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# Model catalysts for Fischer-Tropsch synthesis

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## Preface

This Master's thesis is a result of the work of my exchange studies from Spain at the Norwegian University of Science and Technology (NTNU). The work has been completed within the Catalysis group at the Department of Chemical Engineering, Faculty of Natural Sciences and Technology, during the spring 2014.

I would like to thank my home university, Universidad Autónoma de Madrid, for allow me to carry out this year abroad.

This Master's thesis would not have been possible without the help and support from several important people.

I would like to thank my supervisor, Professor De Chen, for accepting me as a part of his research group and giving me the opportunity to work in a field of chemical engineering that I like. I thank his advices during the whole semester to carry out this thesis in a good way sharing his point of view.

I am grateful to my co-supervisor, Michael Markus Wycisk, for helping me to improve my laboratory skills, for having patience and giving me the time required to get experience.

I would like to give great thanks to my family for give me the opportunity to live this experience in a country like Norway, it was awesome. I am proud of my sister, Lucia, for making me feel bigger every day.

Finally, thanks to my old and new friends for their motivation and moral support.

### Declaration of compliance

I declare that this is an independent work according to the exam regulations of the Norwegian University of Science and Technology (NTNU).

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## Abstract

Today, Fischer-Tropsch synthesis is the key process in the production of liquid fuels from synthesis gas (a mixture of CO + H<sub>2</sub>). This mixture can be obtained from fossil fuels (oil, natural gas or coal) and from renewable sources such as biomass. Catalysis has an important role in the reaction since the catalysts can vary the activity and selectivity towards a wide range of products (i.e. methane, olefins, paraffins and alcohols, among others).

The scope of this Master's thesis has been the synthesis of core/shell nanoparticles as catalysts to increase the conversion of CO; increase the selectivity to olefins and C<sub>+5</sub>; and decrease the methane formation. It is known that using metal oxides as promoters in the catalyst formation favor these desired products.

For this objective, it has been selected manganese oxide as promoter. It has been synthesized 10 catalysts with different core/shells. Some catalysts were a formation using Co as core and MnO as shell, coating the surface area of the Co with different percentages (0, 25, 50, 75, 100, and 200%) to understand which conditions are optimal.

On the other hand, it has been synthesized few core/shells catalysts of MnO as core and Co as shell.

Finally, it was evaluated some experiments of lanthanum oxide nanoparticles. It was comparable different precursors to synthesize this oxide: La oleate; La linoleate; La laureate; and La stearate.

The characterization of the catalysts has been done using these techniques: TEM, XRD, and TGA. The catalyst performance has been evaluated in a Fischer-Tropsch reactor.

After evaluate the results, it can be concluded that a catalyst formed by a core/shell of Co as core and coated with multi layer of MnO is the optimal catalyst. This catalyst has a low methane formation and high selectivity to olefins and C<sub>+5</sub> compared with the rest of the catalysts, even pure Co.

Regarding the experiments of lanthanum oxide, lanthanum laureate is the precursor with the lowest decomposition temperature, favoring the reaction to form lanthanum oxide.



# Table of Contents

Preface.....	i
Abstract.....	iii
List of figures.....	vii
List of tables.....	viii
List of symbols and abbreviations .....	ix
<b>1. Introduction .....</b>	<b>1</b>
<b>2. Theory.....</b>	<b>2</b>
2.1 Technology:.....	2
2.2 Fischer-Tropsch synthesis .....	4
2.2.1 FT mechanism.....	4
2.2.2 Kinetics: .....	6
2.2.3 Conversion and selectivity:.....	6
2.3 Nanoparticles:.....	8
2.3.1 Core/shell nanoparticles:.....	8
2.3.2 Base.....	9
2.3.3 Promoter:.....	10
2.3.4 Support.....	11
2.3.5 Catalyst pretreatment: .....	12
2.4 Characterization techniques: .....	12
<b>3. Materials and Methods .....</b>	<b>13</b>
3.1. Catalyst synthesis .....	13
3.1.1. Synthesis Co nanoparticles .....	13
3.1.2. Synthesis MCF-26: .....	14
3.1.3. Synthesis of Manganese oleate complex: .....	14
3.1.4. Synthesis MnO:.....	15
3.1.5. Catalysts preparation:.....	15
3.1.6. Synthesis of lanthanum oxide:La <sub>2</sub> O <sub>3</sub> .....	19
3.2. Catalyst characterization .....	20
3.2.1 Transmission electron microscopy: .....	20
3.2.2 X-ray diffraction: .....	20

3.2.3	Thermal gravimetric analysis:.....	21
3.3	Catalyst testing: .....	21
<b>4.</b>	<b>Results and discussion:.....</b>	<b>23</b>
4.1	Co nanoparticles:.....	23
4.2	Catalysts results.....	24
4.3	Results La <sub>2</sub> O <sub>3</sub> .....	59
<b>5.</b>	<b>Conclusions.....</b>	<b>61</b>
<b>6.</b>	<b>Literature .....</b>	<b>63</b>
<b>7.</b>	<b>Attachments .....</b>	<b>64</b>
7.1	Calculations.....	64
7.2	Tables .....	75



## List of figures

Figure 1. The three main steps in the gas-to-liquids process.[2].....	2
Figure 2. Process scheme GTL.[4].....	3
Figure 3. ASF plot.....	4
Figure 4. Carbide mechanism for FT. ....	5
Figure 5. Structure of a core/shell.....	8
Figure 6. XRD technique. ....	21
Figure 7. General view of the installation of the activity testing.....	22
Figure 8. TEM characterization for the first synthesis of Co nanoparticles. ....	23
Figure 9. TEM characterization for the second synthesis of Co nanoparticles. ....	23
Figure 10. TEM characterization for CAT_J01. ....	24
Figure 11. Frequency vs size of Co nanoparticles. ....	25
Figure 12. Frequency vs size of CAT_J01. ....	25
Figure 13. XRD result for CoO.....	26
Figure 14. XRD result for MnO.....	26
Figure 15. Conversion diagram for CAT_J01 without reduction.....	27
Figure 16. Conversion diagram for CAT_J01 reduction.....	28
Figure 17. Conversion CO vs temperature CAT_J02.....	29
Figure 18. Selectivity vs temperature CAT_J02. ....	30
Figure 19. O/P ratio vs temperature CAT_J02. ....	31
Figure 20. TEM image of MnO nanoparticles.....	32
Figure 21. TEM image CAT_J03, MnO/CoO.....	32
Figure 22. TGA result CAT_J04.....	33
Figure 23. TEM of MnO nanoparticles. ....	34
Figure 24. Figure 24 .TEM image of CAT_J05.....	34
Figure 25. Conversion vs temperature CAT_J05. ....	35
Figure 26. O/P ratio vs temperature CAT_J05. ....	36
Figure 27. Selectivities vs temperature CAT_J05.....	36
Figure 28. 2:1 Conversion CO vs residence time for all the catalysts.....	39
Figure 29. 2:1 O/P C <sub>2</sub> ratio vs CO conversion for all the catalysts.....	40
Figure 30. 2:1 O/P C <sub>3</sub> ratio vs CO conversion for all the catalysts.....	41
Figure 31. 2:1 O/P C <sub>4</sub> ratio vs CO conversion for all the catalysts.....	42
Figure 32. 2:1 Selectivity CH <sub>4</sub> vs CO conversion for all the catalysts.....	43
Figure 33. 2:1 Selectivity C <sub>2</sub> vs CO conversion for all the catalysts.....	44
Figure 34. 2:1 Selectivity C <sub>3</sub> vs CO conversion for all the catalysts.....	45
Figure 35. 2:1 Selectivity C <sub>4</sub> vs CO conversion for all the catalysts.....	46
Figure 36. 2:1 Selectivity C <sub>5+</sub> vs CO conversion for all the catalysts.....	47
Figure 37. 2:1 Selectivity C <sub>3=</sub> vs CO conversion for all the catalysts.....	48
Figure 38. 2:1 Selectivity C <sub>4=</sub> vs CO conversion for all the catalysts.....	49

