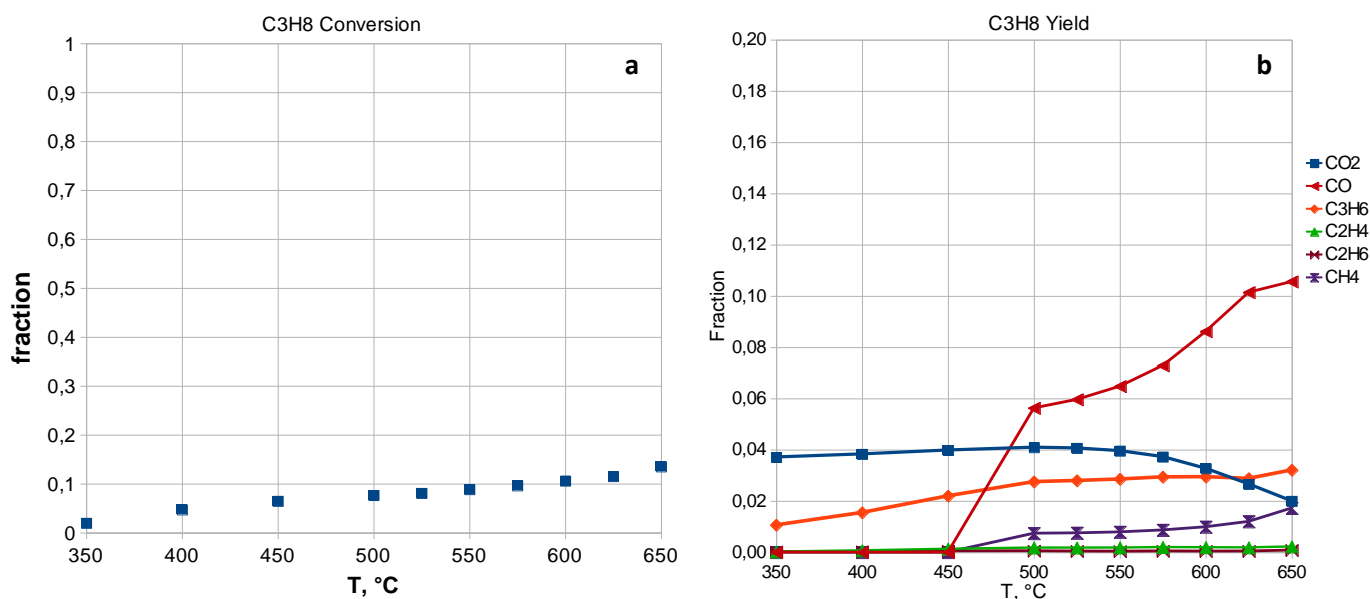
Figure 20: a) propane conversion, b) propane yield as a function of temperature

These two experiments, without hydrogen, can be compared. When the amount of oxygen increased in the reactor, the propane conversion and the propene yield were improved. Oxygen had a positive effect on the system in this case. In both case, all oxygen is consumed, and the main product formed with O_2 is CO_2.

The fifth example is the experiment 6, with high pressure. In this case, 27 % of H_2 was used, with 56 % of C_3H_8 and 16 % of O_2.

The propane conversion jump is visible on the plot. Above 550 °C, the conversion is dramatically improved. The maximum conversion is high, as the propene selectivity to propane and the yield of propane.
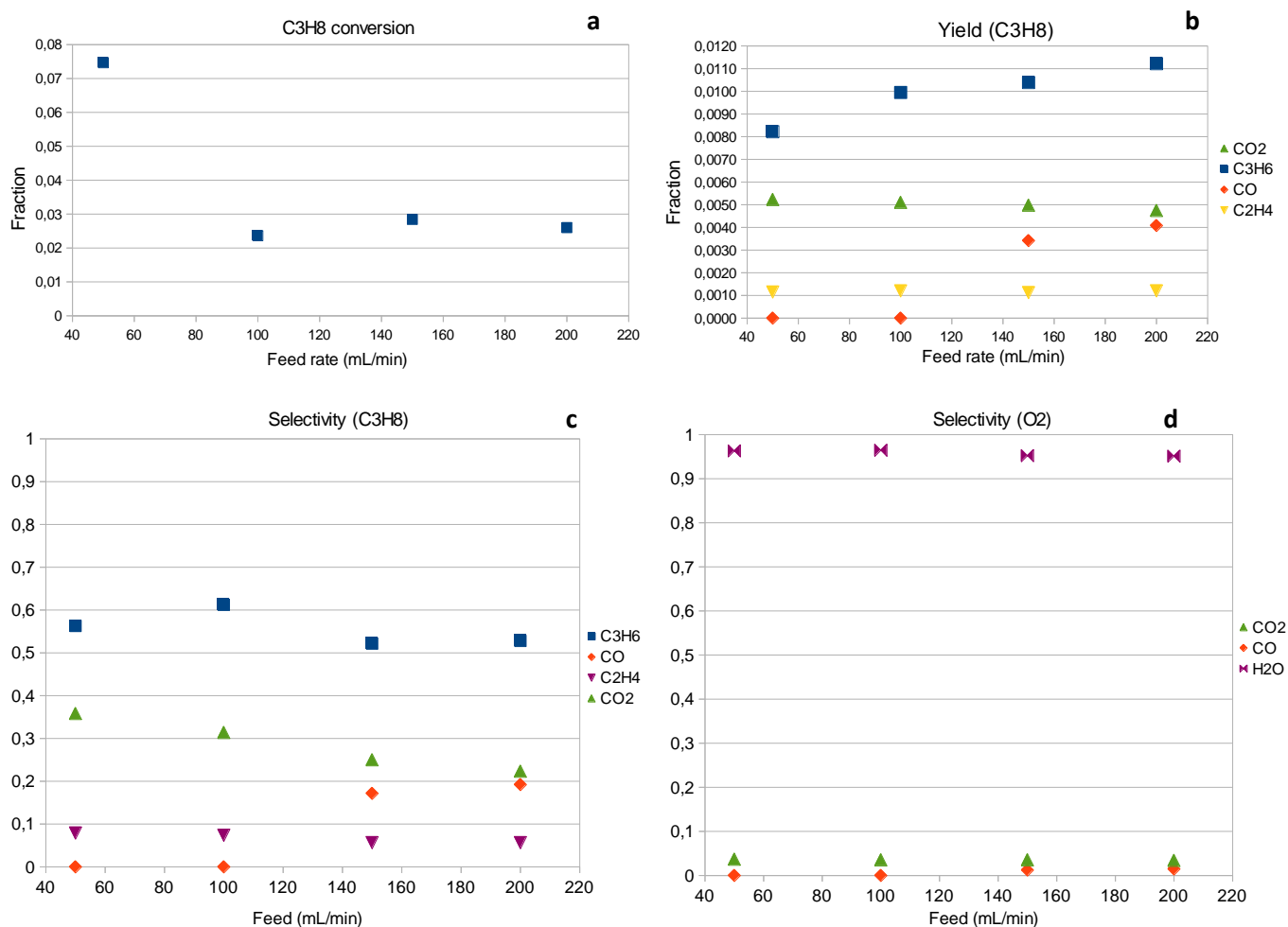

Figure 21: a) propane conversion, b) O2 selectivity, c) propane yield and d) propane selectivity as a function of temperature

5.2.1.3 Feed influence on the reaction

4 experiments were performed. The same ratio of active components was used for the 4 experiments. The ratio of active components is around 37 % of H_2, 44 % of C_3H_8 and 19 % of O_2. The feed rates were 50, 100, 150 and 200 mL/min. The temperature was 575 °C. In each case, O_2 and H_2 were entirely consumed. C_2H_4 and CH_4 were produced, but C_2H_6 was not. CO is produced for a feed velocity superior to 150 mL/min, and the amount of CO increases when the feed increases. The propane conversion is higher when the feed stream is lower (7 % conversion for 50 mL/min).

The propene yield increases when the feed rate increases (from 0.8 to 1.1 %). C_2H_4 yield is quasi constant whatever the feed. The amount of CO_2 decreases quickly when the feed rate increases, whereas the amount of CO increases. CO begins to accumulate when the feed velocity is quite high. It is possible to suppose that CO_2 is produced by a consecutive reaction of CO with O_2. If the feed velocity increases, there is not enough time for O_2 to oxidize CO. Consequently, the amount of CO_2 produced in the reactor decreases, whereas the amount of CO detected by the GC increases. The selectivity of C_2H_4 decreases also slowly (form 1 % to 0.6 %). The yield is poor for this reaction at this temperature. The selectivity of C_3H_6 decreases slowly when the feed increases.

Most of oxygen is used to produce water.

Figure 22: a) propane conversion, b) O2 selectivity, c) propane yield and d) propane selectivity as a function of feed velocity, at 575 °C.

5.2.1.4 Pressure influence on the reaction

The pressure used for the experiments can be chosen. Two different pressures were used for some experiments. Indeed, the same gas mixture was analyzed with high pressure (2 bar excessive pressure) and low pressure (less than 0.1 bar overpressure). The pressure influence was tested both for system with and without catalyst. Indeed, the catalyst was used only for two experiments. For 2 other, only quartz wool was put in the reactor. The feed gas used for the reaction has almost the following composition: H_2: 36 % ; C_3H_8: 46 % ; O_2: 18 %.

First, the reactor was loaded with 0.150 g of catalyst and quartz wool. In this case, the exact compositions of the gas mixtures were at high pressure: H_2 : 37.5 % ; C_3H_8 : 44.6 % ; O_2 : 17.9 % and at low pressure: H_2 : 37.2 % ; C_3H_8 : 44.5 % ; O_2 : 18.3 %. The following plots are the propane conversion as a function of the temperature, at high and low pressure.
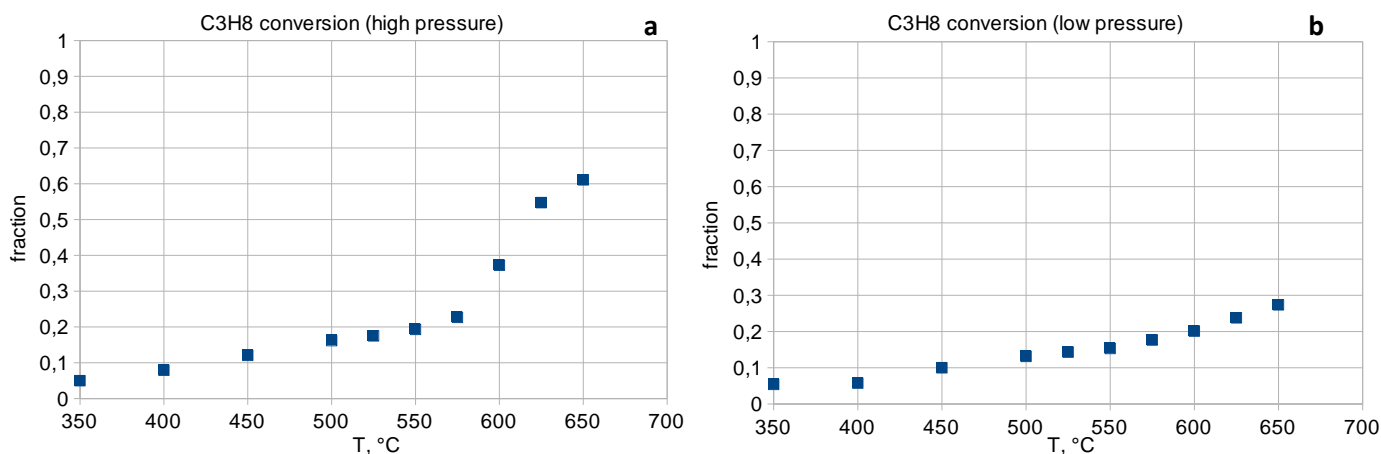

Figure 23: C3H8 conversion as a function of temperature, with a) high pressure (3 bar) and b) low pressure (1.1 bar)

The behavior of the system is quite different according to the pressure. In the first case, at high pressure, there is a jump in propane conversion around 575 °C. This conversion jump is not really significant at low pressure. Before this conversion jump, the conversion was almost the same for the system at high pressure and low pressure (around 19 % conversion at 550 °C and high pressure, 17 % at low pressure). The propane conversion at high temperature and high pressure is quite good, around 60 %. It is less than 30 % at low pressure.

The carbon yield and selectivity were also determinate. The following plots were found:
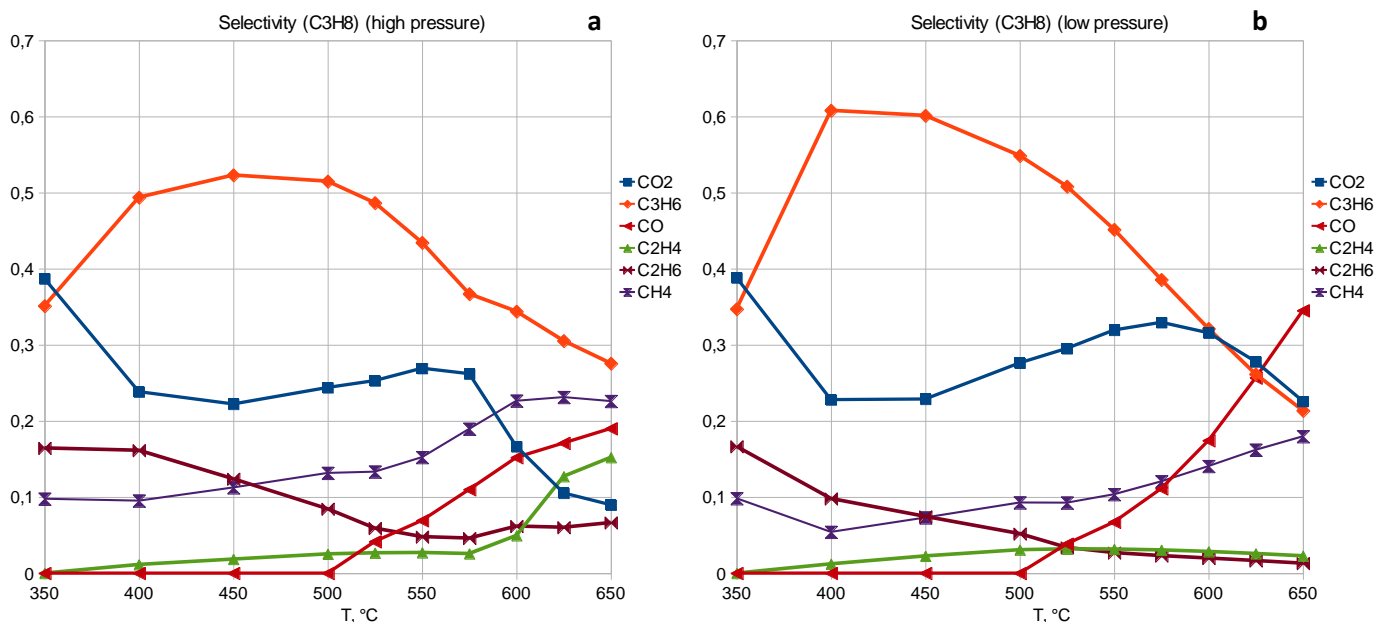
Figure 24: C3H8 selectivity a function of temperature, with a) high pressure (3 bar) and b) low pressure (1.1 bar)

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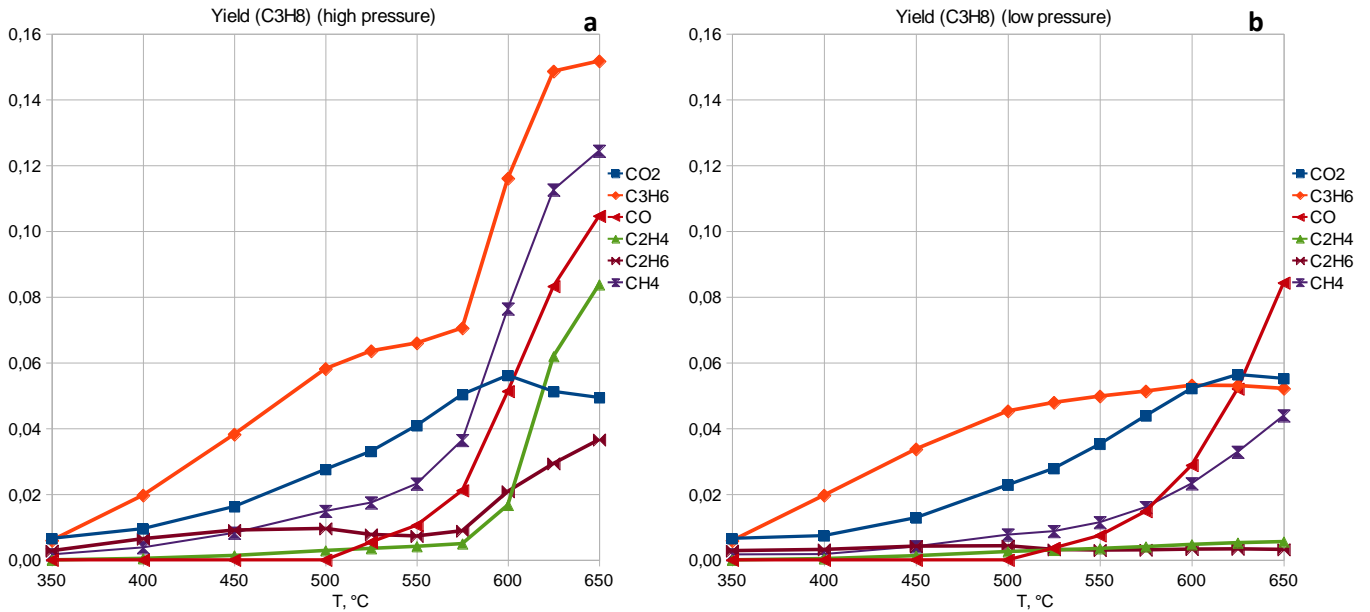
Figure 25: C3H8 yield a function of temperature, with a) high pressure (3 bar) and b) low pressure (1.1 bar)

The maximum selectivity of C_3H_8 from C_3H_6 is a bit better at low pressure (0.52 ; 0.60). The selectivity of ethane and ethylene is less important at low pressure, since less than 2 % of the products formed by the decomposition of propane are these products. The propene yield is better at high pressure.

Finally, oxygen selectivity was studied. O_2 is mainly consumed to produce water, in both cases. Whatever the pressure, CO is formed as soon as the temperature is superior to 500 °C. At high pressure and high temperature, CO_2 and CO are produced in the same quantity.
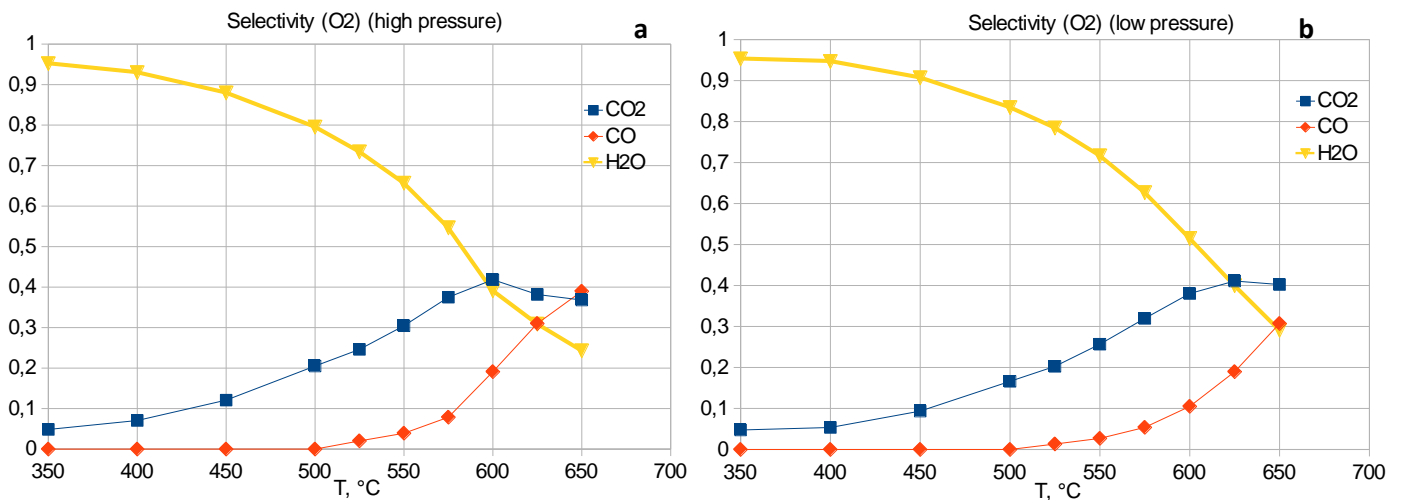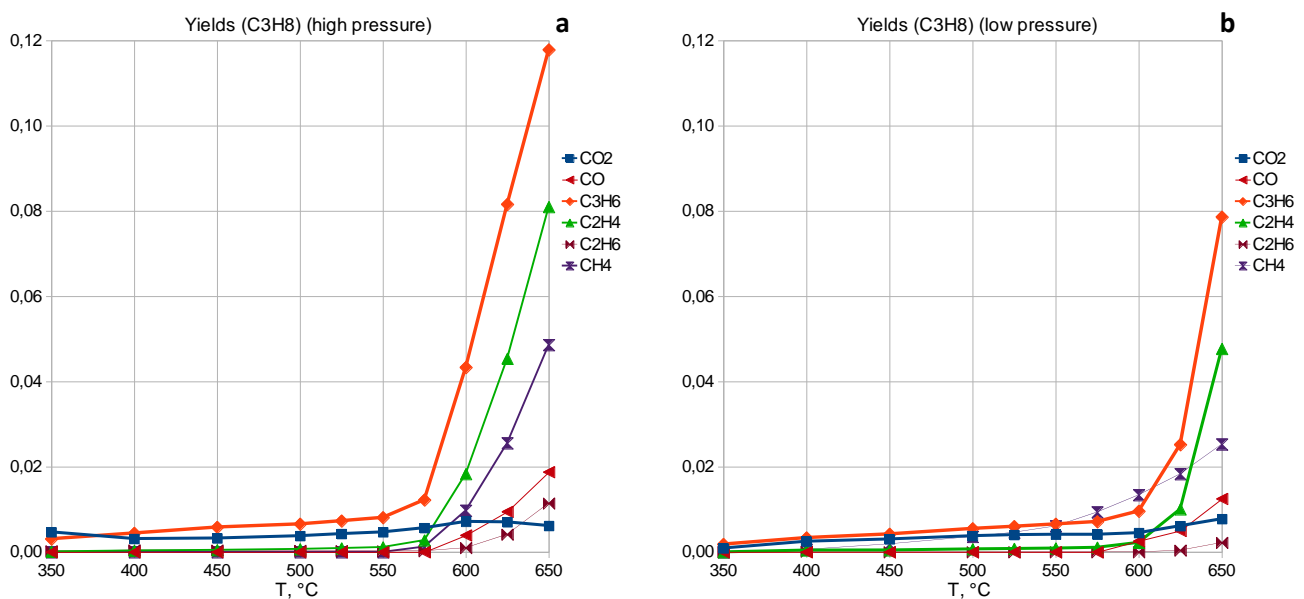

Figure 26: O2 selectivity a function of temperature, with a) high pressure (3 bar) and b) low pressure (1.1 bar)

The same experiments were carried out without catalyst, to know the catalyst activity in the reaction.

The figure 25 shows the propane conversion as a function of the temperature, at low and high overpressure. At low pressure, the exact composition of the feed gas was the following: H_2 : 37 % ;

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C_3H_8 : 45 % ; O_2 : 18 % and at high pressure, the composition was: H_2 : 36 % ; C_3H_8 : 46 % ; O_2 : 18 %. In both cases, there is a pressure jump in propane conversion at high temperature. At high pressure, the pressure increases quickly for a temperature above 575 °C. At low pressure, this increasing happens for a temperature superior to 600 °C. The final value of the conversion rate is 0.37 at high pressure and 0.32 at low temperature (i. e. 15 % increasing). Before this jump, the system doesn't seem to react to the temperature. The behavior of the system without catalyst is similar to the system with catalyst at high temperature. The main difference between the system with catalyst and without is the conversion reached at high temperature. With catalyst, the conversion is superior to 60%, whereas it was 37 % without (i. e. 1.65 times).
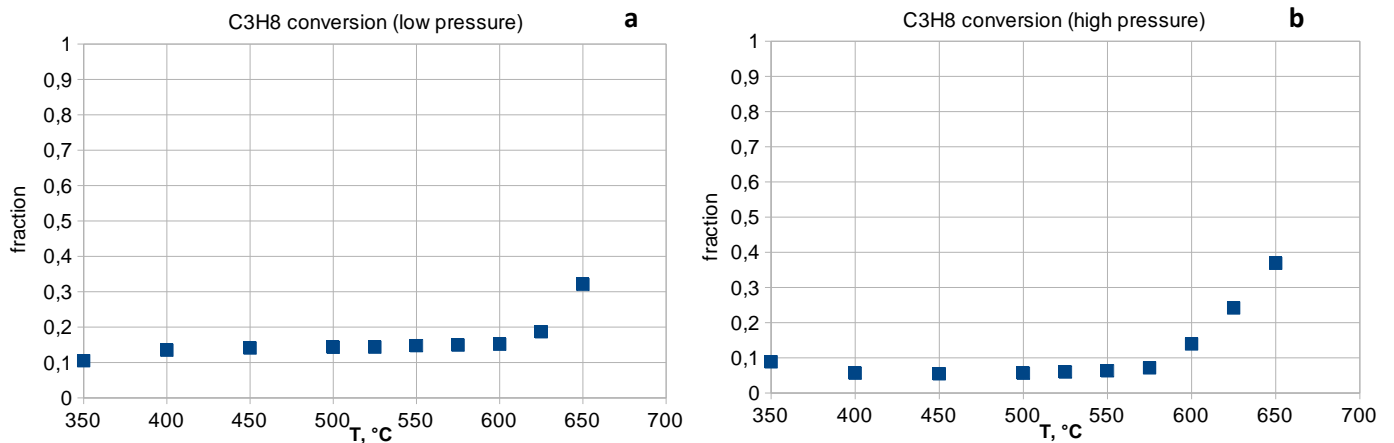
Figure 27: propane conversion a function of temperature, with a) high pressure (3 bar) and b) low pressure (1.1 bar), without catalyst

Concerning the yield (define with the number of C), there is some difference according to the pressure. The maximum propene yield is, at high pressure, around 12 %. At low pressure, it's only 8 %. In both case, ethylene is the second carbon main product concerning the yield, around 8 % at high pressure and 5% at low pressure.

Figure 28: C3H8 yield a function of temperature, with a) high pressure (3 bar) and b) low pressure (1.1 bar), without catalyst
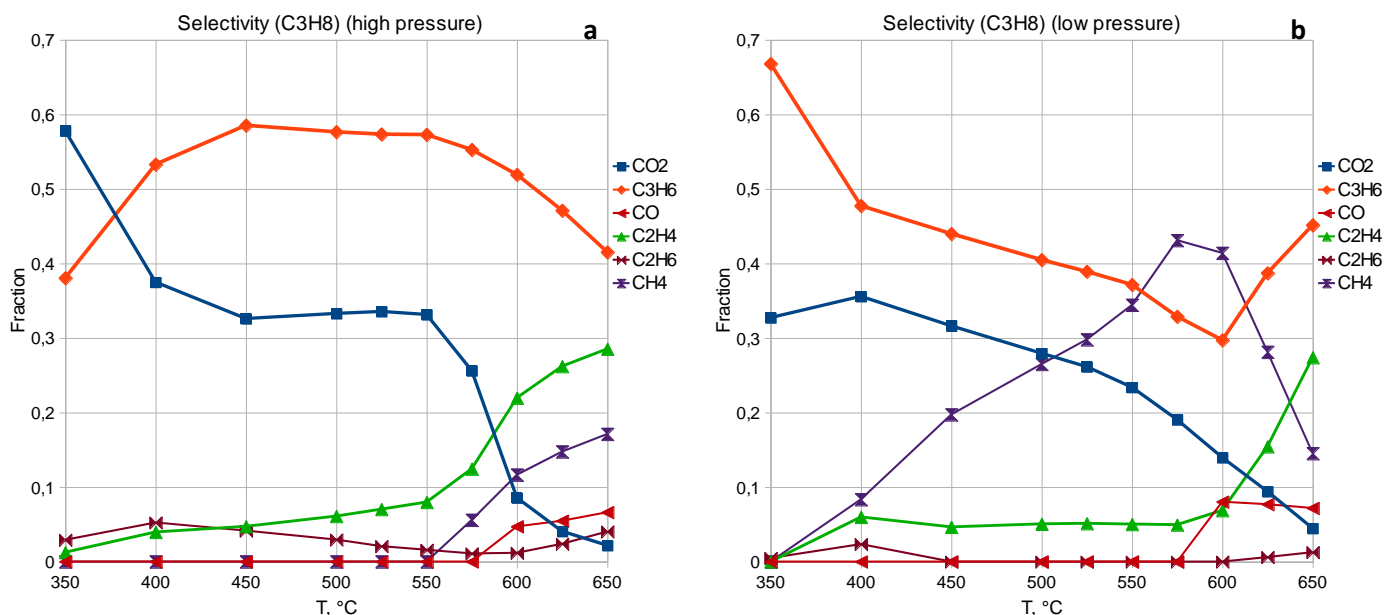
Figure 29: C3H8 selectivity a function of temperature, with a) high pressure (3 bar) and b) low pressure (1.1 bar), without catalyst

During the experiments, O_2 is entirely consumed. In both case, the main product formed with O_2 is water. A small amount of CO_2 is also formed at "low" temperature. When the conversion increases, some CO is also formed. The amount of CO_2 produced is almost constant with the temperature.
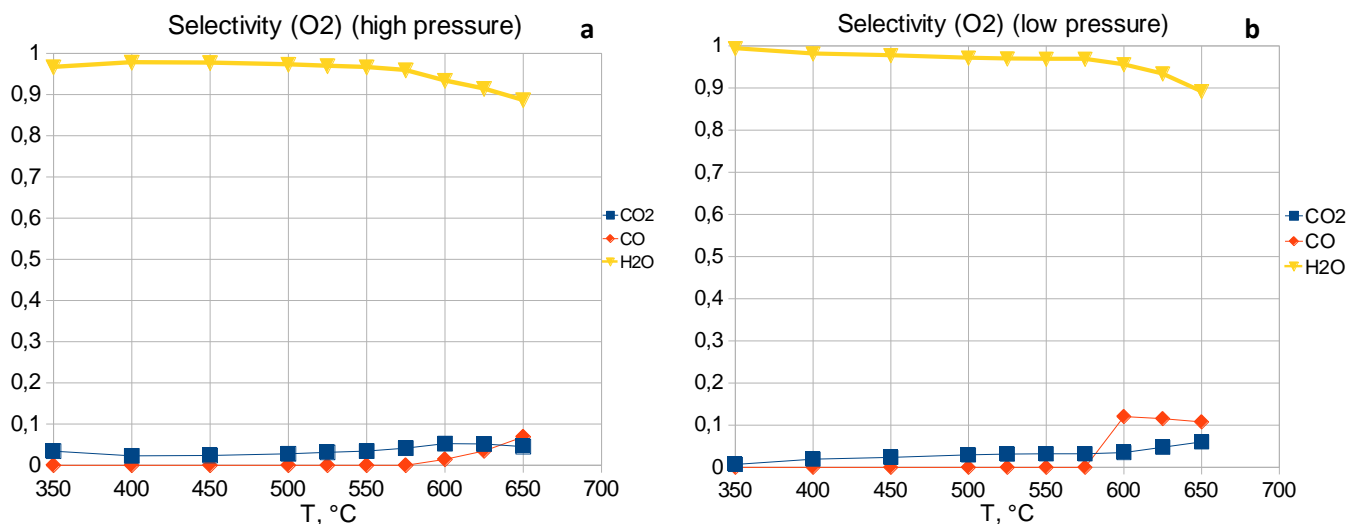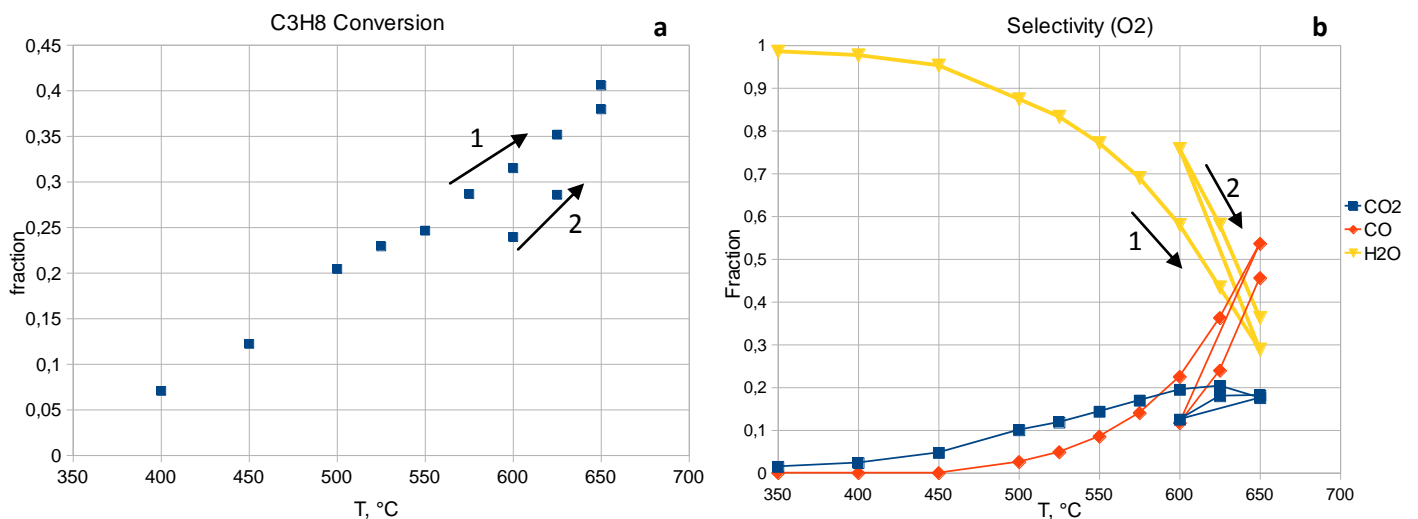

Figure 30: O2 selectivity a function of temperature, with a) high pressure (3 bar) and b) low pressure (1.1 bar), without catalyst

5.2.1.5 Deactivation test

At the end of the activity test, the catalyst color was not homogeneous. Indeed, it was darker at the bottom of the reactor, close to the inlet than near the outlet. Coking on the catalyst is responsible for this black layer on the catalyst. The picture of the reactor illustrates this dark color at the end of the experiment.

Figure 31: Catalytic reactor at the end of the activity test

The reaction should be rapid, and happens mainly at the entrance of the reactor, so all the catalyst is not impacted by coking. A deactivation test was practiced with one gas mixture to highlight this coking. As usual, the catalyst was first reduced, and analyses between 350 °C and 650 °C were done. After the last analysis at 650 °C, the temperature was decreased to 600 °C. Three new analyses were done: at 600 °C, 625 °C and 650 °C. The gas mixture used was 55 % of H_2, 38 % of C_3H_8 and 15 % of O_2. This kind of experiment gives some clue about deactivation of the catalyst. The second time at 600 °C, the conversion rate is lower than the first time. This means that the catalyst is deactivated at high temperature. After a first use at high temperature, it is not possible to obtain the same good conversion rate. A picture of the reactor after the reaction is given with the conversion, yield and selectivity plots.
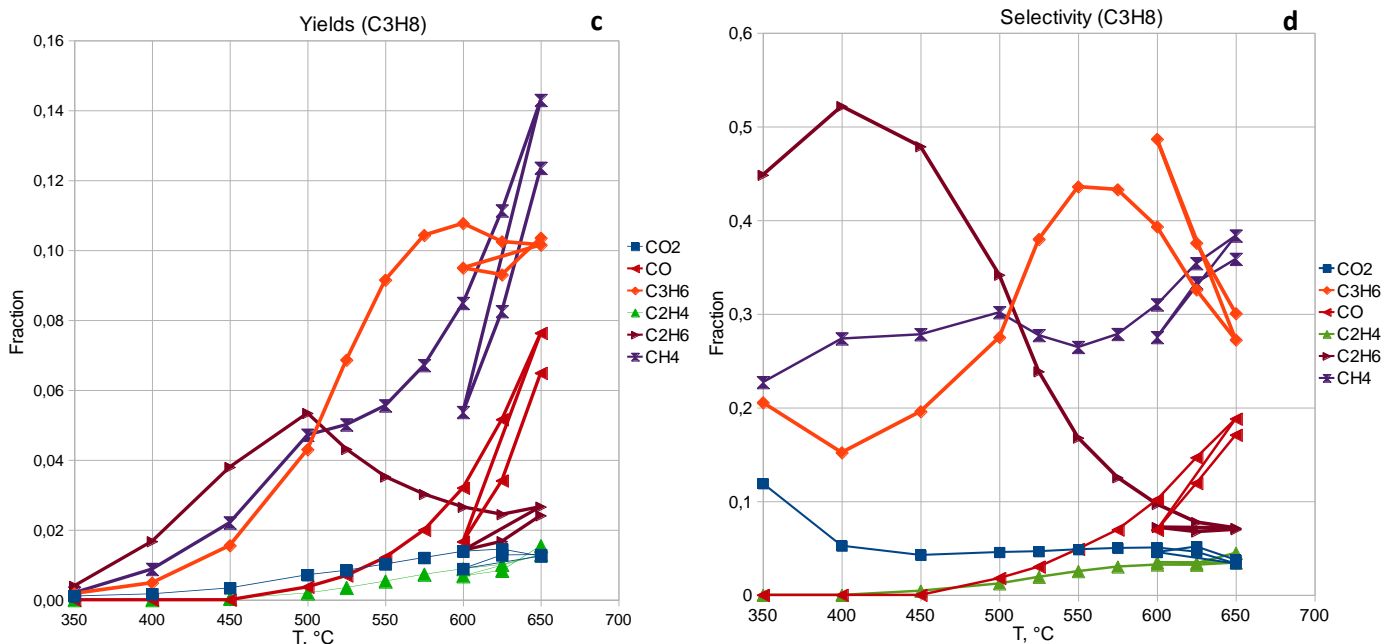
Figure 32: Dehydrogenation test: a) propane conversion, b) O2 selectivity, c) propane yield and d) propane selectivity as a function of temperature

5.2.1.6 Without catalyst

- Feed test analysis

Some gas phase reactions are believed to take place into the reactor. To check this assumption, experiments were performed without catalyst. These kinds of reactions are favored at high temperature. So, for this series of experiments, analyses were done for only 2 different temperatures: 600 °C and 650 °C. The feed gas compositions were almost the same than with catalyst. The overpressure was low for all the experiments, less than 0.1 bar. Without catalyst, all oxygen was not consumed with some feed gas. 10 experiments without catalyst and without oxygen in the feed gas were done in this case, and the main results are summed up in the following table:

N°	Composition (active components)			C_3H_8 conversion		C_3H_6 selectivity		C_3H_6 Yield		Full consumption of O_2
	H_2	C_3H_8	O_2	600 °C	650 °C	600 °C	650 °C	600 °C	650 °C	
1	0	55	45	2.8	2.3	0.109	0084	0.006	0.028	No
2	0	70	30	3.9	4.0	0.067	0.110	0.007	0.013	Yes
3	24	45	31	7.5	17.8	0.038	0.154	0.004	0.042	No
4	26	58	16	7.6	5.1	0.524	0.257	0.008	0.022	Yes
5	5	61	34	2.7	17.5	0.043	0.191	0.003	0.041	No
6	0	92	8	8.8	3.3	0.586	0.489	0.007	0.018	Yes
7	59	33	8	2.8	4.9	0.553	0.643	0.003	0.041	Yes
8	33	60	7	0.4	3.0	0.817	0.495	0.006	0.018	Yes
9	38	48	14	9.2	15.2	0.297	0.452	0.010	0.079	Yes
10	17	59	24	3.5	14.8	0.223	0.494	0.006	0.054	No

Table 5: Main results of gas tests

- Low temperature analysis

Another series of experiments were done, at low temperature. The purpose was to study at which temperature the gas phase reaction started. Some quartz wool was put in the reactor, without catalyst. The feed gas composition was nearly the same that for the experiment 12 (37 % H_2, 44% C_3H_8 and 19 % O_2). The temperature rank was between 100 °C and 225 °C. At 225 °C, the gas phase reaction had already started, so the experiment was stopped.
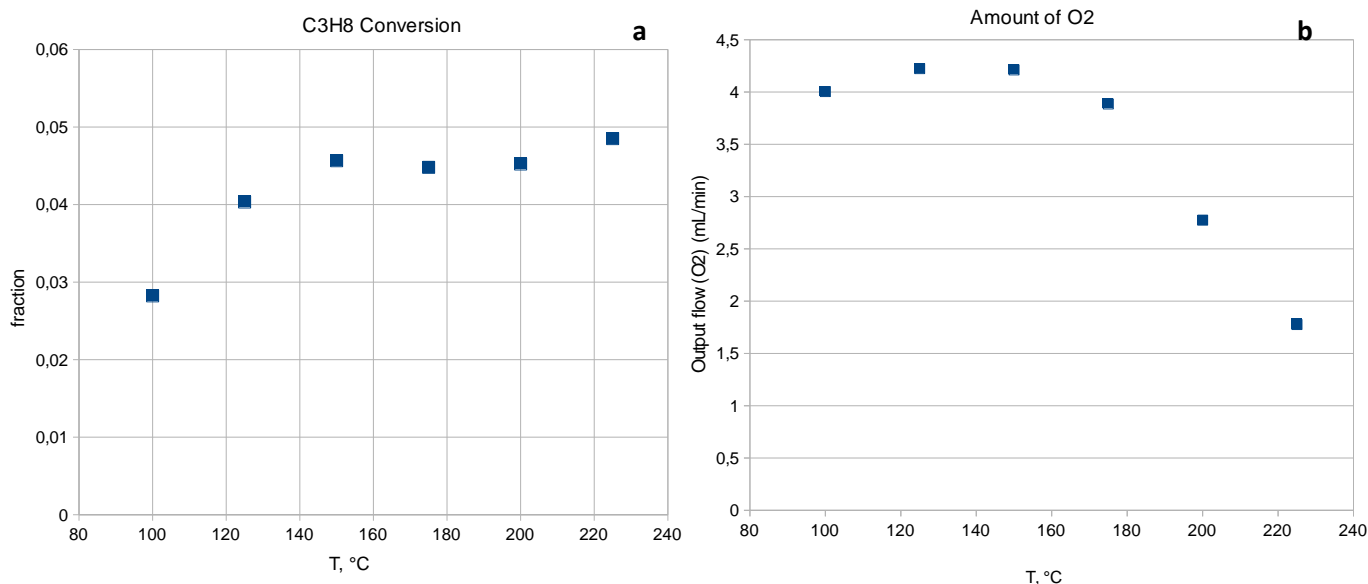

Figure 33: a) C3H8 conversion and b) amount of O2 as a function of temperature, without catalyst

A small amount of propane is consumed as soon as the temperature is superior to 175 °C. The products formed by propane decomposition are CO_2 and C_3H_6. A really few amount of O_2 is consumed until 175 °C, but above this temperature, O_2 started to be consumed. At low temperature, O_2 is consumed to produce mainly a few amount of CO_2. When the O_2 consumption increases, it is due to the formation of a bigger amount of H_2O. CO did not accumulate in the reactor for a temperature under 225 °C. It was not detected by the GC.