Figure 39. 10:1 Conversion CO vs residence time for all the catalysts.....	50
Figure 40. 10:1 O/P C <sub>2</sub> ratio vs CO conversion for all the catalysts.....	51
Figure 41. 10:1 O/P C <sub>3</sub> ratio vs CO conversion for all the catalysts.....	52
Figure 42. 10:1 O/P C <sub>4</sub> ratio vs CO conversion for all the catalysts.....	53
Figure 43. 10:1 Selectivity CH <sub>4</sub> vs CO conversion for all the catalysts.....	54
Figure 44. 10:1 Selectivity C <sub>2</sub> vs CO conversion for all the catalysts.....	55
Figure 45. 10:1 Selectivity C <sub>3</sub> vs CO conversion for all the catalysts.....	55
Figure 46. 10:1 Selectivity C <sub>4</sub> vs CO conversion for all the catalysts.....	56
Figure 47. 10:1 Selectivity C <sub>5+</sub> vs CO conversion for all the catalysts.....	56
Figure 48. 10:1 Selectivity C <sub>3=</sub> vs CO conversion for all the catalysts.....	57
Figure 49. 10:1 Selectivity C <sub>4=</sub> vs CO conversion for all the catalysts.....	57
Figure 50. TEM La <sub>2</sub> O <sub>3</sub> nanoparticles. ....	59
Figure 51. Comparison TGA of precursors for La <sub>2</sub> O <sub>3</sub> . ....	60
Figure 52. TEM result MnO/CoO with hexadecanediol.....	77

## List of tables

Table 1. Usage ratio of FT reactions.....	7
Table 2. Dependence of the selectivity.....	7
Table 3. Amountsofcompounds. ....	13
Table 4. CAT_J01 Reduction, ratio 2:1. ....	76
Table 5. CAT_J01 Reduction, ratio 10:1, GHSV: 0,9 l/g/h. ....	75
Table 6. CAT_J02, ratio 2:1. ....	77
Table 7. CAT_J02 Reduction, ratio 2:1. ....	76
Table 8. CAT_J02, ratio 10:1. ....	77
Table 9. CAT_J08, ratio 2:1. ....	78
Table 10. CAT_J08 Reduction, ratio 2:1. ....	79
Table 11. CAT_J08, ratio 10:1. ....	80
Table 12. CAT_J09, ratio 2:1. ....	81
Table 13. CAT_J09 Reduction, ratio 2:1. ....	82
Table 14. CAT_J10, ratio 2:1. ....	83
Table 15. CAT_J10, ratio 10:1. ....	84

## List of symbols and abbreviations

CO	Carbon monoxide	nm	nanometer
Co	Cobalt	O	Olefin
Fe	Iron	OA	Oleic Acid
FT	Fischer-Tropsch	OD	1-Octadecene
GTL	Gas-to-liquids	O/P	Olefin/paraffin ratio
GC	Gas chromatograph	P	Paraffin
g	gram	TEM	Transmission electron microscope
h	hour	TOA	Trioctylamine
La	Lanthanum	TGA	Thermal Gravimetric analysis
m	mass	V	Volume
mL	Milliliter	X	Conversion
MnO	Manganese oxide	XRD	X-ray diffraction
MCF-26	Siliceous mesocellular foam	°C	Celsius degree
M	Molar mass	$\rho$	Density
n	Mol number		



# 1. Introduction

There are three sources of primary energy in the world: coal, oil and natural gas.

The most used until now has been oil, but the limited availability of crude oil has brought to search alternatives.

In consequence, natural gas and coal have an important role nowadays. It is well known that gas reserves exist in different areas in the world.

This is the reason why the GTL (Gas to Liquids) industry has increased in the last years. To synthesize fuels, natural gas is converted to synthesis gas, followed by Fischer-Tropsch (FT) synthesis to obtain hydrocarbons with different chain-length.

Regarding the environmental aspect, the products of FT are clean; and on the economic point of view, oil has high prices due to its limited availability on earth.

Fischer-Tropsch process is favored when a catalyst is used.. Bonds are formed between the catalyst and the reacting molecules and the chemical reaction accelerates at much lower temperatures and pressures.

There are two types of catalysis: homogeneous and heterogeneous catalysis.

In homogeneous catalysis, the catalyst and the reactants are in the same phase, gas or liquid. Otherwise, in heterogeneous catalysis the catalyst is solid and it catalyzes reactions where the molecules are in gas or solution. The solids catalysts are usually impenetrable, exception of the porous, and the catalytic reaction occurs at the surface. Nanotechnology is the goal here due to using nanoparticles as catalysts it will be a high surface area to bond with the reactants.[1]

The scope of this project is to find catalysts using nanoparticles that can increase the selectivity to olefins by the Fischer-Tropsch reaction.

## 2. Theory

### 2.1 Technology:

Fischer-Tropsch has a high interest in Gas-to-Liquids (GTL) industry nowadays. The high availability of natural gas reserves in the world is the reason.

The GTL process is based in three steps: synthesis gas production, Fischer-Tropsch synthesis and products upgrade.

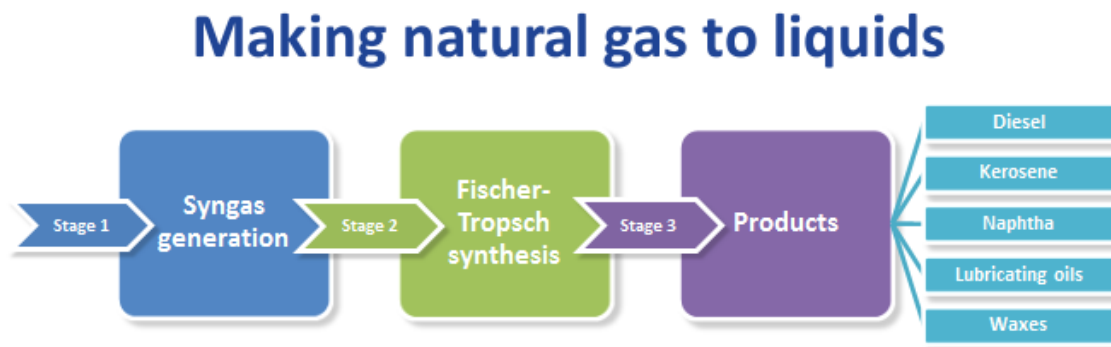


Figure 1. The three main steps in the gas-to-liquids process.[2]

FT technology consists in three steps:[3]

1. Gas synthesis preparation: Gas synthesis is prepared from a feed with carbon and should contain hydrogen to increase the efficiency. If it doesn't contain hydrogen, water can be used, but it would be necessary a higher amount of energy to break the molecule. Sometimes, synthesis gas is produced from natural gas by means of methane reforming. This process is cheaper than coal conversion.
2. FT synthesis: The production of Fischer-Tropsch depends on the gas composition, catalyst formulation and operating temperature. Depending of the desired productions it would be used different values of the parameters. For example, by increasing the temperature it will increases methane production and deactivation mechanism but increases also the reaction rate.

This step is the most important in this project, because the catalyst formulation will be the main parameter that can be changed in order to know the variation of the product distribution by FT. Depending on the catalyst, the conversion and selectivity to various products will change.

3. Product upgrading: Separation and hydroprocessing take place after FT synthesis to produce special final products. One of the most dominant products is diesel converted from olefins.