5.4.2 Without O_2

5.4.2.1 Hydrotalcite catalyst

Four different experiments were performed without O_2, with different gas ratio of H_2, He, and C_3H_8. For 3 experiments, the pressure inside the reactor was low (less than 0.1 bar overpressure). For the last one, the overpressure was 1.25 bar. For each experiment, the propane conversion, the carbon selectivity and the yield were determinate. To find the results, a mass balance was done. An example, for an experiment at low pressure, is given.

First, the initial gas mixture was analyzed.

Component	He	H_2	C_3H_8	N_2	O_2
Height or surface area	319 702	72 913	44 580	0	0
Molar fraction	0.70	0.08	0.2	0	0
Flowrate (mL/min)	36.0	4.0	10.0	0	0

Table 8: Feed gas composition

The total flowrate is supposed to be 50mL/min and constant whatever the temperature. This data was used for the calculation of the partial flowrate. The percentage of active gas is ascertained according to the following calculation, for H_2 for example: $\% \, H_2 = \frac{4.0*100}{4.0+10.0+0}$

At 550 °C, the average height of the He peak is 307 405 A.U. Thanks to a correlation, the molar fraction of He is found: 0.70. The flow of He is the same before and after reaction, because He did not react (inert gas), so the output flow of He is equal to 36.0 mL/min. Concerning H_2, the height of the peak is 90 689 A.U. The flowrate after reaction is 5.65 mL/min. For the other products, the surface area is used. Thanks to some calibrations, the molar fractions and the flowrate were found.

Component	C_3H_8	C_3H_6	C_2H_6	C_2H_4	CH_4
Surface area	34 175	6 098	1 522	1 673	877
Molar fraction	0.154	0.027	0.001	0.001	0.005
Flowrate (mL/min)	8.00	1.38	0.056	0.058	0.25

Table 9: Outlet gas composition

The propane conversion was calculated with the following formula:

$$C_3H_8 \, conversion = \frac{10.0 - 8.0}{10.0} = 0.02$$

The formulae used for the calculation of yield and selectivity are given in appendix. The total amount of by product and propane is the following: $Total = 1.38 + 2 * \frac{0.058}{3} + 2 * \frac{0.056}{3} + \frac{0.25}{3} = 1.55$

C-Selectivity and yield:

Component	C_3H_6	C_2H_6	C_2H_4	CH_4	Total
Selectivity	0.90	0.019	0.025	0.055	1
Yield	0.14	0.003	0.004	0.1	0.247

Table 10: C-selectivity and C-yield

In this example, the relative error on carbon element is 4.6 % and on H_2 is 3.6 %. Various parameters can explain this error. The first one is a problem in the total flow rate. Indeed, it is assumed to be 50ml/min but it is not measured during the experiment. Second error is due to small amount of coke which is supposed to be formed during the reaction, and deposited on the catalyst. This coke is not taking into consideration for the calculation, and explains a lack of carbon in the mass balance. The correlations which established a link between the area/high of peak are empirical formulae. Consequently, vagueness may occur with it. Finally, some measurement errors may happen with the GC.

The results of one experiment without O_2 are given as example in this part. The composition of the gas mixture in this case was 28.8% of H_2 and 71.2% of C_3H_8. The pressure was around 1.1 bar. At low pressure and high temperature, the maximum C_3H_8 conversion is around 20%. A maximum C_3H_8 conversion, yield and C_3H_6 selectivity is reached at 550 °C.
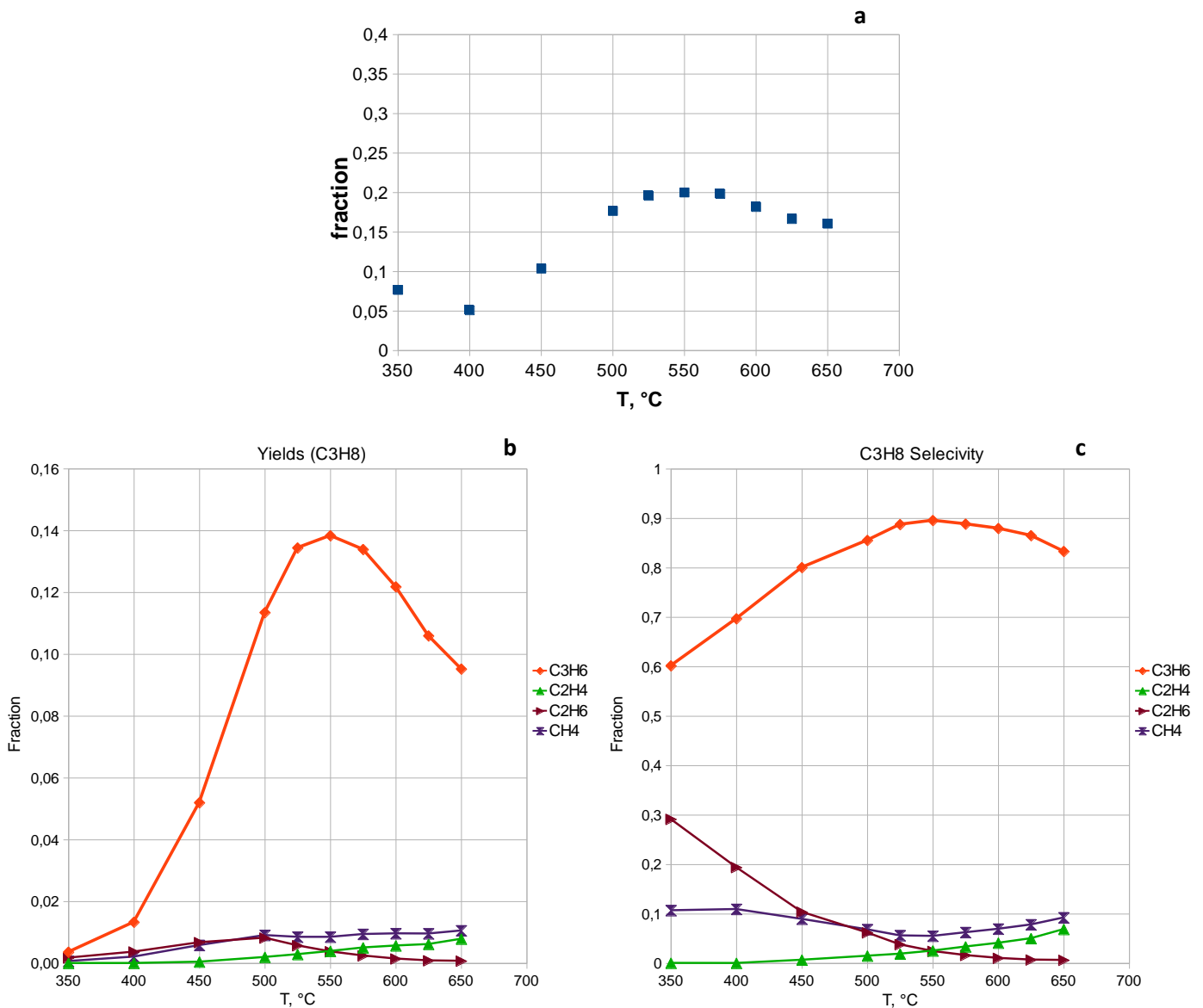
Figure 34: a) propane conversion, b) propane yield and c) propane selectivity as a function of temperature

Ethylene was produced for temperature above 450°C. The amount of ethene reached a maximum for a temperature of 550°C, and then decreased slowly. The amount of CH_4 increased slowly into the reactor.

One experiment was performed with higher pressure (2.2 bar). The propane conversion was improved in this case, as the propene yield and selectivity. In this example, there were 59 % of H_2 and 41 % of C_3H_8 in the feed gas. The best C_3H_8 conversion/yield/C_3H_6 selectivity is obtained for this mixture and this pressure.
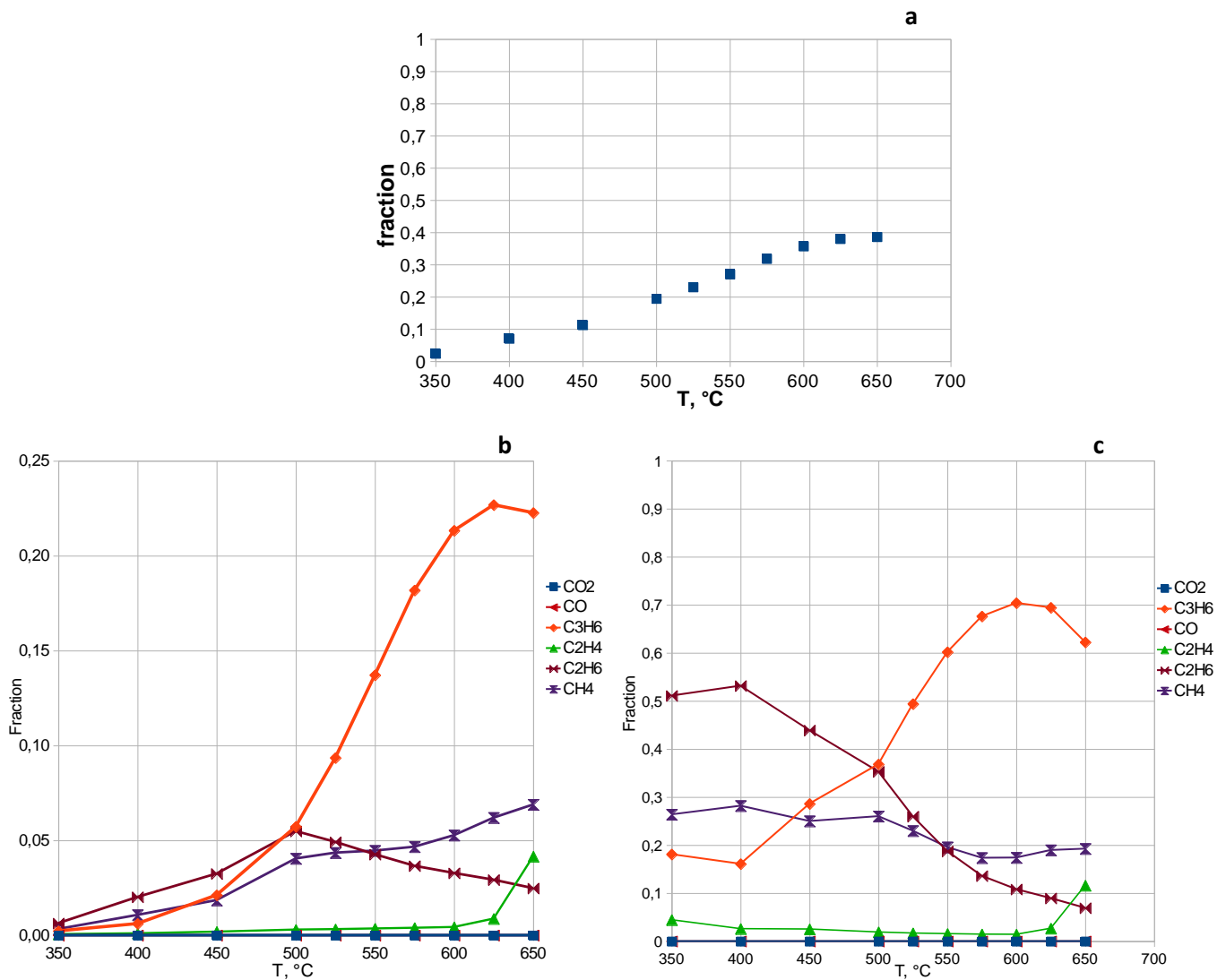
Figure 35: Figure 31: a) propane conversion, b) propane yield and c) propane selectivity as a function of temperature

Concerning the other experiments, the mixture with 81 % of H_2 and 19 % of C_3H_6 gave quite good conversion, but a really poor selectivity as soon as the temperature was above 500 °C.

The last one experiment without oxygen was also without hydrogen. The active component in the feed gas was only propane. It was used as an inert dilute. With only propane in the feed gas, the propane selectivity to propene is very good, but the propane conversion and the propene yield are very low (maximum conversion inferior to 10 %, maximum yield around 5.5 %).

The results for the two last experiments, at low pressure and without O_2 were put in appendix 3, 4 and 5.

5.4.2.2 Without catalyst

Experiments with the same feed gas composition were done, but without catalyst. Measured were done at 600 °C and 650 °C. The main results of these experiments are summed up in the following table:

Feed gas composition	C_3H_8 : 71 H_2 : 28		C_3H_8 : 60 H_2 : 40		C_3H_8: 100 H_2 : 0	
Temperature (°C)	600	650	600	650	600	650
C_3H_8 conversion (%)	0.04	2.9	1.1	3.2	5.1	7.8
C_3H_6 selectivity (%)	78.3	56.1	76.9	54.7	81	57
C_3H_6 yield	0.004	0.017	0.004	0.019	0.003	0.015

Table 4: Without catalyst, main results

Without catalyst and at low pressure, the conversion of propane is really poor. As soon as the conversion increases a little bit, the selectivity to propene decreases dramatically. As for selectivity, the yield of propylene is not good. This process, without catalyst and O_2 cannot be used for dehydrogenating propane with a correct yield. This illustrates the interest of having a catalyst in the case where O_2 is not added in the feed gas.

6 DISCUSSION

6.1 Characterization

The BET results show that all catalysts have a high surface area. The structure of the material did not collapse after the preparation or the calcination, as expected and reported in the literature. The surface areas vary between 136 $m^2.g^{-1}$ and 202 $m^2.g^{-1}$, with a higher surface area for the support HT30, and 2% weight of platinum. However, there is a strange surface evolution. Indeed, the surface area of the support hydrotalcite HT 63 is the lowest, with Pt or just calcined. A different result was expected. The value of the surface area should be between 188 $m^2.g^{-1}$ and 233 $m^2.g^{-1}$ that is to say between the HT 30 and the HT 70. Nevertheless, the behavior of the two catalysts HT 63 supported is coherent: the surface area decreases when platinum is added to the support.

The XRD-patents allow to notice a MgO phase after the calcination of the support. The structure of all the catalysts seems the same, whatever the support. The Pt particles were not detected with the EVA software, but it could be interesting to test other methods to see them. A more accurate measurement, with huge quantity of cycle, might be useful to determinate the size of the Pt particles. If the particles cannot be seen, it might be because they are too small, under the detection limit, but other tests have to be done before claiming this.

The chemisorption test showed a good dispersion of the metal on the support (55 %). The Pt particles were quite small, with an average size of 2.0 nm. These results are in accordance with the results found in the literature [6]. The physical properties of this catalyst are interesting. Indeed, if the dispersion of metal on the catalyst is good, the catalyst is supposed to be very active.

6.2 With oxygen

Concerning the activity test, the GC analysis shows that propene was formed during reaction, but also a lot of by-products. At low temperature, there was not methane or carbon dioxide, but these products were formed as soon as the temperature reached 400 °C for CH_4, 500 °C for CO. Even at low temperature, there was a cracking of the propane molecule, with the formation of carbon dioxide, ethane and ethene molecules. The formation of CO_2 proves that oxidation reaction occurred. Oxidation of propane, but also of produced propene might take place to produce CO_2. The amount of CO_2 formed decreased with the increasing temperature, opposite of the amount of CO and CH_4. One possible way to explain the formation of CO is a propane steam reforming reaction, or a partial oxidation of propane. Another way for producing CO is a reaction between oxygen and coke. For all the experiments, oxygen was totally consumed. It is possible to find the amount of formed water thanks to a balance on the oxygen. The amount of formed water decreased slowly when the temperature increased. The shrinkage of water may corroborate a steam reforming reaction. Finally, the formation of higher alkane (C_4, C_5, C_6…) but also propadiene was not detected by the GC. However, these products may be produced during the reaction of propane dehydrogenation. For example, propadiene may be formed at temperature superior to 600 °C [52, 53].

- Support influence

Concerning the conversion analysis, the best conversion is obtained for the support HT 63, with 2% weight platinum at 650 °C. It is interesting to notice that, at 550 °C, whatever the catalyst, the conversion rate is almost the same: around 0.15. Different behavior of the catalyst is observed for temperature above 550 °C. Indeed, the lowest conversion rate is for the catalyst HT 63 with 1% weight Pt, which is only 0.26 at 650 °C. This catalyst is also the catalyst with the smallest surface area, as it was noticed after the BET analysis. The best conversion rate at 650 °C is 0.59 for the catalyst HT63 support with 2% Pt. This catalyst has also a small surface area compared with the others. Indeed, the highest surface area found was 202.9 $m^2.g^{-1}$ for the 2 % weight Pt, HT 30 supported. This catalyst has a poor conversion rate at 650 °C, only 0.34. So, it seems that there is not link between the surface area and the conversion rate. Other parameters must be taken into consideration to explain the results. The values of the conversion rate are quite similar to those found in the literature [6].

The selectivity of each catalyst was determinate, based on propane consumption. In a first case, it is a selectivity based on carbon number. The selectivity calculations are given in appendix 2. In order to compare exactly the selectivity of the various catalysts, the conversion rate must be the same for all of them. In this case, the propane conversion rate reached during the experiment is a bit different for temperatures above 600 °C. For temperatures lower than 600 °C, the selectivity of the catalysts for producing propene is similar. The maximum selectivity is reached around 450 °C or 500 °C, and then decreases quickly with the temperature. So, when the conversion rate increases, the selectivity of the catalysts decreases. The maximum selectivity is around 55 %, for all the catalysts. There is a slowdown of the decrease after 600 °C. The selectivity can be compared between all the catalysts at 550 °C, when all the conversion rates are 0.15. At this temperature, the best selectivity is 50 % for the catalyst 1 % Pt HT 70, and the worst is 39 % for the 2 % Pt HT30. At 650 °C, the selectivity is around 30 % for all catalysts except 2 % weight Pt HT 30, with only 20 % selectivity. So, it is the catalyst with the highest surface area which has the worse propane selectivity. The selectivity of the reaction is not influence by the amount of platinum on the catalyst. Indeed, the selectivity of propane decreased a little with 2 % instead of only 1 % Pt for HT 30 and HT 63, but did not change for HT 70.

The evolution of the selectivity of the catalyst to produce CO_2 is noticeable. Indeed, the selectivity decreases when the temperature increases. The quantity of CO_2 formed during the activity test is significant. Consequently, a cracking of the propane molecule to produce CO_2 may happen, instead of only dehydrogenation. When the temperature increases, carbon dioxide and methane are also produced by the reaction.

The plots showing the O_2 selectivity for H_2O, CO and CO_2 are given in the Appendix 3. When the temperature is low, O_2 is mainly used to produce water. Indeed, the selectivity of water is around 90 % for all the catalysts. At low temperature, there is not CO. When the temperature is higher than 575 °C, the selectivity of CO_2 is the highest. However, for the two supports HT 30 and HT 70, the CO becomes the most selective product above 625 °C. The catalyst with the best selectivity to water is the HT 63 with 2% Pt.

The energy of activation of the reaction can be determinate, for a temperature inferior to 575 °C. Below 575°C, the conversion rate is less than 0.15, so it is possible to determine the rate. For this, the reaction rate has to be calculated, per gram of catalyst, according to the following equation:

$$r = \frac{initial\ propane\ flow * conversion\ rate}{catalyst\ weight}$$

At low temperature (i.e. below 575 °C), the conversion rate is low, which means the concentration of the product can be considered constant for calculation. So, the energy of activation can be found by using the Arrhenius equation.

$$r = A\ e^{-\frac{E}{RT}}$$

By plotting the logarithm of the rate as a function of the inverse temperature, the energy activation value can be found. A straight line is obtained, excepted for the catalyst 2 % Pt HT30. In this case, one point was removed to determinate the activation energy. This point can indicate the presence of transfer diffusion limitation. The following graph, for the catalyst 1 % Pt HT63, is given as example.
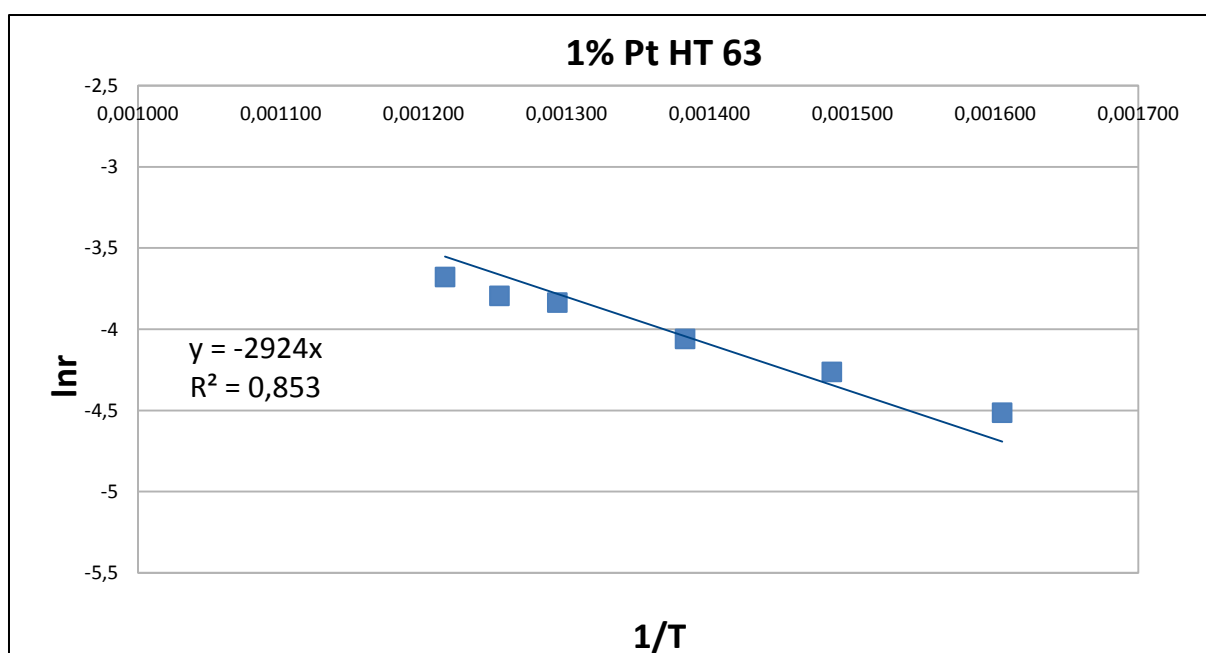
Figure 36: reaction rate as a function of inverse temperature

After calculation, the results are:

Catalyst	Energy of activation (kJ.mol^{-1})	Catalyst	Energy of activation (kJ.mol^{-1})
2Pt HT30	20	1Pt HT30	24
2Pt HT63	21	1Pt HT63	24
2Pt HT70	20	1Pt HT70	25

Table 5: Activation energy for the various kind of HT

The energy of activation decreases when the percentage of Pt increases. These energies of activation are not very high. The reaction of propane dehydrogenation started with a really slow rate.

The temperature must be high to obtain an acceptable conversion rate. There is not a huge difference in energy activation value between the three supports. Indeed, only the quantity of propane per gram of catalyst seems to play a part in the activation mechanism. The found values are lowest than the literature value. Indeed, it is usual to find around 22 kcal.mol⁻¹, i. e. 90 kJ.mol⁻¹ for propane dehydrogenation in hydrogen flow [54]. In steam flow, the activation energy is reported to be about 15 kcal.mol⁻¹. In most of the studies, the dehydrogenation of propane is not oxidative. The oxidation reactions are supposed to be very rapid during the reaction. So, oxygen must change the mechanism of the reaction. Some transfers limitations may be involved in the process.

A comparison between all the catalysts was done. It seems there is not a huge influence from the support in the catalytic dehydrogenation of propane reaction. The best conversion is obtained for support HT 63, with 2 % weight platinum, and the best selectivity for 1 % Pt HT 70. The propane selectivity decreases when the conversion rate increases. One explanation is the presence of labile hydrogen atoms in the produced propene. This atoms act as center for consecutive attacks, and so the obtained amount of propene decreases [55]. The catalyst HT 70 with 2% of platinum is a great compromise between selectivity and conversion. Catalysts with 2 % in weight platinum seem better than with only 1 %. Indeed, the surface areas are higher and the conversion rates reached during the catalytic test are also more significant (for a same amount of platinum). Only the selectivity is not improved when the amount of platinum per gram of catalyst increases.

The conversion rate is very low below a temperature of 600 °C, whatever the catalyst. Above 600 °C, the reaction rate soars. But a decreasing of carbon selectivity takes place in the same time than the increasing of the conversion rate. The mechanism of the reaction is supposed to be changed. Indeed, new products such as CO and CH_4 appear at high temperature. Below 600 °C, all the catalysts have exactly the same behavior, with a best selectivity at 0.55 at 550 °C.

- Feed gas influence

The catalyst HT 63 with 1 % Pt was selected for further experiments. In presence of oxygen, oxidative reactions happened in the reactor. Indeed, for each experiment, CO and CO_2 are formed as by-products by the reaction. Oxygen is entirely consumed by the reaction in all cases, whatever the feed gas composition.

The example 1, which is given in the results part, is discussed in the following paragraph. It was the experiment 12.

To find the various results, the analysis of the data from the GC was done. To exemplify this, a carbon balance was done, at 400 °C. The propane feed rate was 9.79 mL/min. The amount of propane which passed through the reactor is: $n_{C_3H_8} = \frac{pV}{RT} = \frac{1.1*10^5*9.79*10^{-3}}{8.314*773} = 0.1676 \, mol$

Consequently, during one minute, $0.1676 * 3 = 0.5027 \, mol$ of carbon went through the reactor.

The amount of containing carbon products are known thanks to the GC analysis, and the molar amount of product can be calculated thanks to the same relation than for the inlet reactant. The following data were found:

Outlet rate	Molar amount
V_{C3H8} = 9.230 mL/min	n_{C3H8} = 0.1580 mol
V_{C3H6} = 0.190 mL/min	n_{C3H6} = 0.0033 mol
V_{C2H6} = 0.047 mL/min	n_{C2H6} = 0.0008 mol
V_{C2H4} = 0.006 mL/min	n_{C2H4} = 0.0001 mol
V_{CO2} = 0.220 mL/min	n_{CO2} = 0.0038 mol
V_{CO} = 0.000 mL/min	n_{CO} = 0.0000 mol
V_{CH4} = 0.05 mL/min	n_{CH4} = 0.0009 mol

Table 6: Molar amount of products at 400 °C, for the experiment 12

The total amount of carbon which was detected by the GC after reaction was:
$$3*0.1580 + 3*0.0033 + 2*0.0008 + 2*0.0001 + 0.0038 + 0.0009 = 0.4904 \; mol.$$

The error on the carbon balance is $\frac{0.5027-0.4904}{0.5027}*100 = 2.4 \, \%$.

The yield based on propane was calculated.

C-Selectivity and yield:

Component	C_3H_6	C_2H_6	C_2H_4	CH_4	CO	CO_2	Total
Selectivity	0.61	0.098	0.012	0.05	0.0	0.23	1
Yield	0.02	0.003	0.0004	0.002	0.0	0.07	0.095

Table 7: C-Selectivity and yield, for the experiment 12

O-selectivity

Component	CO_2	CO	H_2O	Total
Selectivity	0.05	0.0	0.95	1

Table 8: O2 selectivity for the experiment 12

At low temperature, the products formed by the reaction were C_3H_8, H_2O, CO_2, C_2H_6, CH_4 and a small amount of C_2H_4. Propene is the main product formed by the decomposition of propane. Indeed, propane selectivity and yield for propene, at low temperature, are the best. The propane dehydrogenation took place into the reactor, according to the following reaction: $C_3H_8 \longrightarrow C_3H_6 + H_2$.

At low temperature, O_2 is mainly used to produce water with hydrogen, according to the following reaction: 2 H_2 + O_2 = 2 H_2O. This reaction is exothermic (ΔH^o_f = -285.8 kJ). In this example, hydrogen was not entirely consumed. So, hydrogen was detected by the GC at the outlet of the reactor. Due to hydrogen oxidation, steam was present in the reactor, and could react with other molecules, according to water gas shift or steam reforming reaction. At low temperature, CO was not detected by the GC. The amount of outlet reactor CO is supposed to be too small to be detected. However, CO can be formed, by partial oxidation of propane, according to the following reaction: C_3H_8 + 3 H_2O $\longrightarrow$ 3 CO + 7 H_2. In this case, CO reacted as soon as it was formed with water, according the water gas shift reaction: CO + H_2O = CO_2 + H_2. This reaction is a reversible and exothermic reaction (ΔH^o_f = -40.6 kJ). It is an equilibrium controlled reaction. The equilibrium of water gas shift reaction depends only of the temperature. Indeed as the number of moles of reactant and products are not modified during the reaction, the pressure has not influence on the equilibrium. The equilibrium constant depends on the temperature according to the following formula: Kp= exp [(4577.8/T) - 4.331] [56]. If the temperature increases, the equilibrium will be displaces. The reactants (CO and H_2O) will be favored instead of the product.

Propane selectivity to CO_2 was quite high (between 22 and 39 % at low temperature). The water gas shift reaction is not enough to explain the CO_2 formation. Oxidation of propane in CO_2 should be considered. The following reaction happened in the reactor: $C_3H_8 + 5\ O_2 \longrightarrow 3\ CO_2 + 4\ H_2O$.

Even at low temperature, there were ethane and methane into the reactor. Cracking of propane molecule took place into the reactor, to form ethene and methane: $C_3H_8 = C_2H_4 + CH_4$. However, the amount of measured ethene is low. Ethene molecules may be hydrogenated to form ethane: $C_2H_4 + H_2 = C_2H_6 + CH_4$. This reaction is not equilibrium limited, so it is possible to think that it took place in the reactor. A direct reaction between propane and hydrogen can also give these products: $C_3H_8 + H_2 = C_2H_6 + CH_4$. This reaction is a hydrogenolysis of propane. It is difficult to say which one of this reaction is the most important to form ethane molecules.

At high temperature, there was also CO formed in the reactor and detected by the GC. Oxygen selectivity to water decreased dramatically with the temperature, whereas it increased to CO as soon as it appears in the system. It increased to CO_2 until 575 °C, reached a maximum and decreased above this temperature. In this case, CO may be formed by partial oxidation of propane and consumed by water gas shift reaction. Indeed, as the equilibrium constant of water gas shift reaction decreases with the temperature, the reaction happens slower in the reactor [57]. Consequently, the amount of CO increases whereas the amount of CO_2 decreases in the reactor. Another possible reaction, at high temperature, which produces CO is the steam methane reforming. CH_4 is produced by cracking of propane. Then, the following reaction happens: $CH_4 + H_2O \longrightarrow CO + 3\ H_2$. This reaction is strongly endothermic ($\Delta H° = 201.6$ kJ/mol) [58]. However, the partial oxidations which happen in the reactor can supply the necessary heat requires by SMR [59]. Boudouard's reaction ($2\ CO = CO_2 + C$) can also explain the equilibrium ratio between CO and CO_2. Moreover, this reaction explains coke formation on the catalyst, and so the dark color on the catalyst at the end of the experiments.

The maximum propane conversion is around 30 %, at high temperature (650 °C). The propene selectivity is good with low propane conversion, so at low temperature. But as soon as the temperature increases, the propene selectivity decreases. The propene selectivity is plot as a function of propane conversion.
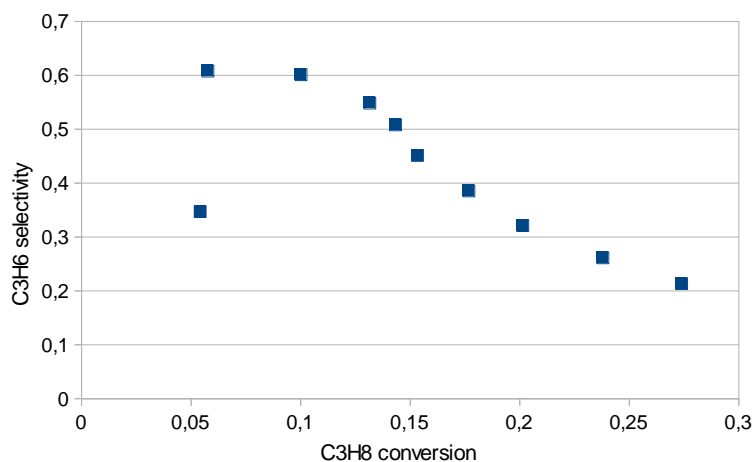
Figure 37: C3H8 selectivity for C3H6 as a function of C3H8 conversion

The maximum reached by the selectivity is around 5% conversion. The main product is propene, but the amount of by-products increased when the propane conversion increased.

Concerning the second example given in the previous part, the main difference is the oxygen selectivity. Indeed, the oxygen selectivity was better to CO_2 than to H_2O. However, H_2O is produced even at low temperature (around 40 % of O_2 is used to form water), and the oxygen selectivity to water decreased when the one for CO increased – similar evolution than for the first example. The small amount of hydrogen in the feed gas can explain this result. Indeed, the same behavior is observed in the case where there is not H_2 in the feed gas. The propane conversion was a bit better for this example than for the first one, around 40 %. The propane selectivity to propene was not good, but increased to reach a maximum around 450 °C, before decreasing.

Two examples of experiments with O_2 but without H_2 in the feed gas were given. For the three experiments without H_2 in the feed gas but O_2, the selectivity of oxygen for CO_2 is superior to the selectivity to H_2O. This reaction could happen to consumed excess of oxygen, which did not react with hydrogen. This reaction explains the small increases of ethane yield at low temperature, whereas ethene is not produced yet. When the amount of oxygen increases, the propane conversion increases. The selectivity to propene or the propene yield was a little bit improved when there is more oxygen in the reactor. In both cases, less than 10 % of consumed propane is used to form CH_4, but the amount of CO_2 at low temperature and CO at high temperature are significant.

For all the experiments with oxygen in the feed gas, oxygen is entirely consumed. At low temperature, O_2 is mainly used to produce water with hydrogen, according to the following reaction: $2 H_2 + O_2 = 2 H_2O$, provides there is enough hydrogen to consume it in the feed gas. This reaction is exothermic (ΔH^o_f = -285.8 kJ [62]). If extra hydrogen is not added to the feed gas, at low temperature, hydrogen is not detected by the GC. In one other case with hydrogen in the feed gas, this molecule is not detected by the GC at the outlet of the reactor. Consequently, hydrogen produced by the propane dehydrogenation and contained in the feed gas is entirely consumed, mostly by the reaction of water formation. A small amount of H_2 is also used to produce CH_4 and C_2H_6. For the other experiments, some amount of hydrogen is still detected by the GC. However, even when hydrogen is produced at low temperature, the amount of hydrogen decreases in a first time with the increasing of the temperature. O_2 reacts more with H_2 than with carbon molecules (to form CO_2). The amount of hydrogen increased at higher temperature, 400 or 450 °C in most of the case. At high temperature, the propane conversion is better, so the amount of hydrogen formed by the reaction increases. Some water molecules were in the reactor, so steam methane reforming and water gas shift reactions could take place into the reactor. In the same time, at low temperature, a small amount of carbon dioxide is formed.

Concerning the O_2 selectivity, in most of the cases, the CO plot cruise the CO_2 plot, which means the oxygen selectivity to CO is more important than to CO_2 at high temperature. As oxygen is entirely consumed, we can suppose that there is not enough oxygen to oxidize totally CO by a reaction such as $CO + ½ O_2 = CO_2$. The equilibrium for the WGS reaction may be reached in this case, so the amount of CO_2 cannot increase more.

The various feed gas composition were chosen according to an experimental plan. Thanks to all this data, some convenient calculations and presentations of the results can be done. Indeed, these results were used by I. V. Goreklin to plot composition properties diagrams. The results of his

work are given in the following paragraph. This work is a part of his Doctoral Thesis. More details about the theoretical calculations could be found in his thesis, as soon as it will be published. For this presentation, the errors due to experimental measurements or calculations are not taken into consideration.

The parameters taken into consideration in this work are the feed gas composition and the temperature. There are three active components in the feed gas: C_3H_8, H_2, and O_2. A triangle representation of the results is given. The amount of the three active gases can be found on the side of the triangle. The amount of one component is in the range from 0 (the gas is not present) to 1 (there is only one kind of gas). All the possible compositions were not studied during the experiments. Consequently, there is not more than 44 % of O_2 in the system, neither more than 84 % of H_2. The results at six different temperatures are given (525, 550, 575, 600, 625 and 650 °C). One triangle represents the conversion or the yield of one product, at one temperature and with all the feed gas composition tested.

The first series of triangles (figure 38) is the conversion of propane.

Concerning the conversion of propane, the dotted line represents the stoichiometric composition. Whatever the temperature, the lowest propane conversion is always almost for this composition. In this case, the maximal amount of water is produced. O_2 and H_2 mainly react together to produce water, but this reaction does not help the dehydrogenation. The conversion lines look symmetric, with the stoichiometric line as symmetry axe. It is possible to explain this behavior. Indeed, if there is a lot of H_2, the catalyst will stay active longer. H_2 prevents coke formation by forming CH_4. Consequently, the propane will be converted in products in higher amount than without H_2. On the other part of the triangle (the right side), if the amount of O_2 increases, the propane conversion increases. In this case, CO and CO_2 are formed by partial or full oxidation of the coke. The result is the same than with an excess of H_2. The catalyst is more active, and the conversion is improved if O_2 is present in the feed gas. So, even if it is not the same mechanism for both components, excess of H_2 or excess of O_2 is good for the conversion of propane. The minimal valley at low temperature is a little bit above the stoichiometric line, i.e. with excess of O_2. At low temperature, oxidations are not favored, and the reaction with H_2 to form water is really favored. On the other hand, at high temperature, the minimal valley is a bit under the dotted line, in H_2 excess part. At high temperature, O_2 is more likely to react with C than H_2. This composition is less favorable for the reaction of propane conversion.

Finally, it is possible to notice that this presentation of the results emphasizes the increasing of the propane conversion with the temperature. The conversion is improved when the temperature increases, whatever the composition (*i.e.* in all the parts of the diagram).
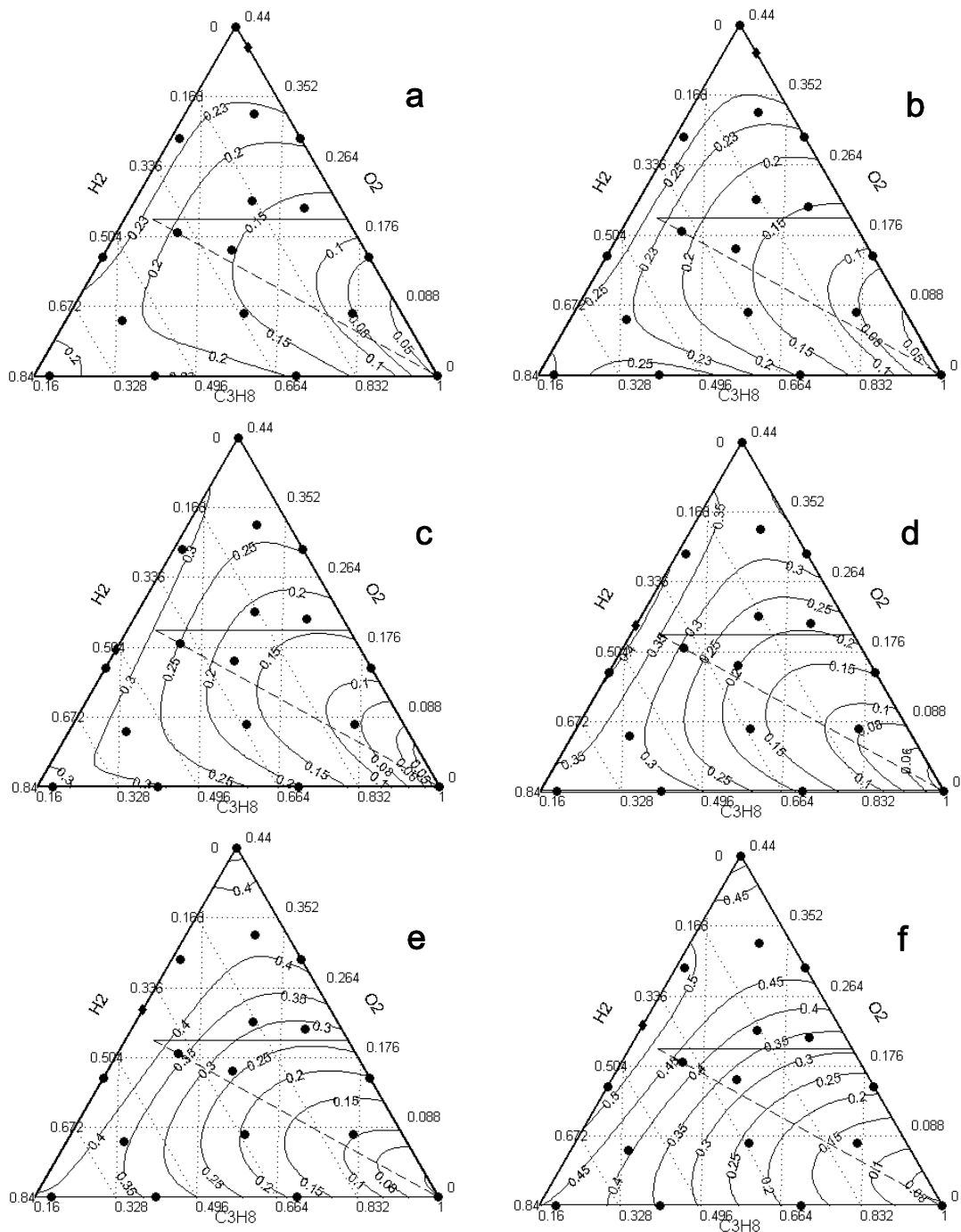
Figure 38: Conversion of propane at temperatures : a) 525, b) 550, c) 575, d) 600, e) 625, f) 650 °C