In the next figure it is showed a process scheme from the sources, coal and natural gas, until the final products:

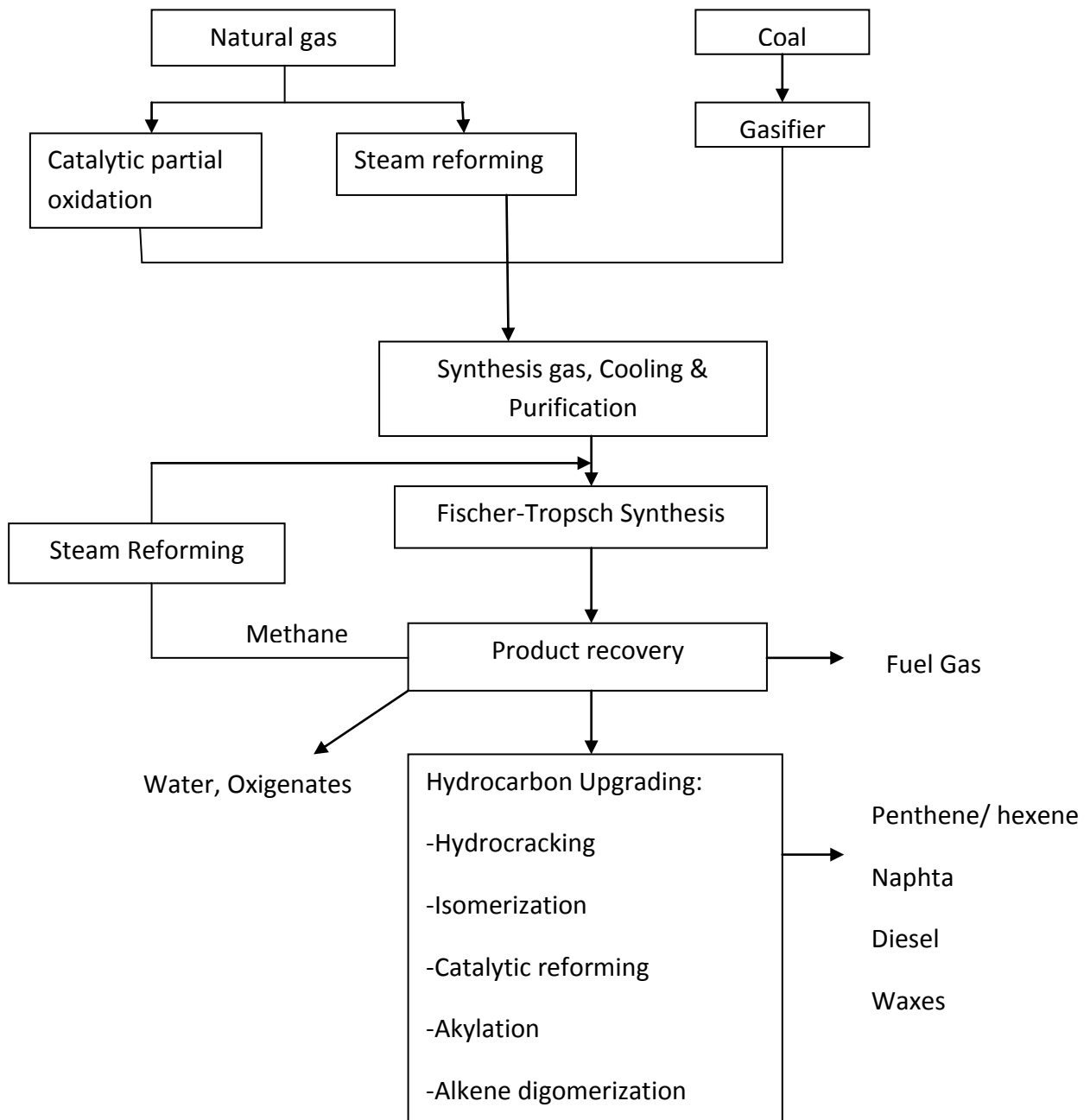


Figure 2. Process scheme GTL.[4]

## 2.2 Fischer-Tropsch synthesis

FT synthesis is the main step in this project. FT will be explained from the mechanism used; the reactions that take place for the desired products; and an explanation about the dependence of the conversion and selectivity on some parameters.

### 2.2.1 FT mechanism

The FT is a polymerization reaction, with the addition of a single carbon monomer on the catalyst surface, and it is presented, by Herington, Anderson and Flory as:[3]

$$\text{Log}(W_n n) = n \log \alpha + \text{constant} \quad (1)$$

where  $W_N$  is the mass fraction of the species with carbon number  $n$ , assuming  $\alpha$  to be independent of chain length.

The classical Anderson–Schulz–Flory (ASF) distributions showed in the following plot, which shows the chain growth probability ( $\alpha$ ) and weight fraction of HC of chain length dependence. [5]

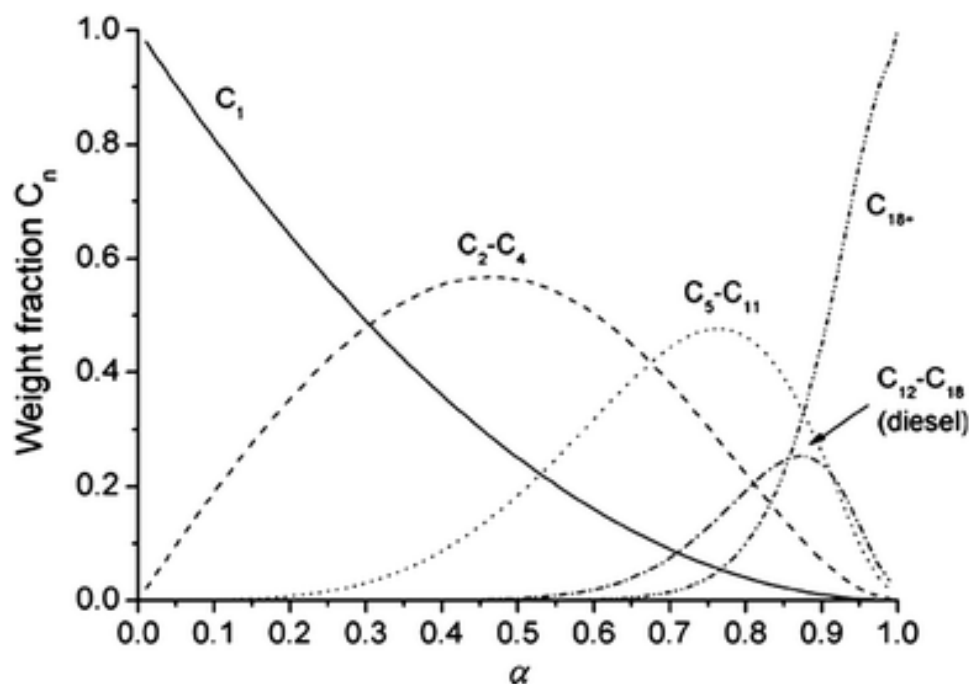


Figure 3. ASF plot.



FT follows these steps: [6]

1. Reactant adsorption
2. Chain initiation;
3. Chain growth;
4. Chain termination;
5. Product desorption;
6. Readsorption and further reaction.

There is a variety of mechanisms to describe the chain growth step, the most important for the hydrocarbon of the VIII metals (Co, Fe and Ru) is the surface carbide mechanism by insertion of methylene ( $\text{CH}_2$ ). Where CO and  $\text{H}_2$  are assumed to adsorb in a dissociative way.[7]

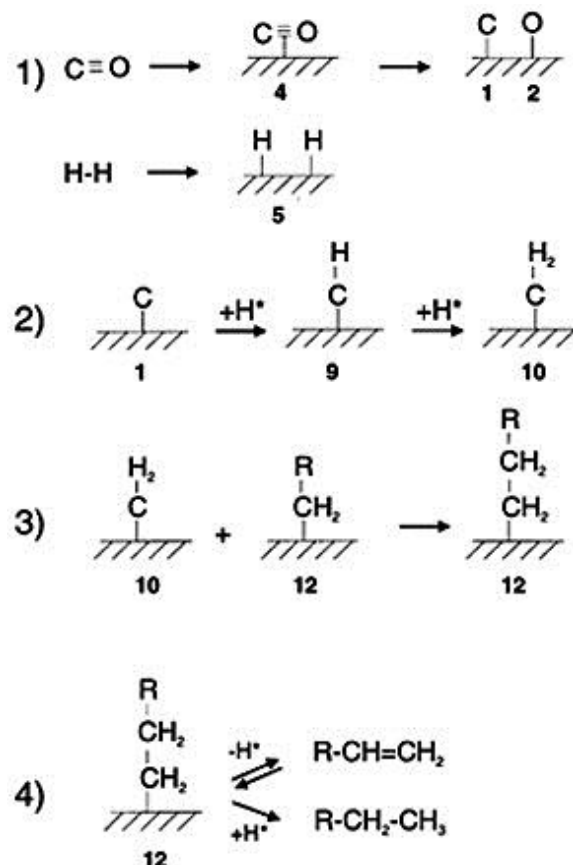
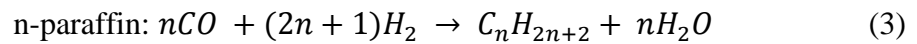
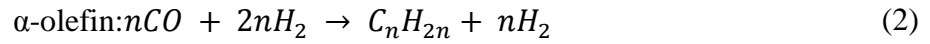


Figure 4. Carbide mechanism for FT.