The yields of propene seem to be influenced by the ratio of all the components in the feed gas. It is possible to see two major behavior of the yield of propane. If H_2 is in excess, that is to say if the part under the stoichiometric line is considered, the lines with the same yield are paralleled to each other. The amount of H_2 is an important factor of the amount of C_3H_6 formed. In the low part of the triangles, the main reaction of dehydrogenation happens: $C_3H_8 \longrightarrow C_3H_6 + H_2$. The behavior of the system involving excess of O_2 is more complex. A minimal valley can be seen, above the stoichiometric line. If O_2 is the excess reactant, a lot of by-product such as CO and CO_2 can be formed. This prevents a good yield of propylene, even if the conversion of propane is good. At low

and average temperature, for an excess of O_2, the amount of propane in the feed gas is only responsible for the propene yield, especially if the amount of propane is low. Indeed, the lines of yields are vertical on the left part of the triangles, so with a low amount of propane. This means propane is the only factor which influences them. On the triangles, the full line represents the amount of O_2 where half of H_2 in the system (feed and produced) is completely burnt (in ideal case). The intersection between the stoichiometric line and the full line, for a feed gas containing 1/5 of O_2 is an important point. It represents the point where all the hydrogen fed to reactor is burnt and this amount of hydrogen is equal to one produced. The yield of propane, for this point, is good whatever the temperature (always around the maximal yield). Consequently, it is check that this interesting theoretical composition is a great mixture for the dehydrogenation of propane.
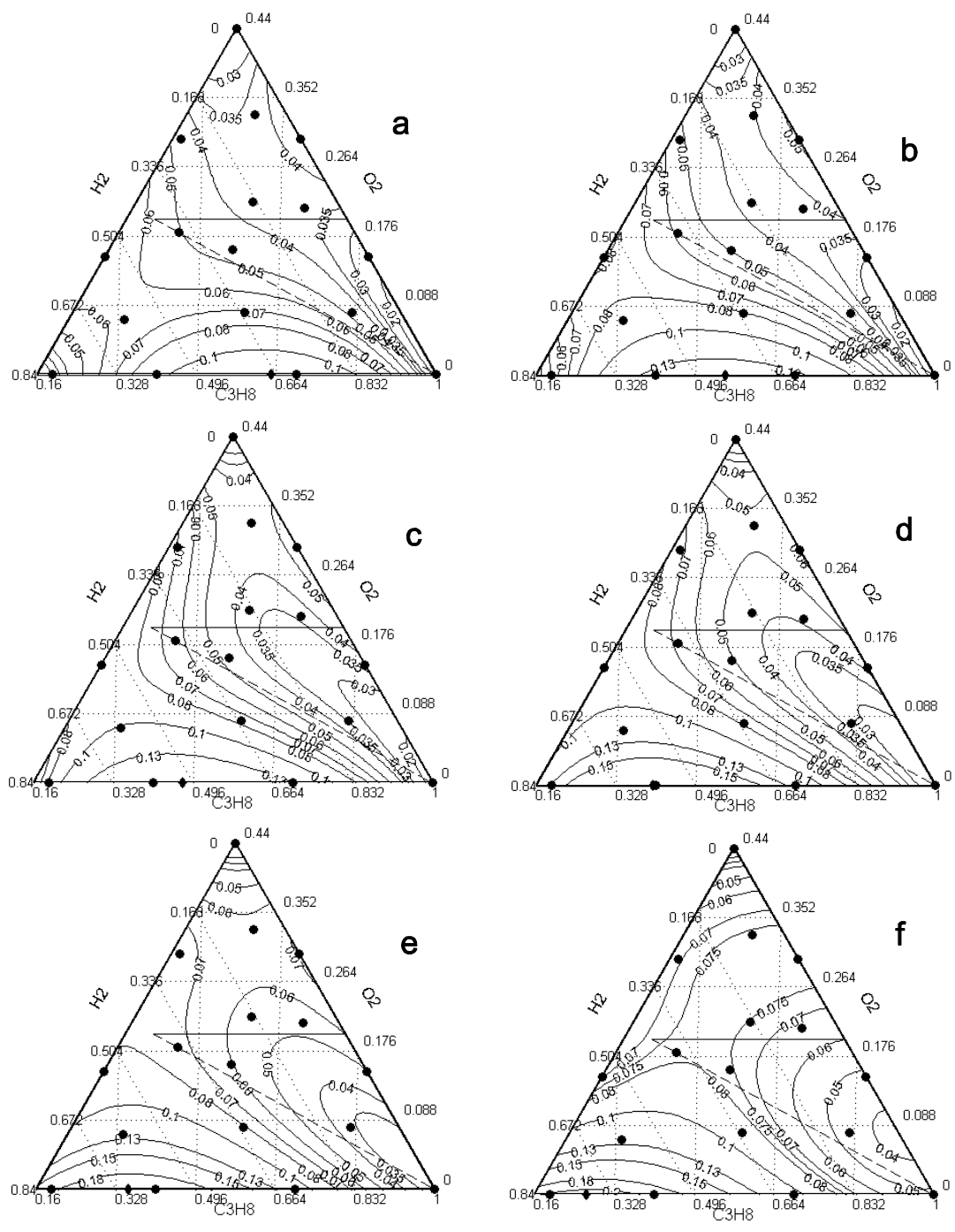
Figure 39: Yields of propylene at temperatures: a) 525, b) 550, c) 575, d) 600, e) 625, f) 650 °C

Concerning the yields of CO_2, it is obvious that the yield depends on O_2 concentration in the feed gas. Whatever the temperature, the yield of propane increases when the amount of O_2 increases. The yields are quite the same whatever the temperature, with a maximum yield around 0.15, when the amount of O_2 is maximum. These results are not surprising. Indeed, if the amount of oxygen increases, a reaction between C and O_2 are favored, such as this reaction:

$C_3H_8 + 5\ O_2 \longrightarrow 3\ CO_2 + 4\ H_2O$. Moreover, the more O_2 is present in the feed gas, the more likely a complete oxidation of C is possible. It was possible to see, thank to the feed velocity test that the amount of CO_2 produced at high feed rate is not really good, whereas CO starts to be detected by GC at high temperature. This means that a part of CO_2 is formed by oxidation of CO. So, to succeed to form CO_2 instead of CO, a huge quantity of O_2 is necessary. If there is not enough O_2, CO will be the main component involving C and O.
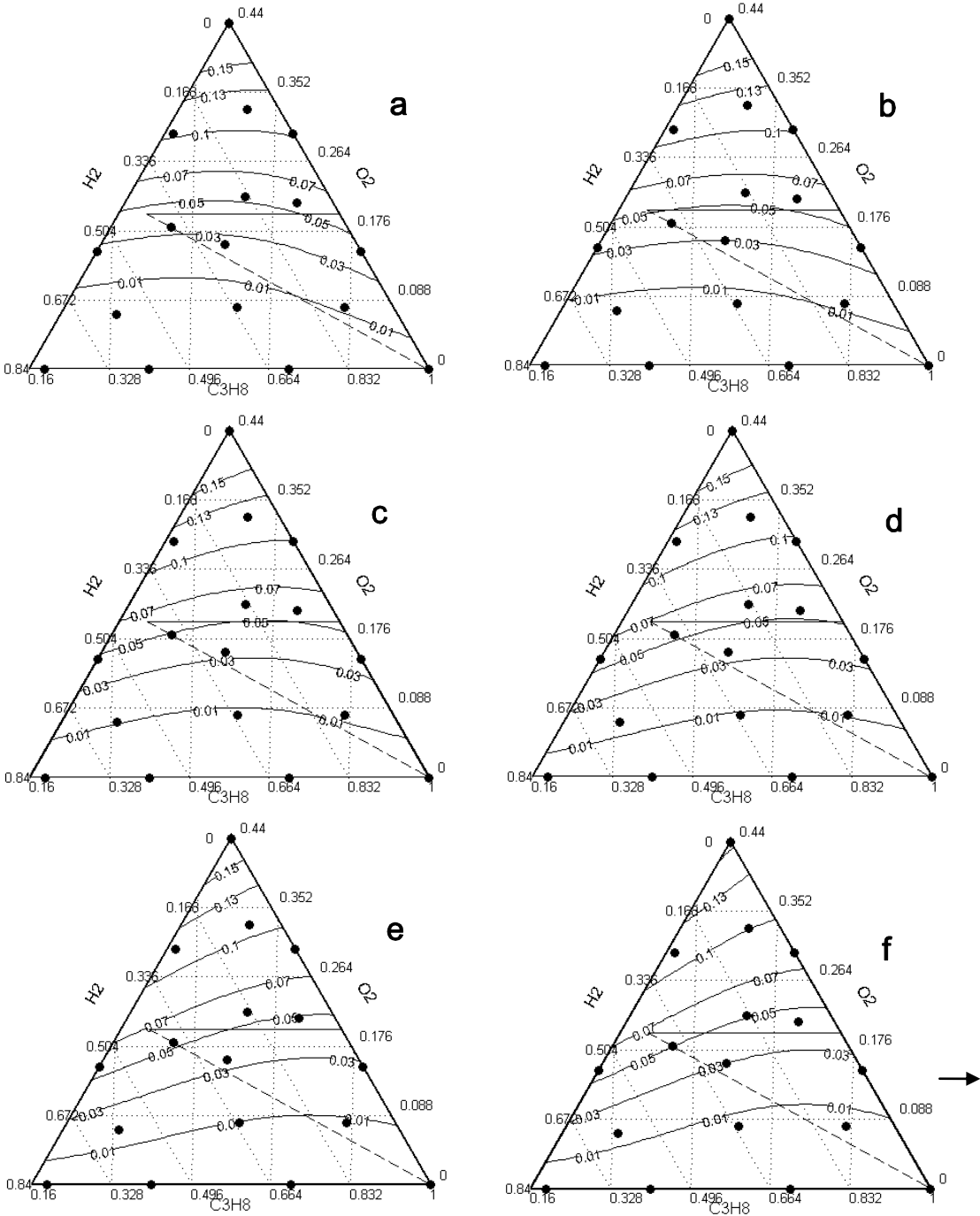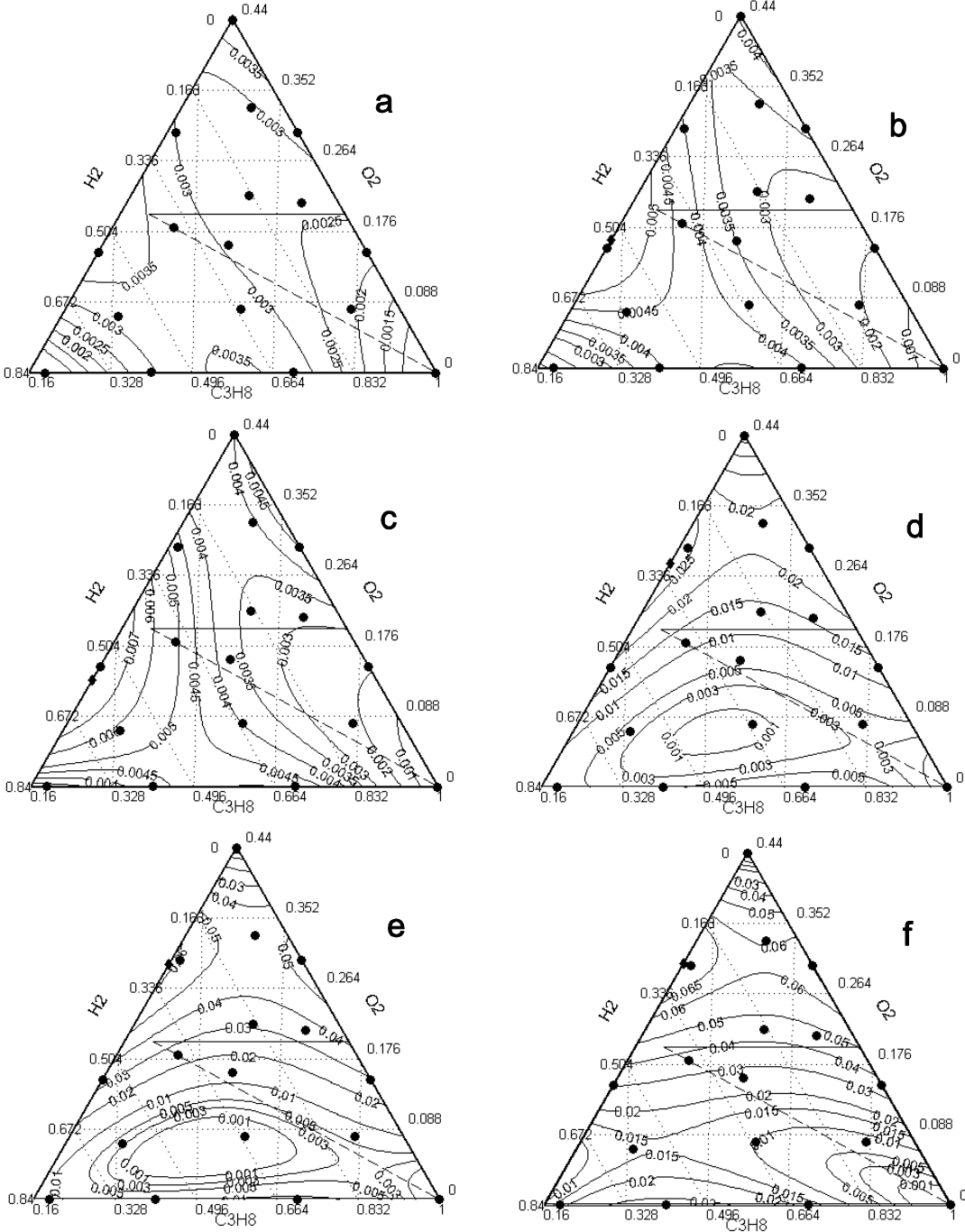

Figure 40: Yields of CO2 (C3H8) at temperatures: a) 525, b) 550, c) 575, d) 600, e) 625, f) 650 °C
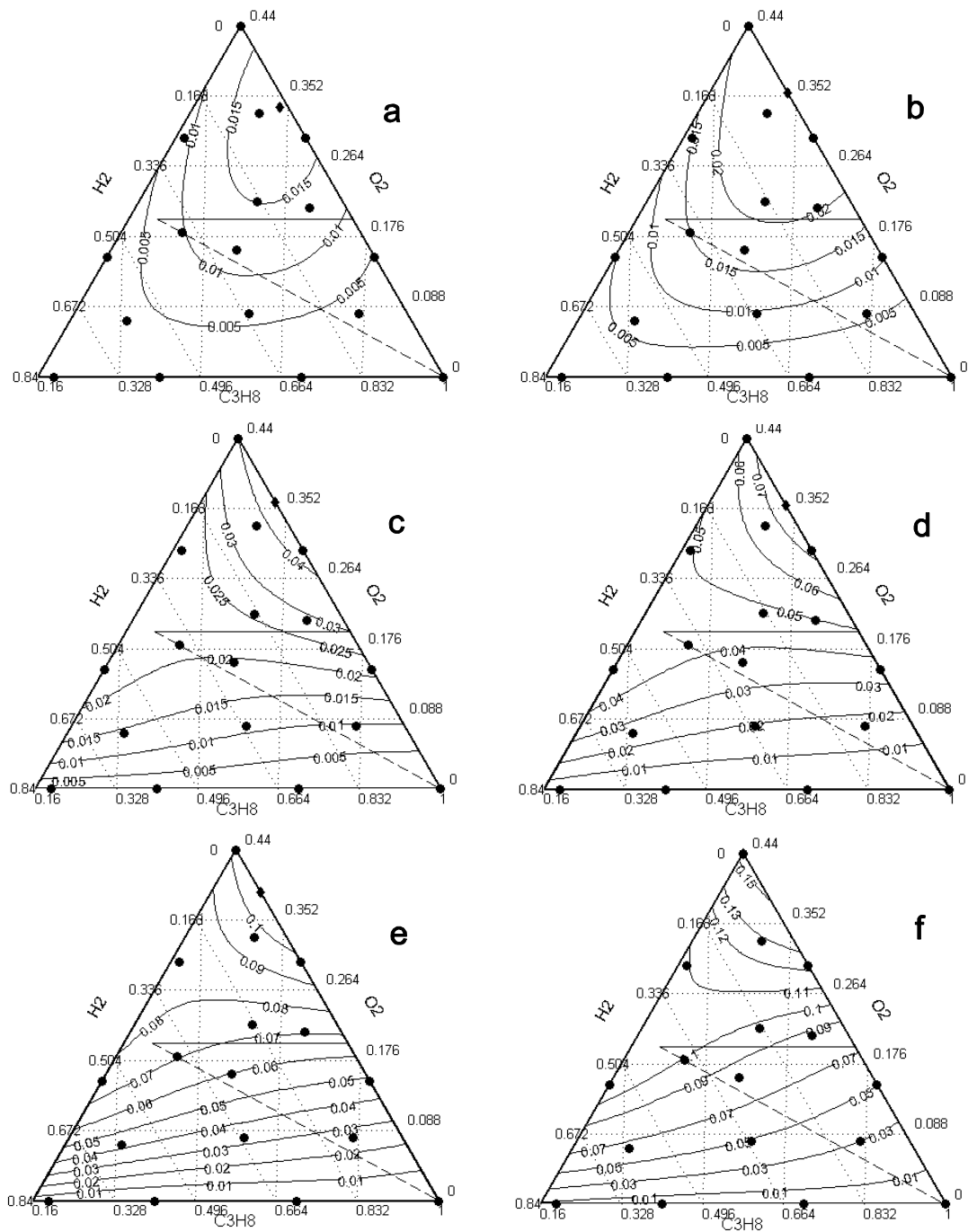
Figure 41: Yields of CO (C3H8) at temperatures: a) 525, b) 550, c) 575, d) 600, e) 625, f) 650 °C

The behavior of the yield of CO changes a little bit according to the temperature. At low temperatures, a minimal area can be noticed, for the experiments with a small amount of O_2 or a big amount of H_2. When the amount of H_2 is low and the amount of O_2 high, the yield of CO is maximal at low temperature. At high temperature, two different behaviors are visible on the triangle. If there is not O_2 in the system, of course CO cannot be produced. And in the lowest part of the triangle –with a small amount of O_2, it is only this component which influences the amount of CO produced. If O_2 is in excess, a full oxidation of CO to form CO_2 is supposed to take place in the reactor. At high temperature, it is possible to see vertical lines on the triangles. This means that the amount of

63

propene plays also a role in the yield of CO, and is the most important parameters if there is not a lot of propene present in the feed gas.
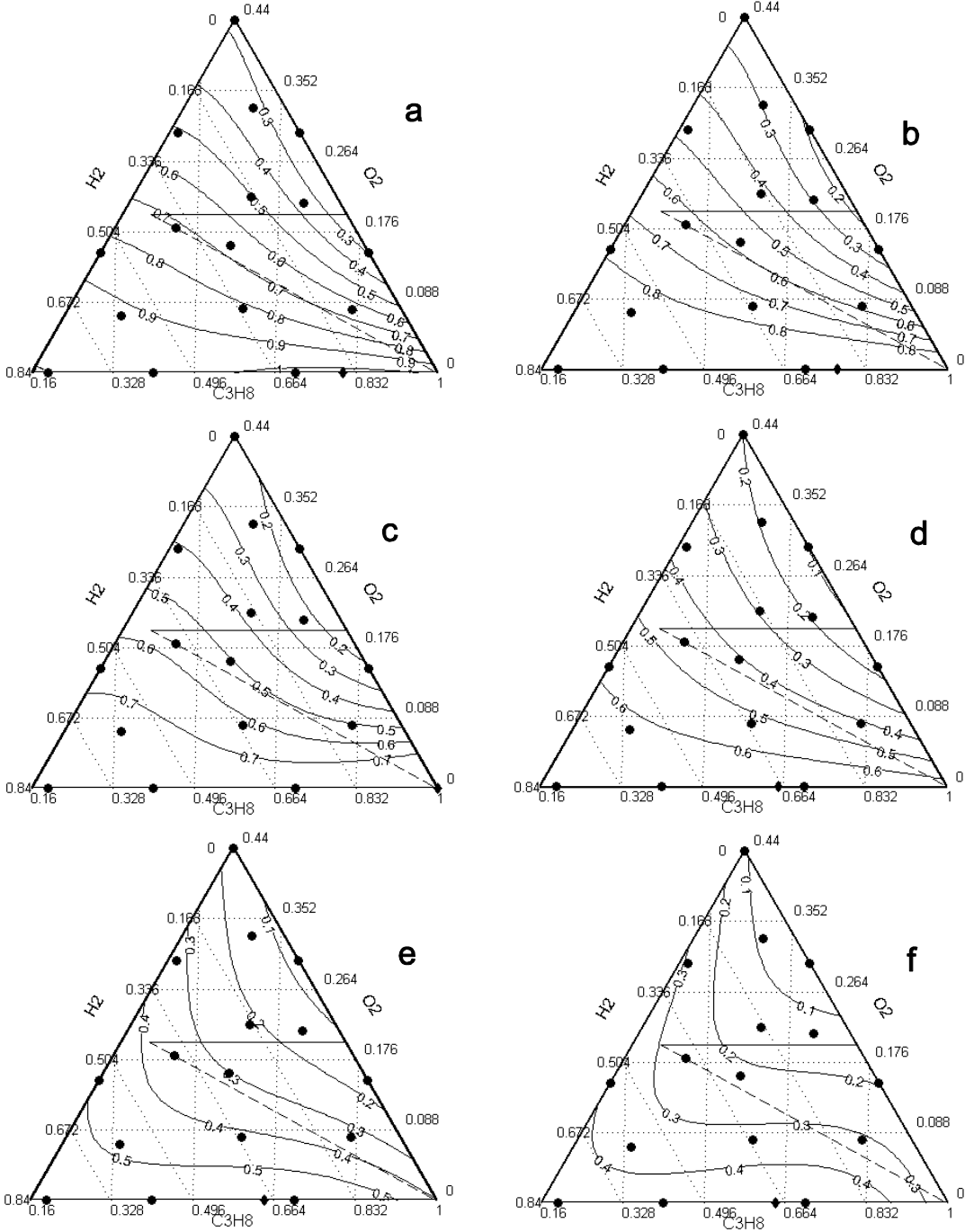
Figure 42: Yields of H2O (C3H8) at temperatures: a) 525, b) 550, c) 575, d) 600, e) 625, f) 650 °C

The best yields of water are obtained at low temperature. At low temperature, thanks to the triangle, it is possible to see than both H_2 and O_2 influence the yields. Indeed, the yields lines are parallels to each other, and parallels to the stoichiometric line. When the amount of O_2 decreases and the amount of H_2 increases, the yields of water is improved. Indeed, if more hydrogen is

available, it is easier to produce water in the system. At average temperature (triangles c and d), the yield lines are almost parallels to the concentration lines of H_2. This means that H_2 plays a major role in the formation of water. At high temperature, the behavior of the system is modified. If there is an average amount of C_3H_8 in the feed gas, the main factor which influences the yields of water is the amount of O_2 (horizontal lines in the middle of the triangles). If there is a small amount of C_3H_8, it is C_3H_8 which determinates the amount of water (vertical lines in the left part of the triangles). And finally, if there is a huge amount of C_3H_8, it is the amount of H_2 which influences mainly the production of water.

The three following triangle series concerns the by-products C_2H_6, C_2H_4 and CH_4. These triangles can be interesting to know which feed gas composition gives too much undesirable products, and so to avoid it for improving the reaction of dehydrogenation of propane.

At low temperature, the yields of C_2H_6 depend mainly on the amount of H_2 in the feed gas. It is possible to see on the triangle a that if the amount of H_2 increases, the yield increases. To produce C_2H_6, a cracking of propane and a hydrogenation of the formed molecules are necessary. Consequently, a high amount of H_2 is required to form C_2H_6. However, it is possible to notice that at low temperature, the methane yield is less good with a small amount of H_2 (less than 10 %) than without H_2, and this whatever the amount of O_2. . At low temperature, this yield seems mainly influence by the amount of propane in the feed gas. When the temperature increases, the concentration of O_2 in the feed gas starts to play a role in the yield of C_2H_6. At medium and high temperature, the minimum yield of C_2H_6 is obtained for a stoichiometric ratio between H_2 and O_2.
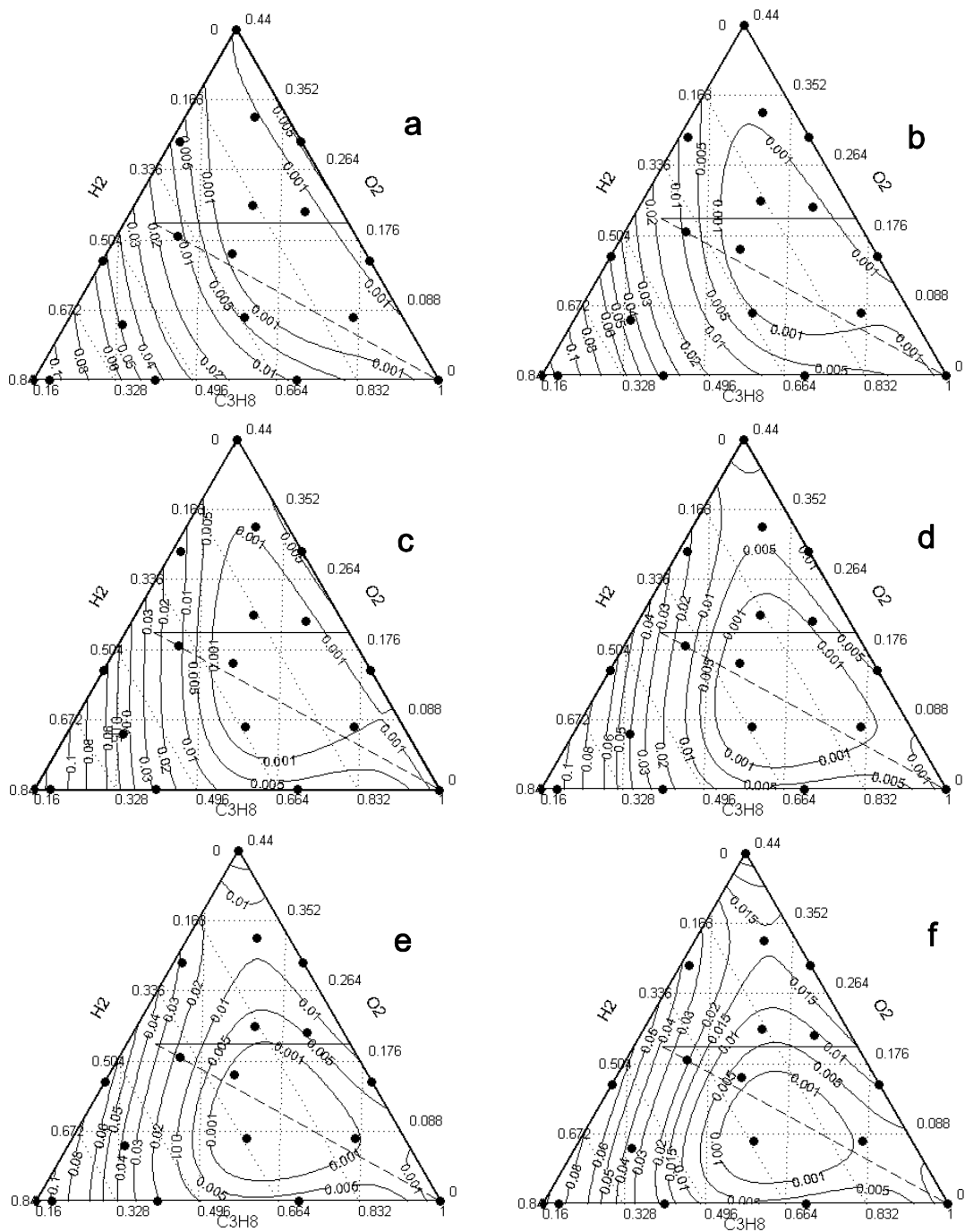
Figure 43: Yields of C2H6 (C3H8) at temperatures: a) 525, b) 550, c) 575, d) 600, e) 625, f) 650 °C

At low temperature, the C_2H_4 yields follow the amount of H_2. The more H_2 is present in the feed gas, the less C_2H_4 is produced during the reaction. However, at low temperature, the yield of C_2H_4 is very small. The behavior of the system changes a lot with temperature. Indeed, the minima yields of propane are displaced from high amount of O_2 to small amount at high temperature. When the temperature increases, the yields are favored with a high amount of O_2 and a small one of H_2. The compositions which give minima yield are surprising, because they are neither the lowest

concentration in H_2 nor in O_2. At high temperature (*i.e.* 650 °C), the yield of C_2H_4 depends only on the amount of O_2 in the feed gas. Some unknown reactions are supposed to happen in the reactor, which involves oxidative reactions since the amount of oxygen is the main factor which influences the ethylene yield.

Figure 44: Yields of C2H4 (C3H8) at temperatures: a) 525, b) 550, c) 575, d) 600, e) 625, f) 650 °C
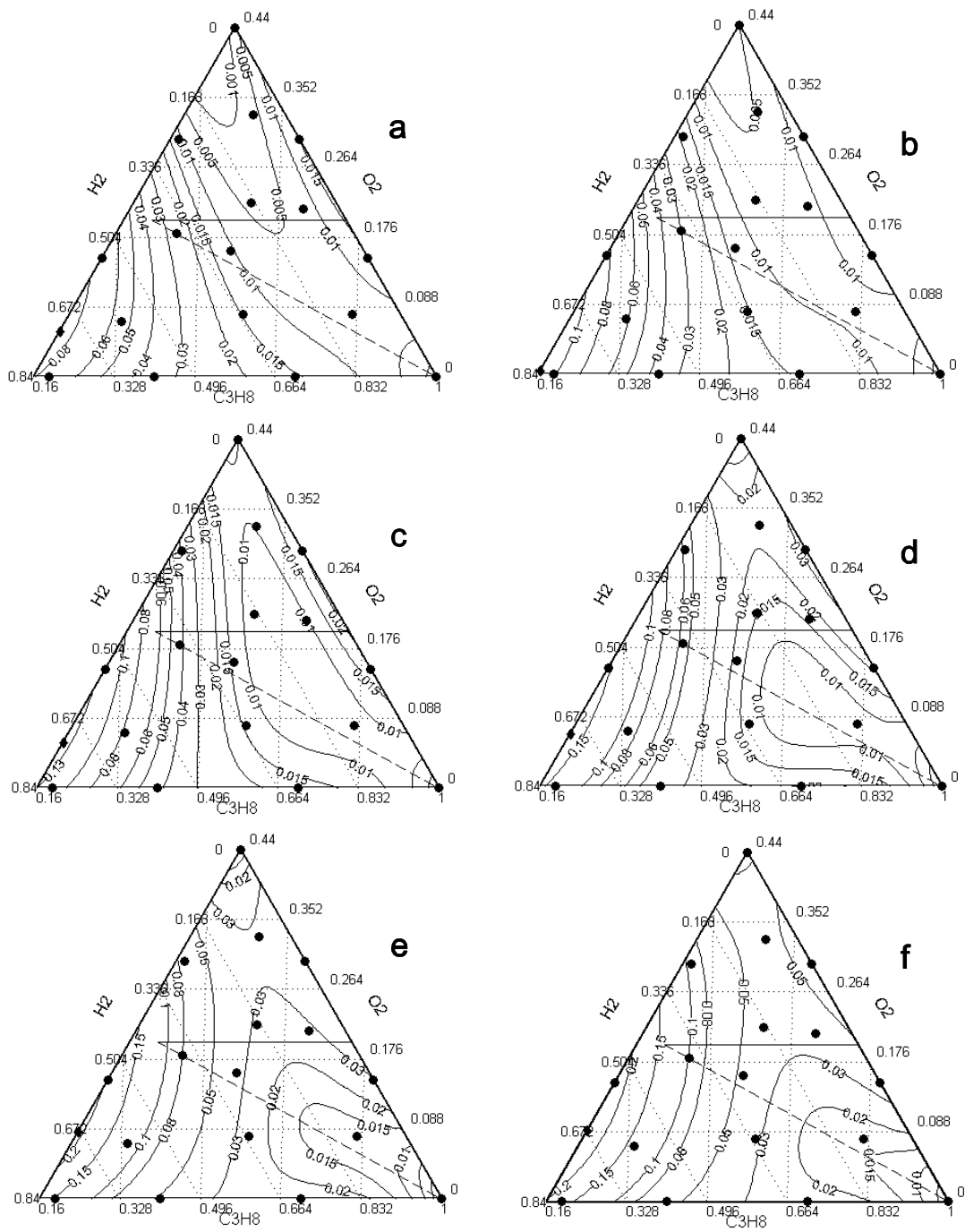
Figure 45: Yields of CH4 (C3H8) at temperatures: a) 525, b) 550, c) 575, d) 600, e) 625, f) 650 °C

Concerning CH_4, the yields depend on the amount of H_2 in the feed gas. The 'iso-conversion' lines show that H_2 is the main factor at low temperature to explain the amount of formed methane. Nevertheless, some strange points can be underlined. The minima yield is obtained with a low concentration in H_2. However, if there is no H_2 at all in the feed gas, the yield is better than with a small quantity. The behavior of the system changes when the temperature increases. Indeed, above 550 °C, the amount of O_2 seems playing a role for the CH_4 yield. The minimal yield is obtained around the stoichiometric composition between H_2 and O_2. When the amounts of H_2 or O_2 increase, the yield

decreases. The yield is more influence by the H_2 concentration than by the O_2 concentration, since the lines are tighter.

Despite the fact that only three reactants are involved in the process (propane, hydrogen, oxygen), the system is complex. Numerous by-products are formed. The feed gas composition influences all the parameters of the system: the conversion of propane, the yield of the desirable product and the by-products. According to the objectives of the process, different feed gas composition can be chosen: the conversion can be favored, or the selectivity. Some by-products such as water or CO_2 can be less damageable for the system.

As it was noticed in the previous part, the color of the catalyst was not homogeneous at the end of the reaction, especially in the case where the feed gas contained O_2. This illustrates the different reactions which take place in the different place of the reactor [60]. Indeed, in presence of O_2, near the inlet of the reactor, mainly oxidative reactions take place. Propene, water and carbon oxide are formed. Further in the reactor, close to outlet, non-oxidative reactions are predominant. Different areas in the catalytic bed can be determinate. However, it is not a real border between the two areas, and some reactions, both oxidative and non-oxidative could happen simultaneously. The inhomogeneous color is a piece of evidence of coke formation, which induces deactivation. The deactivation of the catalyst is a problem. To avoid coking, some solutions are available. For example, the coke can be burnt in oxygen flow. It is possible to know the amount of formed coke during the reaction, thanks to the GC. When the coke is burned in oxygen flow, it reacts with O_2 to form CO_2, and CO_2 can be detected by the GC. The method allows to have an accurate carbon mass balance.

The pressure is a significant parameter for the system. Indeed, at high pressure and with the catalyst, the propane conversion is better and the propane selectivity to propene is also improved. Some unknown reactions could explain this improvement. The system is complex, and it is not possible, just with these experiments, to determinate all the reactions which happen in the reactor. For example, it is possible to have first a cracking of propane, and then a recombination of CH_2 or CH_3 with C_2H_3 or C_2H_4 to produce propene. Some gas phase reactions happen in the reactor, but they are not enough to explain the results. Indeed, without catalyst, the system seems less influenced by the pressure. For the experiment 12, the propane conversion is 36 % at low pressure and 37 % at high pressure. The propene selectivity is not modified neither according to the pressure, and the yields are very similar whatever the pressure.

Increasing the feed velocity decreases the propane conversion and the propane selectivity to propene, but increases the propene yield. The difference between the propane conversion for a total flow rate of 50 mL/min and 100 mL/min is the most significant, with almost 8 % conversion for 50 mL/min and only less than 3 % with 100 mL/min. CO is detected by the GC at 575 °C if the feed gas is superior to 150 mL/min. It is not detected at low feed velocity. It can be assumed that CO is fully oxidized in CO_2 if the feed rate is low. If it is rapid, the gas mixture does not stay enough time to obtain a total oxidation. The partial oxidation at high speed explains the presence of CO. With high gas velocity, the residence time of gases in the reactor is reduced.

The test at low temperature without catalyst shows reactions between propane and oxygen start as soon as the temperature is superior to 175 °C. The reactions which happen in this case are gas phase reactions, involving propane and oxygen. This emphasizes that not only gas-solid reactions are important in the dehydrogenation, but also the gas phase reactions help the desirable reaction. A

few amount of propane is consumed at low temperature, to produce propene and some by-products. However, with this low temperature and without catalyst, the propane conversion is really low.

With the zeolite support, the propane conversion was similar to the one with hydrotalcite support. The propane selectivity to propene is a bit improved in this case. The load of Pt on the catalyst has also an influence on the conversion in this case.

6.3   Without oxygen

At low temperature, we can assume that two main reactions happened in the reactor. Propene was produced with 60 % carbon selectivity. The main reaction which produced propene is: $C_3H_8 = C_3H_6 + H_2$. A second reaction, producing ethylene, should happen. The cracking of the propane molecule by hydrogenolyse took place in the reactor, according to the following reaction: $C_3H_8 + H_2 = C_2H_6 + CH_4$.

At high temperature, the amount of C_2H_6 decreased. Instead of C_2H_6, C_2H_4 was produced. Thanks to the selectivity plot, we can notice that also the amount of CH_4 decreased slowly. The same reaction than at low temperature must happen. In addition, two different kinds of reactions allow producing ethylene. The first one is a catalytic reaction: $C_3H_6 + H_2 = C_2H_4 + CH_4$. The second reaction which can happen is a gas phase reaction. In this case, the catalyst is useless. The reaction is: $C_3H_8 = C_2H_4 + CH_4$

The propene selectivity as a function of the propane conversion was plotted. The selectivity increases when the conversion increases which implies there is not consecutive reaction to C_3H_6 degradation. The phase gas reaction is expected to be responsible for the ethylene production.
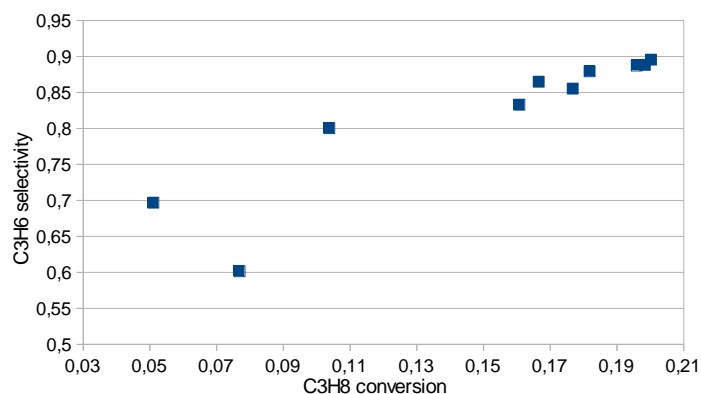
Figure 46: C3H8 selectivity for C3H6 as a function of C3H8 conversion

The molar ratio $\frac{C_2H_4+C_2H_6}{CH_4}$ is different from 1. For this experiment and at 550°C for example, this ratio is 0.46. This means that there was more CH_4 produced than ethene and ethane. To explain this result, a cracking of ethane or ethene have to be considered. This molar ratio is inferior to 1 for three experiments, whatever the temperature. However, at low temperature (i. e. 350 or 400 °C), the ratio is closer to 1 than at high temperature. When the temperature increases, some successive cracking may happen in the reactor, such as: $C_2H_6 + H_2 = 2 CH_4$. This reaction can also explain why the yield and carbon selectivity for ethane decreased when the temperature increased.

The same experiment was performed without catalyst, at high temperature (600°C and 650°C). The pressure was the same and the inlet gas mixture also. In this case, C_2H_4 molecules were still produced, but not C_2H_6, neither at 600°C nor 650°C. C_2H_6 may be formed during the reaction, but consumed as soon as formed, and so not detected by the GC. The propane conversion was really poor without catalyst (only 2 % at 650°C), and the propene selectivity was around 56 %.

This illustrates the interest of the catalyst. In this case and with this feed gas composition, it is absolutely necessary to use it for dehydrogenation of propane.

- Temperature inside the reactor

During the experiments, the thermocouple was outside the reactor, really close to the inner surface. Some calculations were done to check the temperature value given by the thermometer.

For the determination of the temperature, some hypotheses were done: the reaction was supposed to be adiabatic, the steady state reached when the measurements were done, and oxygen was entirely consumed by the reaction. The temperature is calculated for the first measurement, that is to say to confirm that the temperature is around 350 °C. The feed gas is composed by 56 % of C_3H_8 and 44 % of O_2, for the active components. There was not hydrogen in the feed gas, and at 350 °C, H_2 is not detected by the GC. This means that the H_2 formed by the catalytic dehydrogenation of propane is consumed by consecutive reactions as soon as it is produced. Only three products were detected by the GC, and they can be formed by these two kinds of reactions:

$C_3H_8 + 5\ O_2 = 3\ CO_2 + 4\ H_2O$
$2\ C_3H_8 + O_2 = 2\ C_3H_6 + 2\ H_2O$
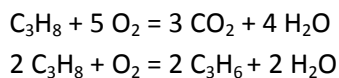
So, if we combine these reactions:

$3\ C_3H_8 + 6\ O_2 = 3\ C_3H_6 + 6\ H_2O + 3\ CO_2$
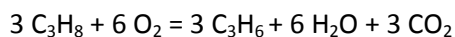
If we consider the flowrate, the feed gas had the following composition: C_3H_8: 38.88 mL/min, O_2: 7.87 mL/min, N_2: 32.03 mL/min.

We can determinate the molar amount of each component entering the reactor during one minute thanks to the following equation:

$$n_{O_2} = \frac{pV}{RT} = \frac{1,2.10^5 * 7,87.10^{-3}}{8,314 * 623}$$

	3 C_3H_8	+ 6 O_2	= 2 C_3H_6	6 H_2O +	3 CO_2	N_2
Entering compounds	1,41	0,18	0	0	0	1,16
Exit compounds	1,32	0	0,06	0,15	0,09	1,16

Table 9: Molar balance of the reaction

The calculations were done according to the method of J.B. Riggs [61], and the "sensibly heat" values have been taken from his book. The reference state 25 °C is chosen.
The energy balance reduces to $\Delta H = 0$ because $Q = 0$ (the reactor is supposed to be adiabatic).

We can sum up the data needed for the energy balance in the following table.