### 2.2.2 Kinetics:

This technology converts synthesis gas, hydrogen and carbon monoxide, to hydrocarbon products and provides an alternative way to produce fuels and petrochemicals from non-petroleum sources. The reaction stoichiometry depends on the hydrocarbon product, alkanes and alkenes, is shown in the followings reactions:[8]



These products are mostly liquid at ambient conditions but some of them are gaseous or solids as well. The most abundant product of the reaction between CO and H<sub>2</sub> is methane because of the thermodynamic and reaction conditions, but with FT is possible to produce higher hydrocarbons. The goal is to produce clean hydrocarbons for fuel production, where olefins are distinguished. There are some co-products like nitrogen that can be used to make other products. Subsequently products are sold in different markets.

### 2.2.3 Conversion and selectivity:

The conversion relates the consumption of reactants rather than the appearance of the products. [9] It is expressed following this equation:

$$X_{CO} = \frac{F_{CO,IN} - F_{CO,OUT}}{F_{CO,IN}} \cdot 100 \quad (4)$$

On the other hand, the selectivity is the way in which the resulting products are distributed.

In the FT reactors, in order to obtain useful products, is important the efficiency of the reactants consumption. The selectivity should be controlled to minimize undesired products, as methane.

The product distribution can be varied altering parameters depending on the carbon number: operating temperature, operating pressure, space velocity, H<sub>2</sub>/CO ratio, type of catalyst, amount and type of promoter, or type of reactor. The reaction should be done with the optimal conditions for the desires products.

The main reactor types are:

1. Three-phase fluidized bed reactors or slurry bubble column reactors with internal cooling tubes.
2. Multitubular fixed bed reactor with internal cooling
3. Circulating fluidized bed reactor with circulating solids, gas recycle and cooling in the gas/solid recirculation loop.
4. Fluidized bed reactors with internal cooling.

Regarding the usage ratio of H<sub>2</sub> and CO, it controls the selectivity as is shown in the following table[3]:

Table 1. Usage ratio of FT reactions.

FT product	Reactions	H <sub>2</sub> to CO usage ratio
CH <sub>4</sub>	$CO + 3H_2 \rightarrow CH_4 + H_2O$	3
C <sub>2</sub> H <sub>6</sub>	$2CO + 5H_2 \rightarrow C_2H_6 + 2H_2O$	2.5
Alkanes	$nCO + (2n + 1)H_2 \rightarrow C_nH_{(2n+2)} + nH_2O$	(2n+1)/n
Alkenes	$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$	2
Alcohols	$nCO + 2nH_2 \rightarrow C_nH_{(2n+1)} + (n - 1)H_2O$	2

In the following table is shown how it is controlled the selectivity in FT by process conditions and catalyst modifications: [10]

Table 2. Dependence of the selectivity.

Parameter	Chain length	Chain branching	Olefin selectivity	Alcohol selectivity	Carbon deposition	Methane selectivity
Temperature	↓	↑	*	↓	↑	↑
Pressure	↑	↓	*	↑	*	↓
H <sub>2</sub> /CO	↓	↑	↓	↓	↓	↑
Conversion	*	*	↓	↓	↑	↑
Space velocity	*	*	↑	↑	*	↓
Alkali content iron catalyst	↑	↓	↑	↑	↑	↓

Note: Increase with increasing parameter: ↑. Decrease with increasing parameter: ↓.

Complexrelation: \*.

This project is focused in the olefin, alkenes, production. Multiple factors affect olefin selectivity. It should be taken into account that it is very difficult to obtain high olefin selectivity with high conversion, because of that it is interesting to work with the optimal conditions.

The formation of olefins is favored at low pressure, high space velocity, high temperature, and high CO/H<sub>2</sub> ratio of the synthesis gas.[11]

## 2.3 Nanoparticles:

Nanoparticles have some relevant characteristics that give important properties to the catalyst. The small size increases the surface area, leading more places to form bonds with the catalyst. The properties of nanoparticles can change according the shape or the composition of them. Nanoparticles can be formed from more than one material; in this case core/shell nanoparticles play an important role.

### 2.3.1 Core/shell nanoparticles:

This project will focus in core/shell nanoparticles. The core/shell consists in a combination of different materials coating one of them with the others. Depending on the materials and the different amounts is possible to synthesize various types of catalysts and obtain the desired products.

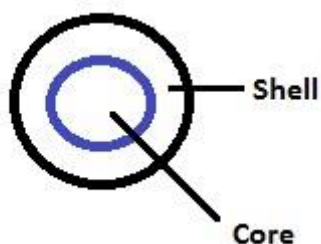


Figure 5. Structure of a core/shell.

There are different classes of core/shell nanoparticles and spherical are the most common. The properties change with the ratio of the core/shell because the properties of the core are modified with the shell coating it.

In addition, on the economic point of view core/shell nanoparticles has an important role as it is possible to reduce the consumption of expensive materials with relevant properties.[12]

It has been found that selectivity of FT synthesis toward high yields of olefins can be achieved by modifying these catalysts.

The goal is to get high selectivity to olefins, so that the olefin-to-paraffin ratio should be high, C5+ production should be high and methane production should be low.

### 2.3.2 Base

Several metals can catalyze the FT reaction and the most important are: ruthenium, nickel, cobalt, and iron.[9]

Nickel was used firstly in this technology but at low pressures were produced too much methane, later on, when the operating pressures were higher because of lower methane production, it has been found out that volatile nickels carbonyls were formed and the nickel was leaking from the reactor. This metal was then abandoned.

Regarding the Ruthenium, it is a very active catalyst, comparing with iron or cobalt, but it is very expensive and the amount available is insufficient for the industry. Therefore, this metal is not viable.

Nowadays, the catalysts for the Fischer-Tropsch synthesis are mostly based on cobalt (Co) and iron (Fe) because they have satisfactory results for commercial purposes.[8]

Iron is very common because its low cost comparing other active metals. Alkali-promoted iron catalysts have been used for many years due to their high water-gas shift activity and high selectivity to olefins.

On the other hand, cobalt catalysts produce predominantly linear alkanes. These catalysts are viable for the production of middle distillates and high molecular weight products.

Comparing Co with Fe, despite the fact that Co is more expensive, “Co-based has higher stability, higher productivity, negligible effects of co-produced water and higher resistance to attrition in slurry bubble column reactors.”[13]

In this project every catalyst has been formed from Co-based catalysts because it represents the optimal choice for synthesis of middle distillate fuels, but the core/shell nanoparticles allow minimizing the cobalt content because of the high cost.

### 2.3.3 Promoter:

Introducing promoters to Co-based catalyst it is possible to control properties of the catalysts, number of cobalt metal sites, characteristics and localization.

Ru, Pt, Re, Zr, Ce and B are promoters that for cobalt catalysts can obtain higher activity, higher C<sub>5+</sub> selectivity, and lower selectivity to methane.[14]

In addition, the promotion with oxides makes the activity and hydrocarbon selectivity favorably. This modification of the catalysts introducing metal oxides as promoters can alter reaction rates, product distribution and catalyst stability.

Different metals to form oxides have been evaluated with various distributions.

-Promotion with Manganese oxide:

Manganese oxide (MnO) as promoter has been used with Co to form the catalyst because it increases the selectivity toward light olefins, increases the selectivity to C<sub>5+</sub> products, increases CO conversion, and decreases the formation of CH<sub>4</sub>. [15]

MnO has ability to improve the selectivity toward to olefins because it can avoid the hydrogenation of C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> that it is favorable for that.[16]

Some experiments have been done changing the core/shell, coating the MnO with Co.