Component	Mol	T(K)	ΔH	ΔH°f (kJ/mol)	ΔH (kJ/mol)
Inputs					
C_3H_8	1,41	623	56 194 - 3563	-103,9	-72,38
O_2	0,18	623	10 343 - 732	0	1,729
N_2	1,16	623	10 183 - 728	0	10,97
				Total	**-59,59**
Outputs	*Assume T =700 K*				
CO_2	0,09	700	18 656 - 912	-393,5	-33,8
H_2O	0,15	700	15 016 - 837	-241,8	-34,1
C_3H_6	0,06	700	39 049 - 2154	20,42	3,4
C_3H_8	1,32	700	90 123 - 3563	-103,9	-4,7
N_2	1,16	700	12 652 - 728	0	13,8
				Total	**-55,42**
ΔH = ΔH$_{outputs}$ − ΔH$_{inputs}$ = 4,16 > 0					
Outputs	*Assume T =650 K*				
CO_2	0,09	650	16 265 - 912	-393,5	-34,03
H_2O	0,15	650	13 183 - 837	-241,8	-34,42
C_3H_6	0,06	650	46 777 - 2154	20,42	3,9
C_3H_8	1,32	650	77 067 - 3563	-103,9	-8,3
N_2	1,16	650	11 144 - 728	0	12,08
				Total	**-60,76**
ΔH = ΔH$_{outputs}$ − ΔH$_{inputs}$ = - 1,17 < 0					

Table 10: Temperature calculation thanks to an energy balance

ΔH = 0 is bracketed. A linear interpolation can be carried out to find the temperature.

$$T = 650 + 0 - \frac{(-1,17)}{4,16 - (-1,17)} * (700 - 650)$$

The calculated temperature inside the reactor is: T = 661 K = 388 °C. This temperature is a bit superior to the value given by the thermometer (350 °C). However, it is a good order of magnitude of the temperature.

6.4 Comparison between oxidative and non oxidative propane dehydrogenation

A comparison between the two different systems can be done, with oxidative and non oxidative reactions.

The propane conversion is better if the feed gas contains O_2. Indeed, at low pressure, the maximum propane conversion is around 20 %. At low pressure but with O_2 in the feed gas, it is often

above 30 % - around 40 % according to the feed gas composition. The selectivity is also improved if some oxygen is added in the feed gas, depending on the composition.

Even if there is oxygen in the feed gas, its composition has an influence on the behavior of the system. Some compositions favor the dehydrogenation of propane, whereas some other favors the formation of by-products. For example, whatever the temperature, the stoichiometric ratio between O_2 and H_2 is the less favorable for the propane dehydrogenation. These two components react together to form water, but do not help the desirable reaction.

Both oxidative and non-oxidative systems are very sensitive to the temperature. It is the main parameter which influences the catalytic dehydrogenation of propane. The propane conversion increases and the selectivity to propene decreases with an increasing of the temperature.

The pressure has also a major influence on the reaction behavior, mostly in the oxidative system. A high pressure increases both propane conversion and propene selectivity.

FUTURE WORK

One main kind of catalyst was used during this work: a platinum catalyst hydrotalcite supported. Several characterizations were done to obtain a better knowledge and understand this catalyst. However, further characterization could be done. For example, a temperature programmed reduction allows to know the reducibility of the catalyst surface. Better reduction conditions can be found thanks to this method.

The influence of the pressure was briefly studied, and it seems that increasing the total pressure in the reactor improves both the propane dehydrogenation and the propane selectivity to propene in the case of oxidative dehydrogenation. However, the mechanisms for these reactions are not well-known. They could be studied more in detail during a future work.

As the pressure was not the same for all the experiments, some points for the experiment plan could not be used. Repeating theses experiments will be a mean to insure the validity of the results, and giving more accurate conclusion.

Finally, it is well-known that alloys with Pt and another metal (Sn…) offer many advantages in comparison with Pt catalyst only. Investigating the effect of pressure variations on mixed catalyst for an oxidative dehydrogenation of propane could be interesting.

CONCLUSION

The catalytic dehydrogenation of propane has an important economic interest for various industries. However, the catalysts used for this reaction suffers from poor conversion rate and selectivity or rapid deactivation. So, finding a better catalyst was an interesting study. During the first part of this work, three kinds of hydrotalcite supports were tested: hydrotalcite 30 (with 30 % of MgO and 70 % Al_2O_3), hydrotalcite 63 (with 63 % of MgO and 37 % of Al_2O_3) and hydrotalcite 70. The influence of the amount of platinum deposited on the catalyst was also tested.

None huge difference was noticed between the three kinds of catalysts. Indeed, a support effect, according to the kind of hydrotalcite, seems to be very small for the dehydrogenation of propane. The conversion rate and the selectivity were not dramatically modified when the support was changed. By contrast, the amount of platinum seems have an influence on the propane conversion rate during the reaction. Indeed, with two supports (HT 63 and HT 70), the conversion rate is better when there is 2 % mass platinum than only 1 %. However for the HT 30, the conversion rate decreases when the amount of platinum increases. The catalyst HT 63 with 2 % Pt showed the best conversion rate. The catalyst 2 % of platinum HT70 supported presented great conversion rate, and quite good selectivity. It is an interesting compromise between these two parameters.

The reaction of oxidative propane dehydrogenation starts slowly at low temperature. Indeed, the conversion rate is very poor below 575 °C, whatever the catalyst. This conversion rate increases rapidly for higher temperatures.

During the second part of this master thesis, the catalyst HT 63 with 1 % Pt was selected. Various experiments were performed with this catalyst. The feed gas composition was varied, and both oxidative and non-oxidative reactions were studied. Oxidative reactions allow a better conversion of propane and selectivity to propene. The oxygen is supposed to play a part in the reaction. The oxidation of some molecules changes the mechanism of the propane dehydrogenation. The system is quite complex, and all the mechanism are not well-known. According to the feed gas composition, the results are modified. An optimal feed gas composition can be chosen to perform he catalytic dehydrogenation of propane thanks to the triangle. For example, it is not relevant to use a stoichiometric composition for O_2 and H_2. Indeed, some compositions favor by-products, such as water, but also as CO_2 or CO, and cracking of propane to form CH_4 or C_2H_6. The energy requires for this kind of dehydrogenation is less important than for non-oxidative dehydrogenation of propane, so these oxidative reactions are really interesting.

The experiments without catalyst showed less good propane conversion and selectivity to propene. Thus a catalyst is really necessary to carry out propane dehydrogenation.

The total pressure is also an important parameter. In presence of oxygen, so for oxidative dehydrogenation, a high pressure seems to have a positive effect, both for the conversion of propane and for the propane selectivity to propylene.

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APPENDIX 1: Preparation of the catalyst

The first catalyst was 2% weight Pt. The solid $H_2PtCl_6,6H_2O$, which molar mass is M=517,8 g.mol^{-1} was used. A preparation with 2g support was done. To know the necessary amount of platinum, the following formula was used.

$$m_{Pt} = 0,02 * (2 + m_{Pt})$$

So, 0,04081g of platinum were necessary. Using $H_2PtCl_6,6H_2O$, there was:

$$m_{H_2PtCl_6,6H_2O} = n_{Pt} * M_{H_2PtCl_6,6H_2O}$$

To obtain a catalyst with 2% weight Pt, a mass of 0,10834g of $H_2PtCl_6,6H_2O$ was added to the support.

For the second series of catalyst, with only 1% weight platinum, the same calculations were done. The amount of platinum was given by:

$$m_{Pt} = 0,01 * (2 + m_{Pt})$$

A mass of platinum of 0,0202 g was obtain, that is meaning only 0,530g of $H_2PtCl_6,6H_2O$ need to be used to obtain a 1% weight Pt catalyst.

APPENDIX 2: Activity test

Thanks to the GC analysis, for each component in the gas mixture, the retention time, the height and the surface area of peak were known. Thanks to some correlation, established after calibration, it is possible to find a relation between the height (for He and H_2) or the area of each peak and the molar fraction of the component. Thus, the molar fraction of each component is determinate in the initial mixture and the mixture after reaction. The total flow rate was 50 mL/min, and it was constant during all the experiments. Thanks to these data, the flow of one component before and after reaction can be found.

For C_3H_6, C_2H_6, C_2H_4, CH_4 and H_2, He is used as a reference to determine the output flow. So the output flow of the component A is given by the following formula:

$$V_{out}(A) = Y_{out}(A) * \frac{V_{out}(He)}{Y_{out}(He)}$$

Where V_{out} (A) is the flow of A after reaction and Y_{out} (A) the molar fraction of A after reaction.

N_2 is used as a reference for CO_2, CO and C_3H_6:

$$V_{out}(A) = Y_{out}(A) * \frac{V_{out}(N_2)}{Y_{out}(N_2)}$$

- Conversion

The conversion rate is defined by the following equation:

$$Conversion = \frac{initial\ flow\ of\ the\ component - flow\ of\ the\ component\ after\ reaction}{initial\ flow\ of\ the\ component}$$

The propane conversion rate was plot in function of the temperature.

- Reaction rate

In this case, the following formula is used for calculating the reaction rate:

$$r = initial\ flow\ of\ propane * \frac{conversion\ rate}{weight\ of\ catalyst}$$

The rate can be expressed in $mol.s^{-1}.g$ of catalyst $^{-1}$. The rate was plot in function of the temperature inverse.

- Carbon selectivity

The selectivity is an important parameter for a catalyst. The selectivity can be defined as the ratio of the molar amount of key reactant converted to desired product divided by the total amount of key reactant converted. The carbon selectivity of each by-product (CH_4, C_2H_6 CO…) can also be determinate by this way.

In this study, the selectivity was determinate by the following calculation:

$$n = \frac{number\ of\ Carbon\ in\ a\ component}{number\ of\ Carbon\ in\ propane}$$

$$Amount\ of\ by\ product = \sum_{by\ product} flow_i * n_i$$

$$Selectivity_j = n_j * \frac{flow_j}{amount\ of\ by\ product}$$

with j a by-product or the propene.

- Oxygen selectivity

During the dehydrogenation of propane, CO_2, CO and H_2O are produced. Some O_2 is necessary to form these products. In order to find the oxygen selectivity, the amount of water produced has to be known. The water cannot be analyzed by the GC. Consequently, a balance based on the molar amount of O_2 is necessary.

When the quantity of water is known, it is possible to find the selectivity. The following formula was used:

$$selectivity\ of\ A = \frac{flow\ of\ A\ after\ reaction}{input\ flow\ of\ O_2 - ouput\ flow\ of\ O_2}$$

where A is CO_2, CO or H_2O.

An example is given to illustrate the calculations:

The catalyst 1% Pt HT63 is considered. First, the initial gas mixture was analyzed.

Component	He	H_2	C_3H_8	N_2	O_2
Height or surface area	127 648	125 624	43 622	23 156	7 946
Molar fraction	0.28	0.16	0.19	0.30	0.08
Flowrate (mL/min)	14.3	8.0	9.6	15.1	3.9

The total flowrate is supposed to be 50mL/min and constant whatever the temperature.

At 600 °C, the average height of the He peak is 133 879 A.U. Thanks to a correlation, the molar fraction of He is found: 0.28. The flow of He is the same before and after reaction, because He did not react (inert gas), so the output flow of He is equal to 14.3 mL/min. Concerning H_2, the height of the peak is 112 889 A.U. The flowrate after reaction is 6.86 mL/min. For the other products, the surface area is used. Thanks to some calibrations, the molar fractions and the flowrate were found. The total amount of by product and propane is calculated.

$$Amount\ of\ by\ product = \frac{1.533}{3} + 0.520 + 0.846 + 2 * \frac{0.069}{3} + 2 * \frac{0.048}{3} + \frac{0.682}{3} = 0.31$$

The propane conversion was calculated with the following formula:

$$C_3H_8 \, conversion = \frac{9.79 - 7.82}{9.79} = 0.02$$

C-Selectivity and yield:

Component	C_3H_6	C_2H_6	C_2H_4	CH_4	CO	CO_2	Total
Selectivity	0.321	0.020	0.028	0.141	0.174	0.316	1
Yield	0.053	0.003	0.005	0.023	0.029	0.0522	0.165

O-Selectivity:

Component	H_2O	CO_2	CO	Total
Selectivity	0.514	0.381	0.105	1
Yield	0.514	0.381	0.105	1

APPENDIX 3: Propane conversion

The following plots are the conversion of propane as a function of temperature. The percentages of active gas in the feed gas are given under each graph.

H_2: 0 - C_3H_6: 56 - O_2: 44

H_2: 0 - C_3H_6: 100 - O_2: 0

H_2: 81 - C_3H_6: 19 - O_2: 0

H_2: 0 - C_3H_6: 70 - O_2: 30

H_2: 0 - C_3H_6: 85 - O_2: 15

H_2: 29 - C_3H_6: 71 - O_2: 0
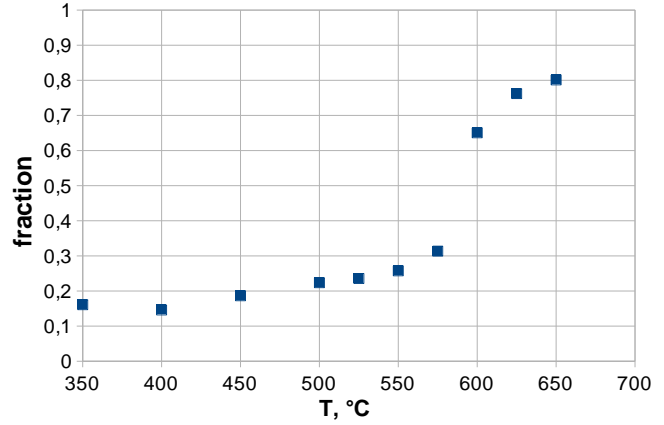
H$_2$: 59 - C$_3$H$_6$: 41 - O$_2$: 0

H$_2$: 25 - C$_3$H$_6$: 45 - O$_2$: 30
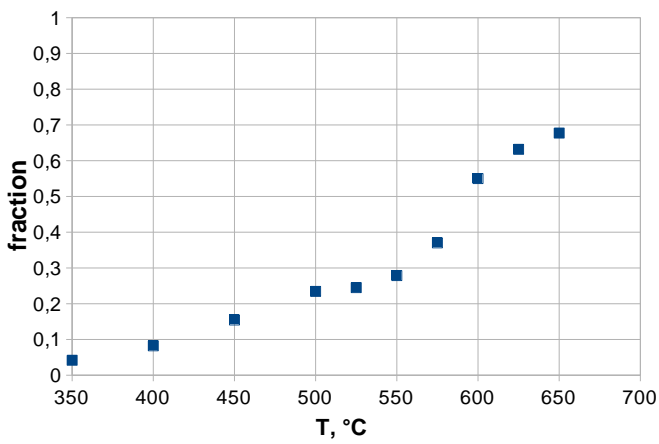
H$_2$: 55 - C$_3$H$_6$: 30 - O$_2$: 15
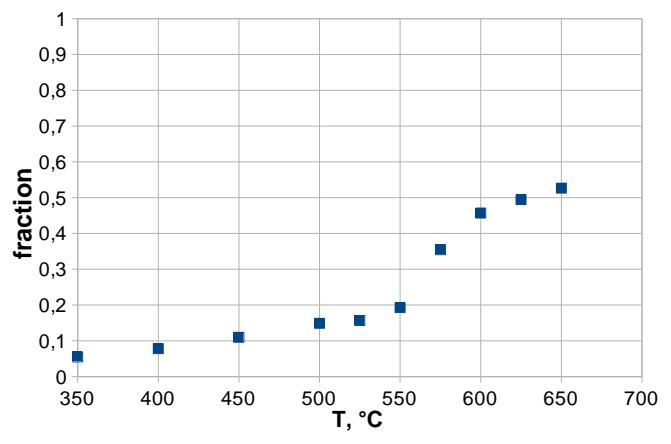
H$_2$: 27 - C$_3$H$_6$: 58 - O$_2$: 15

H$_2$: 7 - C$_3$H$_6$: 60 - O$_2$: 33

H$_2$: 59 - C$_3$H$_6$: 34 - O$_2$: 7

H$_2$: 8 - C$_3$H$_6$: 71 - O$_2$: 21

H$_2$: 34 - C$_3$H$_6$: 59 - O$_2$: 7

H$_2$: 37 - C$_3$H$_6$: 45 - O$_2$: 18


H$_2$: 19 - C$_3$H$_6$: 58 - O$_2$: 23

APPENDIX 4: C₃H₈ selectivity

H₂: 0 - C₃H₆: 56 - O₂: 44
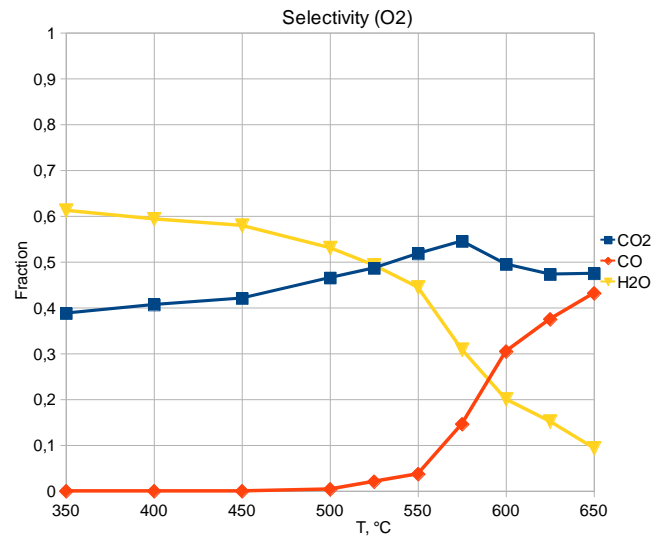

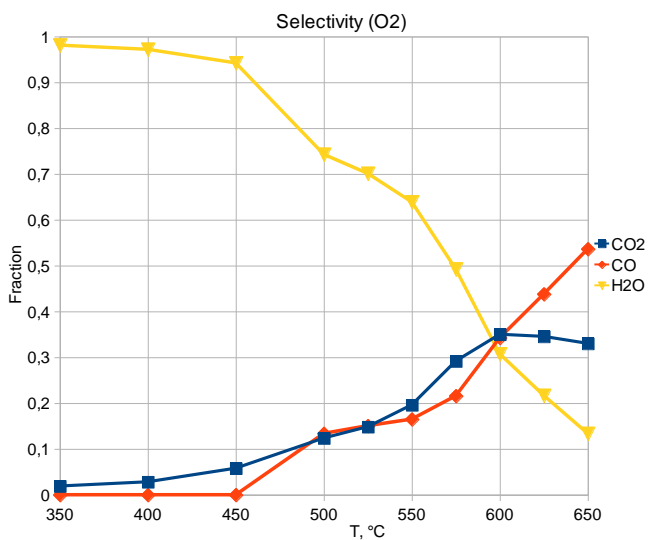H₂: 0 - C₃H₆: 100 - O₂: 0

H₂: 81 - C₃H₆: 19 - O₂: 0

H₂: 0 - C₃H₆: 70 - O₂: 30

H₂: 0 - C₃H₆: 85 - O₂: 15
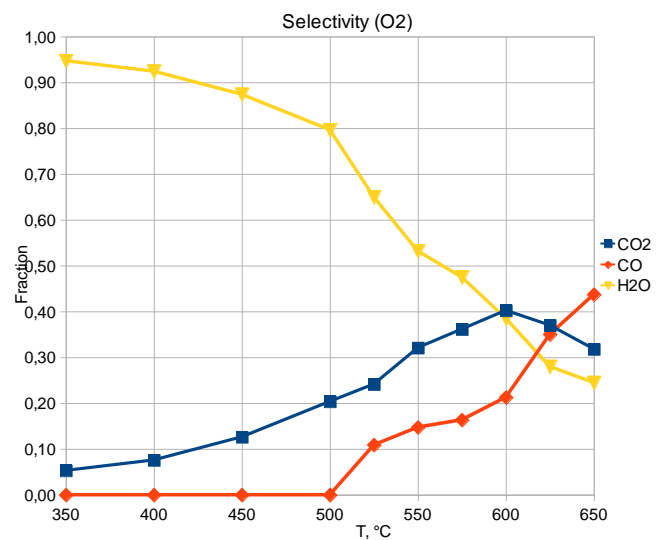

H₂: 29 - C₃H₆: 71 - O₂: 0
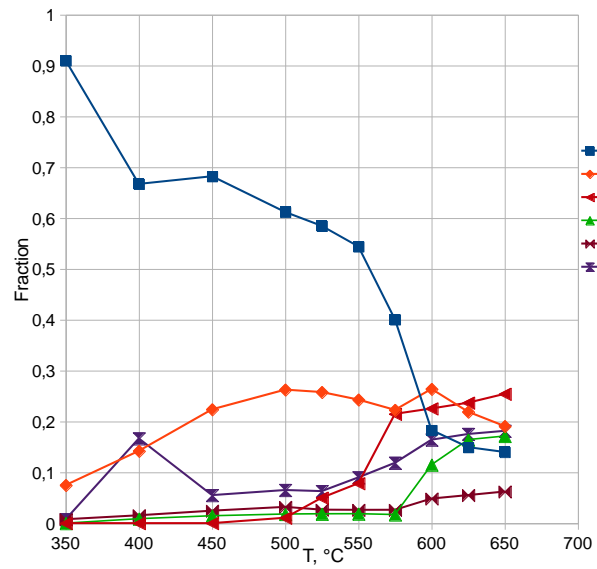
H₂: 59 - C₃H₆: 41 - O₂: 0

H₂: 25 - C₃H₆: 45 - O₂: 30
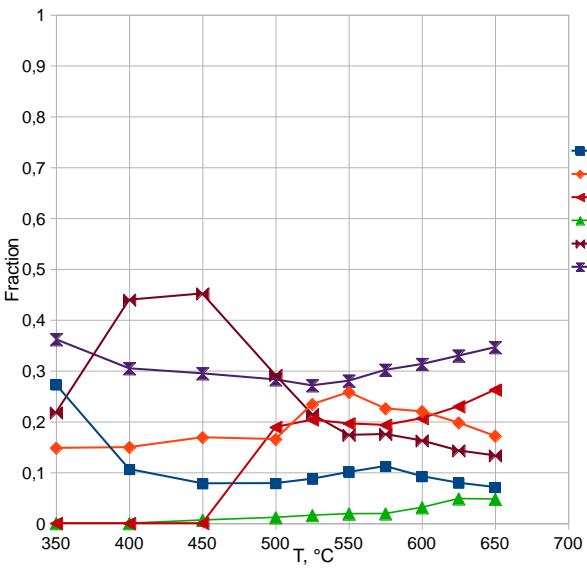
H₂: 55 - C₃H₆: 30 - O₂: 15

H₂: 27 - C₃H₆: 58 - O₂: 15

H₂: 7 - C₃H₆: 60 - O₂: 33

H₂: 59 - C₃H₆: 34 - O₂: 7

H₂: 8 - C₃H₆: 71 - O₂: 21

H₂: 34 - C₃H₆: 59 - O₂: 7

H₂: 37 - C₃H₆: 45 - O₂: 18

H₂: 18 - C₃H₆: 60 - O₂: 22

APPENDIX 5: Carbon yield

The following plots are the carbon yield as a function of the temperature.