-Promotion with Lanthanum oxide:

Lanthanum oxide (La<sub>2</sub>O<sub>3</sub>) can decrease the methane formation and increase the catalytic activity. Also, it is possible to adsorb more CO with a La-cobalt catalyst than in a monometallic cobalt catalyst.[17]

### 2.3.4 Support

As it mentioned above, it is important in catalysis a large surface area; therefore small particles are useful for this reason. The problem is that small metal particles are often unstable and it is necessary to deposit the particles inside the pores of a support. [1]

The function of the catalyst support is to disperse cobalt producing stable cobalt metal particles in the catalysts after reduction.

The preparation of the catalyst support follows some steps.[8]

Firstly, it is important to choose an appropriate catalyst support. The support used in all the catalysts has been siliceous mesocellular foam (MCF-26). The interaction between cobalt and silica-supported catalysts is weak, leading to better cobalt reducibility. Also, MCF has an excellent size exclusion properties and separation capability.[18]

Secondly, impregnation is the choice of method of deposition of the active sites. This method consists in deposit a solution containing cobalt on the pores of a dry support.

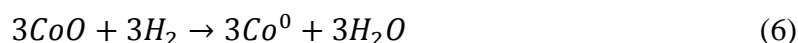
In this projects have been used two methods of deposition depending on the precursor.

On the one hand, incipient wetness impregnation is the most common method to support using cobalt salts. It consists in slowly contact in drops a solution containing the catalyst with cobalt into the dry support being aspired by the capillary forces in the pores. This method is used when the precursor of the catalyst is cobalt acetate tetrahydrate ( $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$ ).

On the other hand, impregnation is a very simple method using cobalt carbonyl solution, withholding transition metals carbonyl on porous oxides. So for the rest of the experiments a method like impregnation used has been used when the precursor was cobalt carbonyl.

### 2.3.5 Catalyst pretreatment:

Some catalysts, synthesized in metal oxide form, become more active when they are pretreated. The reduction is a pretreatment that consists in increasing the temperature around 350°C to generate high metallic surface areas. The reduction occurs when  $\text{Co}_3\text{O}_4$  is reduced to cobalt metal in two steps:



## 2.4 Characterization techniques:

The characterization is an important part of the catalysis process. There are different methods to investigate the nature of an active catalyst and they help to improve catalysts or design new ones. It is used to investigate with spectroscopic, microscopic and diffraction techniques. [1]

The same techniques used for particles are implemented in order to characterize core/shell nanoparticles but it is necessary to use more than one.

The most common techniques are: dynamic light scattering (DLS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermal gravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), photoluminescence (PL), and UV-vis spectroscopy.

The techniques used to characterize the nanoparticles in this project will be explained in the next chapter.



### 3. Materials and Methods

This chapter explains the procedure to synthesis the catalysts, including the synthesis of the cores and shells for them. Also, it explains how to synthesis the silica-support and the type of impregnation used in each catalyst. The associated calculations are included in the appendices.

All the experiments have been performed in a designated setup at NTNU, Gløshaugen.

#### 3.1. Catalyst synthesis

##### 3.1.1. Synthesis Co nanoparticles

Co nanoparticles have been synthesized as core for the catalyst. In total it has been synthesized Co nanoparticles in two experiments following the same procedure.

The formation of Co nanoparticles follows the next reaction:



Where the solvent is O-DCB and the surfactants are Oleic acid (OA) and Trioctylamine (TOA).

In the following table are shown the amounts of the compounds used for both syntheses:

Table3. Amountsofcompounds.

	$Co_2 (CO)_8$ (g)	O-DCB (mL)	OA (mL)	TOA (mL)
First Synthesis	1,08	30	0,4	0,2
Second synthesis	3,24	90	1,2	0,6

##### -First Synthesis:

A total of 1.08g of  $Co_2 (CO)_8$  was mixed with 20mL of O-DCB, 0.4mL OA and 0.2mL TOA in a three neck flask. Then, 10 mL more of O-DCB were added.

The mixed was heated at 150°C for 1 hour stirred with a magnet in nitrogen atmosphere.

Later, it was precipitated with ethanol using a magnet.

Finally, it was dissolved in 30mL of OD, giving a concentration of 0.0124gCo/mL.

It was taken four samples of the solution of 2.5 mL of Co nanoparticles each and left in the fridge (two samples dissolved in 2.5 mL of OD and the other two in hexane).

These Co nanoparticles were used for CAT\_J01, CAT\_J02, CAT\_J06 and CAT\_J07.

### - Second Synthesis:

In the second synthesis was required a higher amount of Co nanoparticles. The procedure was exactly the same as the first one. The amounts were three times the first synthesis.

It was used 3.24 g of  $Co_2(CO)_8$  mixed with 30 mL of O-DCB, 1,2mL OA and 0,6mL TOA in a 3 neck flask. Then, 60 mL more of O-DCB were added.

The mixed was heated at 150°C for 1 hour stirred with a magnet in nitrogen atmosphere.

It was taken from the mixed 11.05 mL for CAT\_J08, explained in the next chapter *Catalysts preparation*.

The rest of the solution was precipitated using a magnet and dissolved in 100mL of 1-Octadecene, giving a concentration of 0.0097gCo/mL. The solution was kept in the fridge.

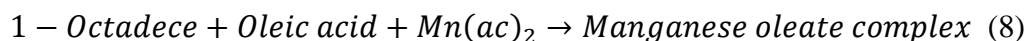
These Co nanoparticles will be used for the catalyts since CAT\_J08 CAT\_J10.

### 3.1.2. Synthesis MCF-26:

Firstly, 4 g of triblock copolymer Pluronic were dissolved in 65 mL of  $H_2O$ , then 10mL of HCl were added and the solution is heated to 40°C with stirring at high velocity for 2h. Afterwards, 9.2mL of tetraethoxysilane (TEOS) was added into the solution and stirred for 5 min. Then the solution was transferred to an autoclave and heated at 40 °C for 20 h. Later on, 46 mg of  $NH_4F$  was added and the mixture in the autoclave is heated at 100 °C for 24 h. Next, when the solution is cooler, it was filtered, washed with water and ethanol, and dried. Finally, the resulting is calcined in air at 900°C for 6h. [18]

### 3.1.3. Synthesis of Manganese oleate complex:

Following the next reaction is possible to obtain the Manganese oleate complex necessary to coat the catalyst of Co nanoparticles and formed a core/shell.



Manganese oleate decomposes in the reaction with the heating in manganese oxide (MnO).

Manganese oleate complex was synthesized mixing the amount of 0.1512 g of Mn acetate required with 5 mL of 1-Octadecene and 0.55mL of OA. The mixed was heated at 180°C for 1.5h.

Manganese oleate was used for CAT\_J01, CAT\_J02, CAT\_J06 and CAT\_J07.

### 3.1.4. Synthesis MnO:

A solution of MnO nanoparticles was synthesized for the later used as core or shell in the catalysts.

The procedure and amounts of the compounds used were found in a publication about nanocrystals of manganese oxide.[19]

It was mixed 0.34605g of Mn acetate with 7.5 mL of 1-Octadecene and 1.676 mL of OA. The mixed was heated at 317°C for 1h. Later on it was separated using the centrifuge and dissolved in hexane.

The concentration obtained was 0.0156gMnO/mL.

This solution was used for some of the catalysts: CAT\_J03, CAT\_J04, and CAT\_J05.

### 3.1.5. Catalysts preparation:

It has been synthesized ten catalysts. The catalysts have been synthesized from Co nanoparticles, Mn oleate or Mn oxide nanoparticles, and the MCF-26 support mentioned above. Using different amounts of them were formed these catalysts.

#### 1) CAT\_J01: Core/ shell Co/MnO.

This catalyst will be coat with multiple layouts of MnO.

To form the core/shell it is necessary to coat Co nanoparticles with MnO.

An amount of 0.062 g of Mn oleate was mixed 2.5 mL of the solution of Co nanoparticles with 2,5mL OD and heated at 317°C for 1 hour. Next, 5mL of Co/MnO were precipitated with hexane, butanol and ethanol. Finally, the particles were dissolved in hexane and 113.7 mg of MCF-26 was added as support by impregnation.

#### 2) CAT\_J02: Core/shell Co/MnO

This catalyst is a core/shell of Co/MnO coating 50% of the Co surface.

A total of 0.01741 g of Mn oleate were mixed with 5 mL of OD, as solvent, and 2,5 mL of Co nanoparticles. The mixed was heated at 210°C at 10°C/min and then until 330°C at 1°C/min. Then it was precipitated with hexane, butanol and acetone using the centrifuge. Afterwards, it was supported in 193.2 mg of MCF-26 by impregnation.

### 3) CAT J03: Core/shell MnO/ CoO

This catalyst is a core/shell of MnO/CoO.

The formation of CoO was done using references from a publication.[20]

The amount of 0.1318 g of Co acetate tetrahydrate was mixed with 0.4mL of OA and 15 mL of 1-Octadecene, the mixed was heated at 180 °C for 1 hour. Later on, 2 mL of the solution of MnO, which concentration was 0.0156 g/mL, was added and heated at 320°C for 30 minutes.

Next, it was cleaned using the centrifuge and mixed with hexane putting into the ultrasound the whole night with 181.1 mg of support MCF-26. Then it was filtered and dried.

### 4) CAT J04: Core/shell MnO/CoO: layout of CoO

It is a core/shell catalyst of MnO coating with a layout of CoO.

For the calculations it is suppose that the molecules are cubic. Following the same steps than CAT\_J03, an amount of 0.218 g of Co acetate tetrahydrate is mixed with 0.6 mL of OA and 15mL of 1-Octadecene. It was heated at 180°C for 1 hour and then 2 mL of the solution of MnO nanoparticles were added and heated at 320°C for 30 minutes.

Later on, the nanoparticles were cleaned with hexane and propanol using the centrifuge. It was really to clean it properly. Finally the nanoparticles were mixed with toluene as solvent.

To put into the support it was used the incipient wetness method; where the solution with 2.87 mL of the catalyst was added directly into 379.1 mg of MCF-26 support.

### 5) CAT J05: Core/shell MnO/CoO:

We tried two experiments for this catalyst.

A total of 0.068466 g of Co acetate (Co(acac)<sub>2</sub>) is mixed with two surfactants: 0,042014 mL of OA and 0,1314mL of Oleylamine (OAm).

It was done twice, in one of the flasks it was added 0.10313 g of 1,2hexadecanediol.

Then, it was mixed with 1 mL of MnO.

After that it was added 5 mL of phenyleter as solvent. The mixed was heated at 220°C at 5°C/min. A shape of TEM was taken from each experiment.

Later on, the temperature was increased until 260°C.

The mixed without hexadecanediol was chosen because it was easier to clean with ethanol.

It was supported with the incipient wetness method in 258.9 mg of MCF-26 support.

#### 6) CAT J06: Core/shell CoO/ MnO: 100%

A total of 34.8 mg of Mn oleate were mixed with 7,5mL of 1-Octadecene and 2,5 mL of the solution with Co nanoparticles (first synthesis) and hexane.

The mixed was heated at 210°C with a rate of 10°C/ min being the setup open on the top to allow the hexane go out. Later on it was heated at 330°C at 1°C/ min and it was at 330°C for 1h.

After the reaction, the solution was precipitate with hexane, butanol and acetone. The precipitated was dissolved in hexane by the ultrasound.

The catalyst was supported in 227.3 mg (12% loading), after one night precipitating in the ultrasound was filtered and dried.

#### 7) CAT J07: Core/shell CoO/ MnO:200%

A total amount of 69.6 mg of Mn oleate was mixed with 7,5mL of 1-Octadecene and 2.5 mL of the solution with Co nanoparticles (first synthesis) and hexane.

The mixed was heated at 210°C with a rate of 10°C/ min being the setup open on the top to allow the hexane go out. Later on it was heated at 330°C at 1°C/ min and it was at 330°C for 1h.

After the reaction, the solution was precipitate with hexane, butanol and acetone. The precipitated was dissolved in hexane by the ultrasound.

The catalyst was supported in 227.3 mg after one night precipitating in the ultrasound was filtered and dried.

#### 8) CAT J08: Core/shell CoO/ MnO: 0%

This catalyst is synthesized with Co nanoparticles of 8.06 nm (second synthesis) and it is coated 0%, pure cobalt.

It was formed with 11.05 mL of Co nanoparticles mixed with 30 mL of ethanol, it precipitated with the magnet. Later on, it was added hexane and put into the ultrasound. Next 1000 mg of the support MCF-26 were added and after one night in the ultrasound, it was filtered.

The catalyst sample was mixed with 500mg SiC, as inert, before testing by FT to ensure isothermal conditions.

#### CAT J09: Core/shell CoO/ MnO: 25%

This catalyst is a 25% coated with MnO. It was formed from Co nanoparticles of 8.06 nm. A total of 0.00661 g of Mn acetate was mixed with 0,025 mL of OA and 6mL of 1-Octadecene. The mixed was heated at 180 °C for 1 hour in a nitrogen atmosphere, then 14 mL of the solution of Co nanoparticles were added into the flask and heated until 210°C at 10°C/ min and the until 320°C at 1°C/min. It was keep at 320°C for 1h, afterwards when the solution is still hot at 100 °C the solution was cleaned with hexane, butanol and acetone in the centrifuge.

Finally, 1000 mg of support MCF-26 were added and keep in the ultrasound for one night, later on it was filtered.

The catalyst sample was mixed with 500mgSiC to test by FT.

#### 9) CAT J10: Core/shell CoO/ MnO: 75%

This catalyst is a 75% coated with MnO. It was formed from Co nanoparticles of 8.06 nm. A total of 0.0198 g of Mn acetate was mixed with 0,072 mL of OA and 6mL of 1-Octadecene. The mixed was heated at 180 °C for 1 hour in a nitrogen atmosphere, then 14 mL of the solution of Co nanoparticles were added into the flask and heated until 210°C at 10°C/ min and the until 320°C at 1°C/min. It was keep at 320°C for 1h, afterwards when the solution is still hot at 100 °C the solution was cleaned with hexane, butanol and acetone in the centrifuge.

Finally, 1000 mg of support MCF-26 were added and keep in the ultrasound for one night, later on it was filtered.

The catalyst sample was mixed with 500mg SiC.

### 3.1.6. Synthesis of lanthanum oxide:La<sub>2</sub>O<sub>3</sub>

This component can increase the activity 100 times.

For the formation of the oxide has been evaluated various precursors:

The first case was tried with oleic acid, following this reaction:



Later on, the La oleate formed produces La oxide. The procedure is the following:

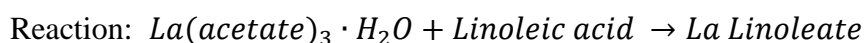
A total of 0.6 g of  $La(acetate)_3$  was mixed with 1.7mL of OA. The mixed was heated at 180°C and frozen the whole night.500mg of La oleate reacted with 10mL of 1-Octadecene at 360°C. There was a problem with the heating because the Teflon of the stir melts.

This high temperature required a magnet cover with glass.

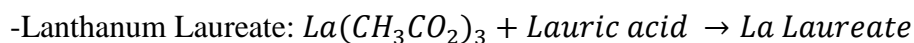
Later on, other 0.500 g of La oleate formed was added with 0.4 mL of OA and 10mL of 1-octadecene and it was heated until 360°C. It was really difficult separate the product.

Other precursor: It was necessary to try to synthesis other precursor that requires a lower reaction temperature.

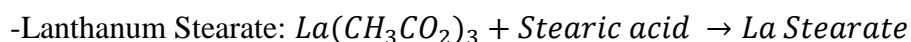
-Lanthanum linoleate: Linoleic acid has 2 doubles bonds, instead of the oleic acid that only has one, with more number of doubles bonds the component is less stable and it can discompose at low temperature.



0.300 g of La acetate were mixed with 0.8395 mL of linoleic acid and heated until 180°C.



0.500 g of La acetate hydrate were mixed with 0.9507 g of Lauric acid.



0.500 g of La acetate hydrate were mixed with 1.3484 g of Stearic acid.

## 3.2. Catalyst characterization

In this chapter the techniques used to characterize the nanoparticles will be explained.