H_2: 0 - C_3H_6: 56 - O_2: 44

H_2: 0 - C_3H_6: 100 - O_2: 0
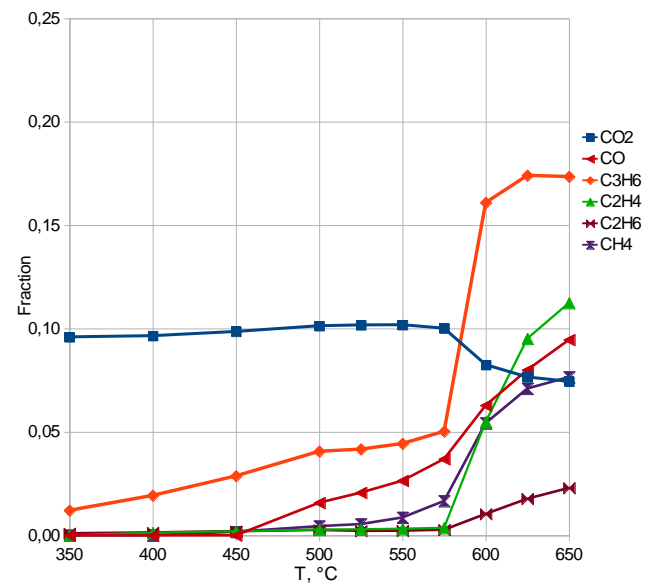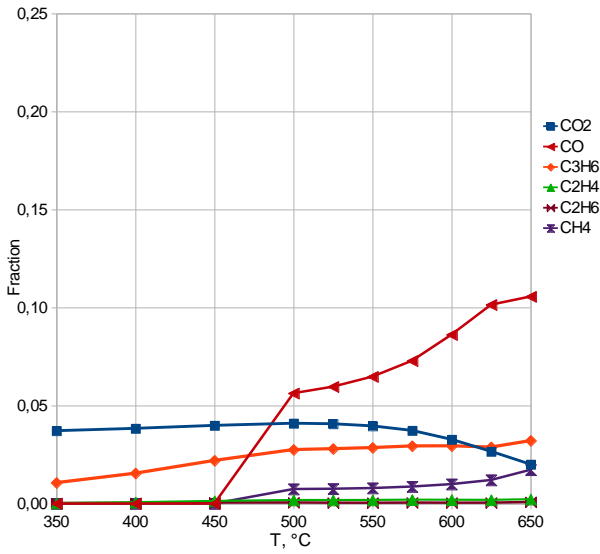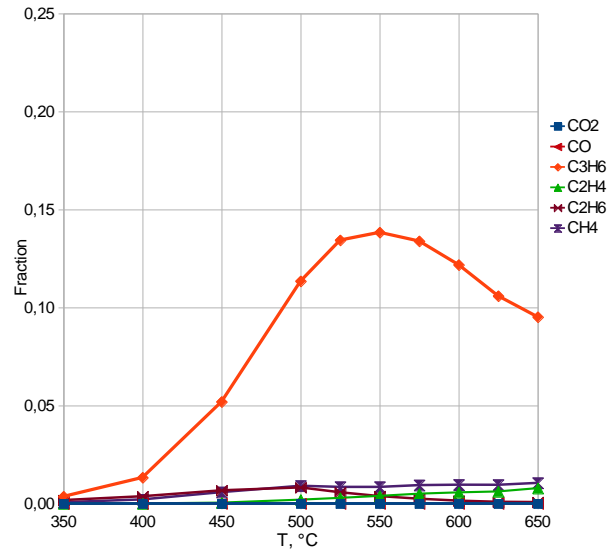
H_2: 81 - C_3H_6: 19 - O_2: 0

H_2: 0 - C_3H_6: 70 - O_2: 30

H₂: 0 - C₃H₆: 85 - O₂: 15
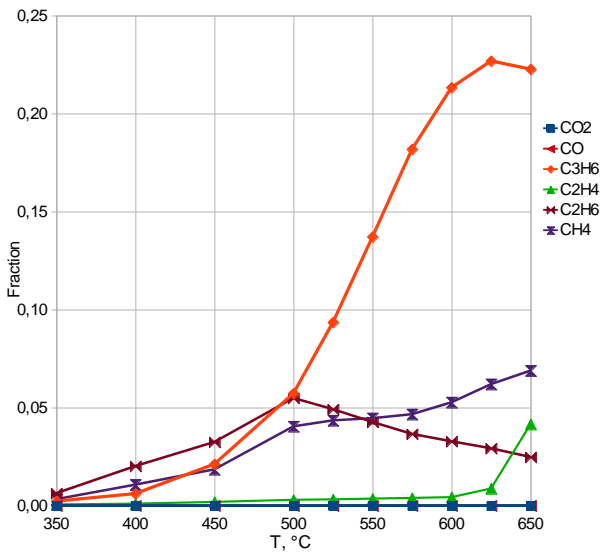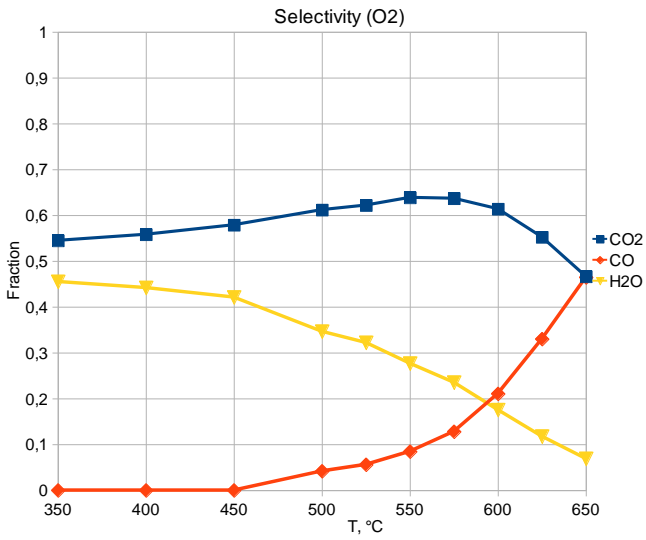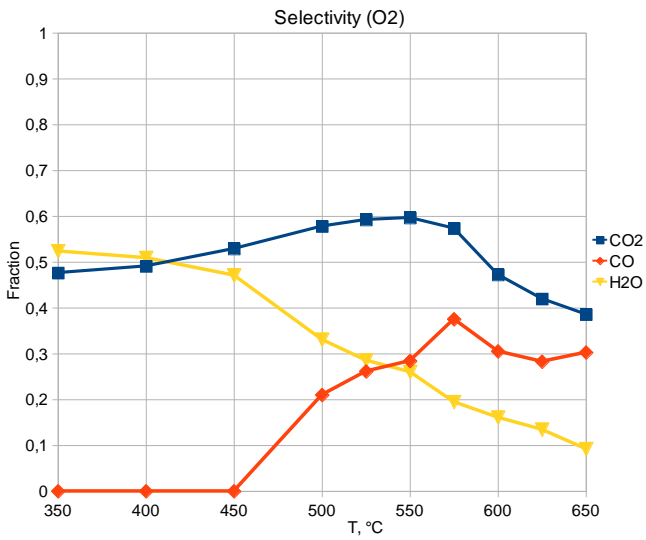
H₂: 29 - C₃H₆: 71 - O₂: 0
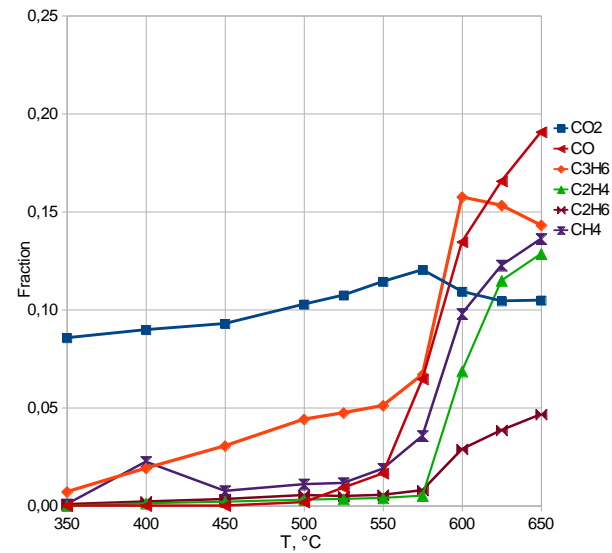
H₂: 59 - C₃H₆: 41 - O₂: 0

H₂: 25 - C₃H₆: 45 - O₂: 30
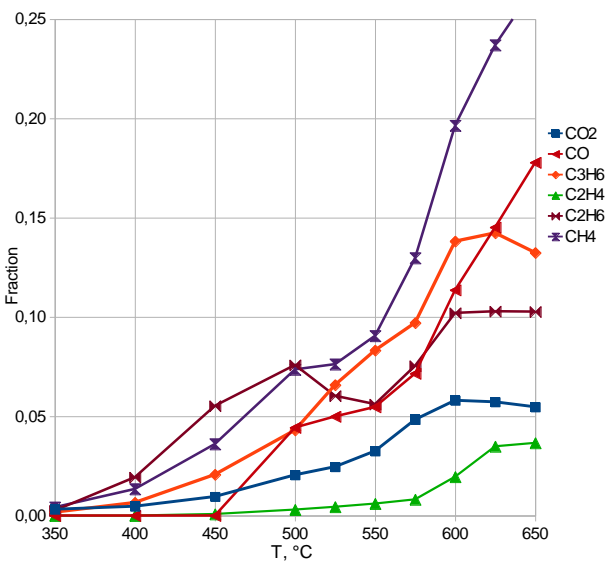
H₂: 55 - C₃H₆: 30 - O₂: 15
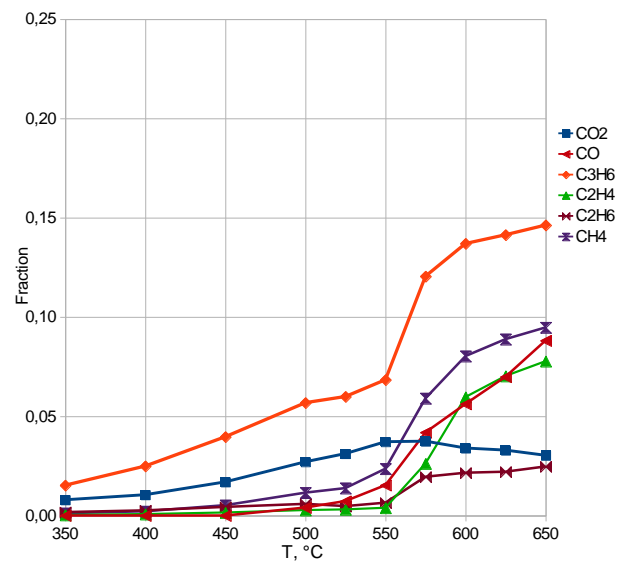
H₂: 27 - C₃H₆: 58 - O₂: 15

H$_2$: 7 - C$_3$H$_6$: 60 - O$_2$: 33

H$_2$: 19 - C$_3$H$_6$: 58 - O$_2$: 23
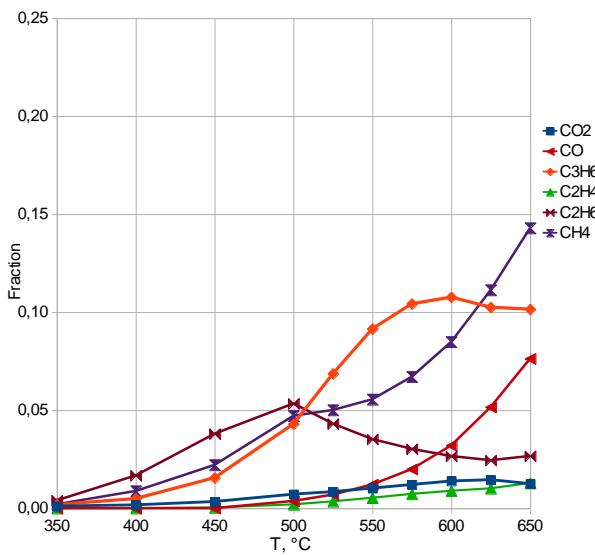
H$_2$: 59 - C$_3$H$_6$: 34 - O$_2$: 7
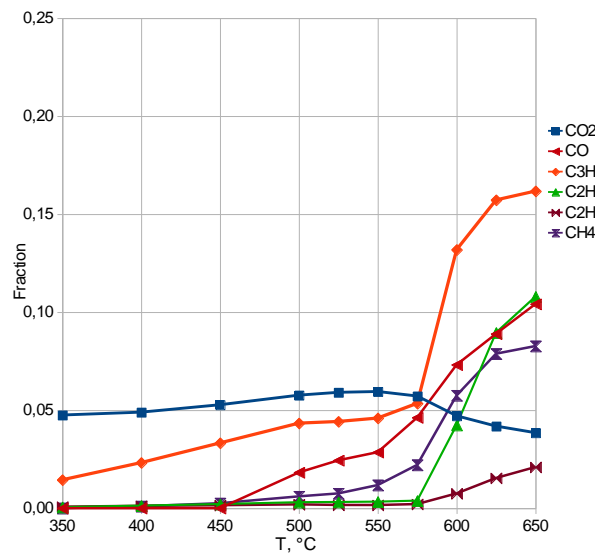
H$_2$: 8 - C$_3$H$_6$: 71 - O$_2$: 21
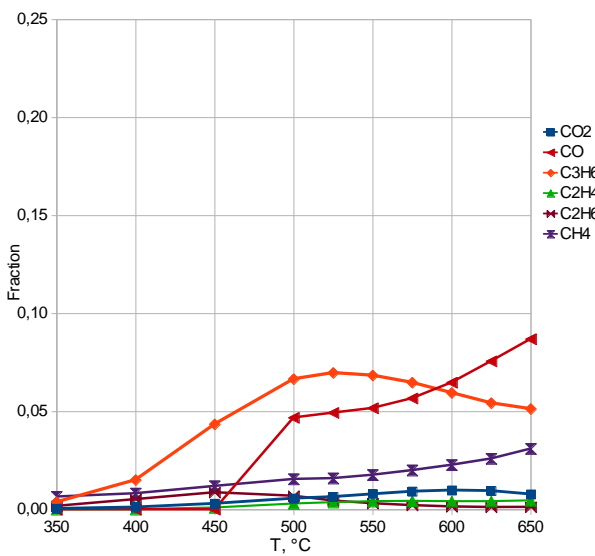
H$_2$: 34 - C$_3$H$_6$: 59 - O$_2$: 7
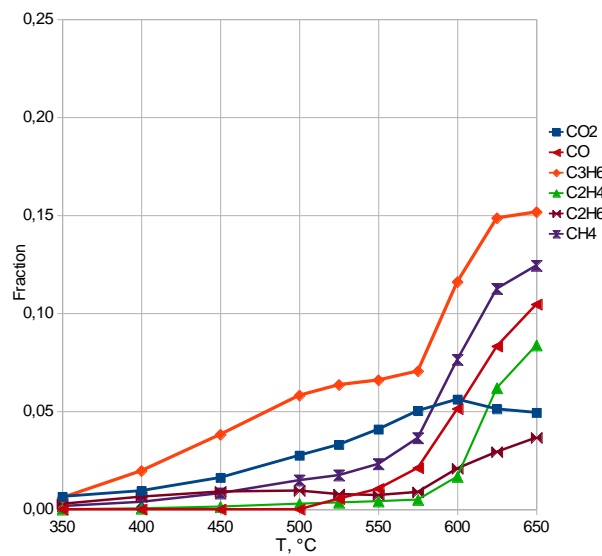
H$_2$: 37 - C$_3$H$_6$: 45 - O$_2$: 18

APPENDIX 6: Oxygen selectivity
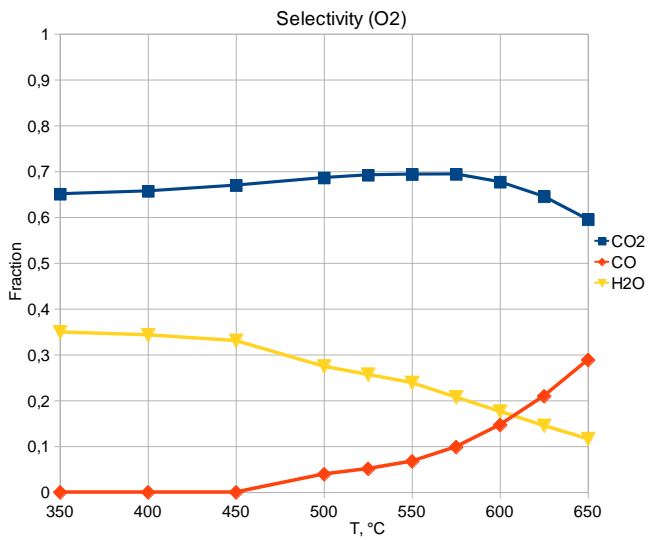
H$_2$: 0 - C$_3$H$_6$: 56 - O$_2$: 44
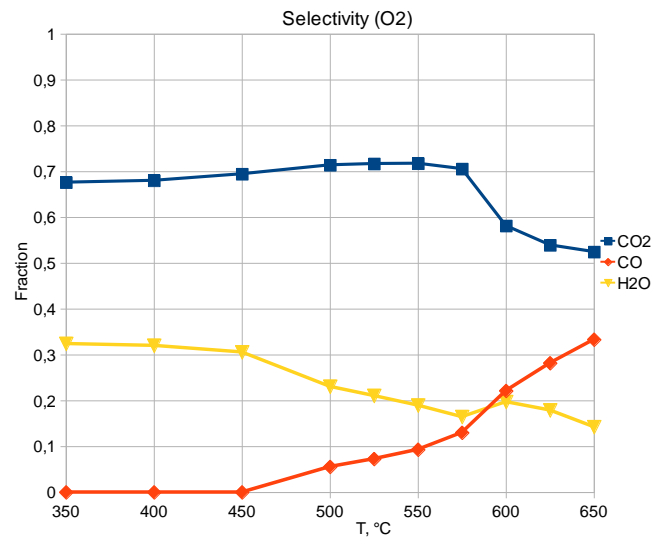
H2: 0 - C3H6: 70 - O2: 30
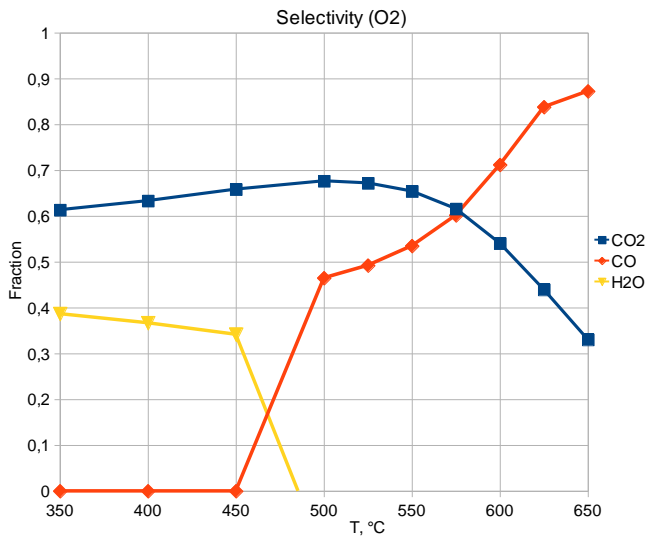
H$_2$: 0 - C$_3$H$_6$: 85 - O$_2$: 15

H$_2$: 25 - C$_3$H$_6$: 45 - O$_2$: 30

H$_2$: 55 - C$_3$H$_6$: 30 - O$_2$: 15

H$_2$: 27 - C$_3$H$_6$: 57 - O$_2$: 16

Selectivity (O2)

H_2: 7 - C_3H_6: 60 - O_2: 33

Selectivity (O2)

H_2: 59 - C_3H_6: 34 - O_2: 7

Selectivity (O2)

H_2: 8 - C_3H_6: 71 - O_2: 21

Selectivity (O2)

H_2: 34 - C_3H_6: 59 - O_2: 7

Selectivity (O2)

H_2: 37 - C_3H_6: 45 - O_2: 18

Selectivity (O2)

H_2: 18 - C_3H_6: 60 - O_2: 22