### 3.2.1 Transmission electron microscopy:

Transmission electron microscopy (TEM) is a tool useful to visualize nanoparticles. Using TEM is possible to obtain details that with light microscopy are inaccessible because it uses a focused beam of high energy electrons instead of light from a torch. The images have a range of grey scale depending on the way the electrons interact.[21]

On TEM image there is a scale bar, TEM provides important information about nanoparticles like confirmation of core/shell formation through contrast difference, overall particle size, core size, shell thickness, uniform or nonuniform shell coating, lattice fringes of the shell material. [12]

### 3.2.2 X-ray diffraction:

X-ray diffraction (XRD) is a method that provides information about the crystal and molecular structure of crystalline. The results of the diffractometer are compared with data collected in the computer to know which compounds with the structure can be forming the material. [22]

“X-ray diffraction occurs in the elastic scattering of X-ray photons by atoms in a periodic lattice. The diffraction of X-rays by crystal planes allows one to derive lattice spacings by using the Bragg relation:

$$n\lambda = 2d\sin\theta ; n = 1,2 \dots$$

Where  $\lambda$  is the wavelength of the X-rays,  $d$  is the distance between two lattice planes,  $\theta$  is the angle between the incoming X-rays and the normal to the reflecting lattice plane,  $n$  is an integer called the order of the reflection.

Measuring the angles,  $2\theta$ , the Bragg equation gives the corresponding lattice spacing characteristic for a particular compound.”[1]



This figure shows how XRD works:

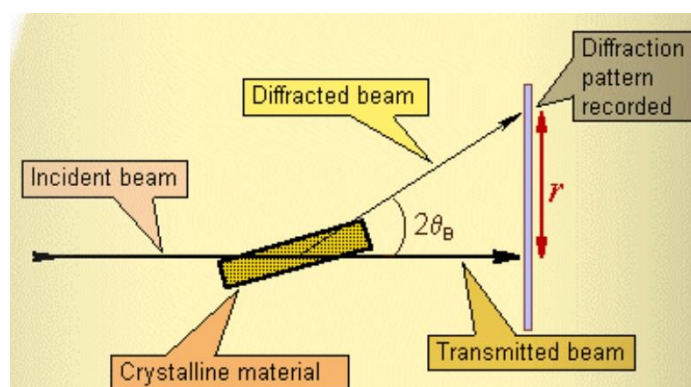


Figure 6. XRD technique.

The results of this technique provide information about how it is the composition of the catalysts and allow knowing if the core/shell wanted has been formed satisfactorily.

### 3.2.3 Thermal gravimetric analysis:

Thermal gravimetric analysis (TGA) is used to characterize the thermal stability of compounds. It works measuring the weight increasing the temperature. The result of this method is the weight loss of the material depending on the temperature.[12]

This technique is useful in this project because it is possible to know if the catalyst contains not stable compounds at high temperature and to know which conditions are better for the reaction. It also allows knowing if it is necessary calcine to remove some compounds before work with it.

### 3.3 Catalyst testing:

The activity testing in FT setup used in all the experiments has been a “Microactivity-Reference” reactor, model MAPGLM3.

“The MICROACTIVITY-Reference is an automatic and computerized laboratory reactor for reactions of catalytic microactivity with reactor bypass, preheater evaporator, pressure control valve and other process layouts in hot box, which avoids the possible condensation of volatile products, at the time that preheats the reactants efficiently.”.[23]

General view:

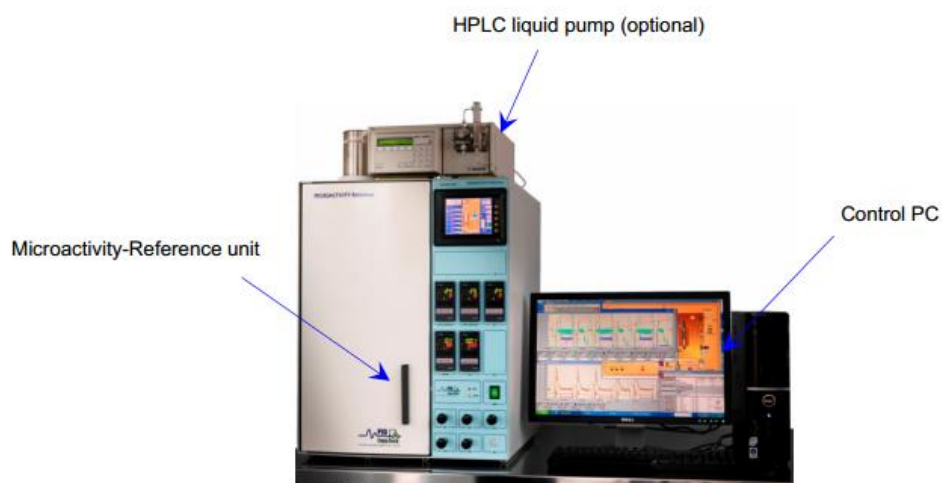


Figure 7. General view of the installation of the activity testing.

Regarding the process parameters, the experiments have been done in this reactor with the same optimal conditions: a temperature of 210 °C; pressure of 1.8bar; and flows of 20, 28, 2 mL/min for H<sub>2</sub>, Ar and CO, respectively. This is the old mass flow controllers with a too big flow range.

For the last three catalysts and number 5, a syngas flow (CO and H<sub>2</sub>) was used for the activity test by FT.

Usually the H<sub>2</sub>/CO ratio has been 2:1, but in some occasions to compare more properly it was of 10:1.

Also, it has been evaluated different values of GHSV (space velocity).

It has been used the same conditions for all the catalyst evaluated, so the product distribution is easily to compare between them.

The reactor is connected to a GC (Gas Chromatograph) machine to analyze samples of the products at different times. The data obtained with the GC is the product distribution of the hydrocarbons that are later evaluated to obtain the dependence of the conversion with the space velocity; and selectivity with the time of residence.

In some cases it has been evaluated the conversion and selectivity with the temperature.

## 4. Results and discussion:

In this chapter, the results and interpretations of the experiments are given.

### 4.1 Co nanoparticles:

The Co nanoparticles were characterized by TEM, providing an image that permits size the particles to compare them when the core/shell is formed.

Results TEM Co nanoparticles:

First synthesis: 4,984 nm

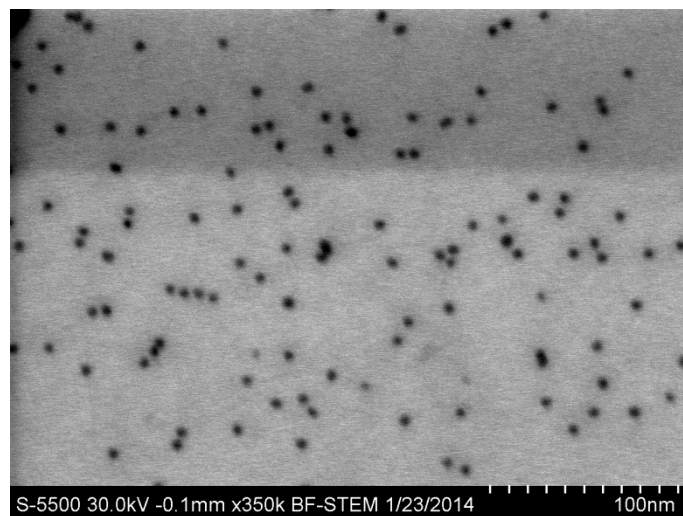


Figure 8. TEM characterization for the first synthesis of Co nanoparticles.

Second synthesis: 8.06 nm.

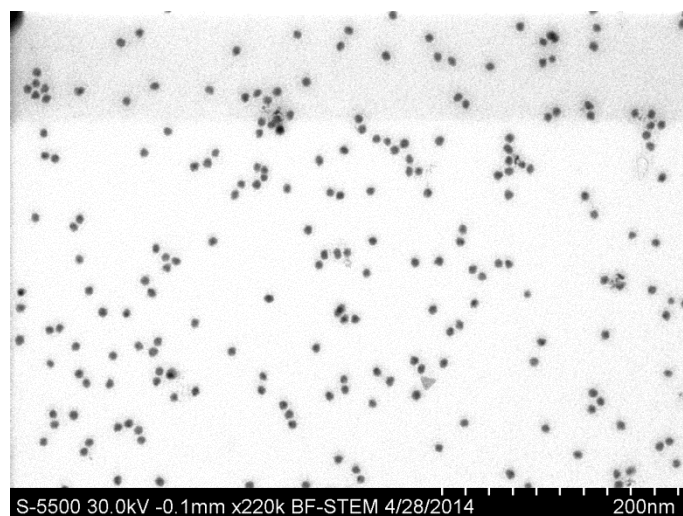


Figure 9. TEM characterization for the second synthesis of Co nanoparticles.

The increment of the nanoparticles is due to the second catalyst was performed in the same setup that the first one using the same size of flask and heating system, but the amounts were three times the first one. So, the heating system doesn't work as the same way for all the nanoparticles.

## 4.2 Catalysts results

- CAT\_J01: Core/ shell Co/MnO: multi layer of MnO.

To know if the catalyst proposed was formed satisfactory were evaluated different properties about the catalyst.

One of the properties that the catalyst satisfied was the magnetism of the particles, it means that Co was present in the catalyst.

Also, the brown color of the catalyst indicates the presence of MnO.

It was submitted by TEM characterization to compare the sizes of the nanoparticles before, only Co nanoparticles, and after the synthesis of the core/shell. Then, it was characterized with XRD to prove which components were presented. Finally, the activity of the catalyst was tested by FT.

TEM:

Co/MnO size 6,337 nm

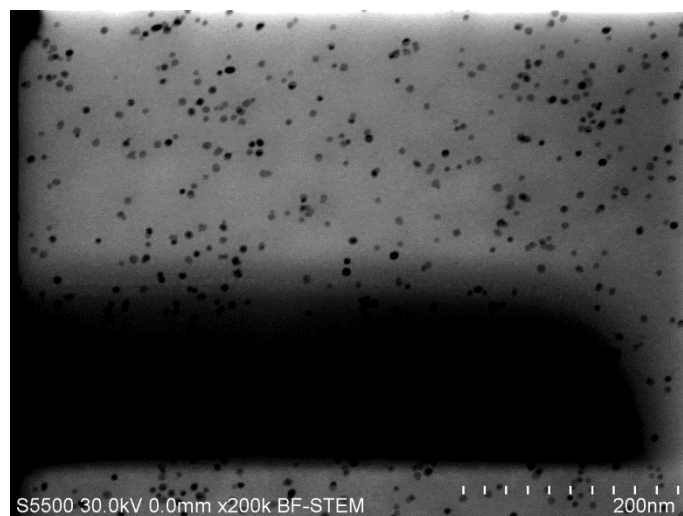


Figure 10. TEM characterization for CAT\_J01.

As it is shown, there is a high increment of the nanoparticles size when Co is coated with MnO. This increment is compared in the following plots where is represented the frequency of the nanoparticles sizes with the size of them.

Co nanoparticles: average 4,984 nm

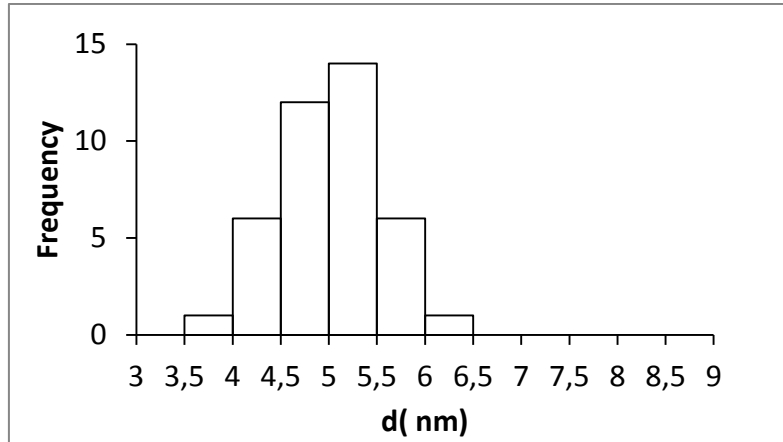


Figure 11. Frequency vs size of Co nanoparticles.

Co/MnO: average 6,337 nm

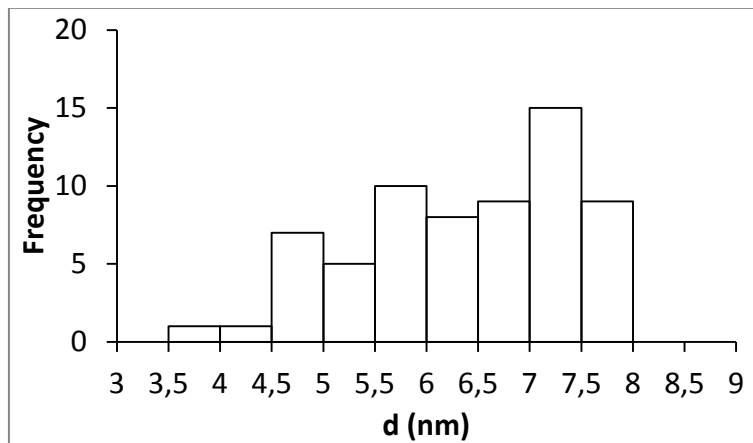


Figure 12. Frequency vs size of CAT\_J01.

Co nanoparticles have a high frequency of size around 4.5-5.5 nm, although the catalyst formed has a high frequency in a size around 7 nm. It means that most of the nanoparticles were formed because the increment of the size.

XRD:

CoO

JNS\_001 (Coupled TwoTheta/Theta)

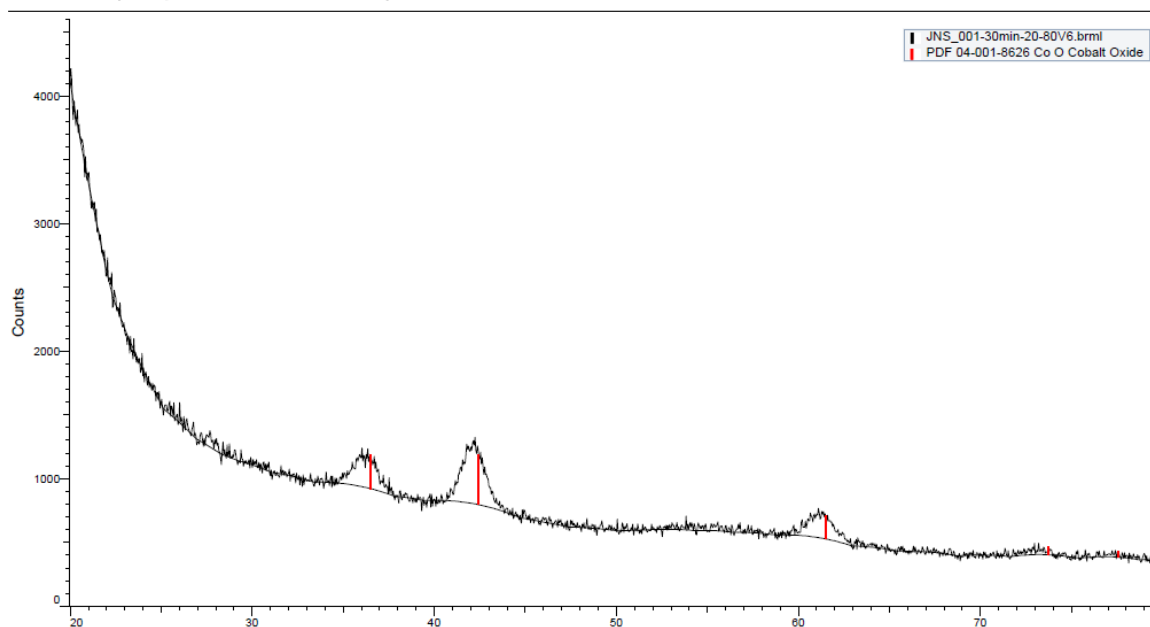


Figure 13. XRD result for CoO.

MnO

JNS\_001 (Coupled TwoTheta/Theta)

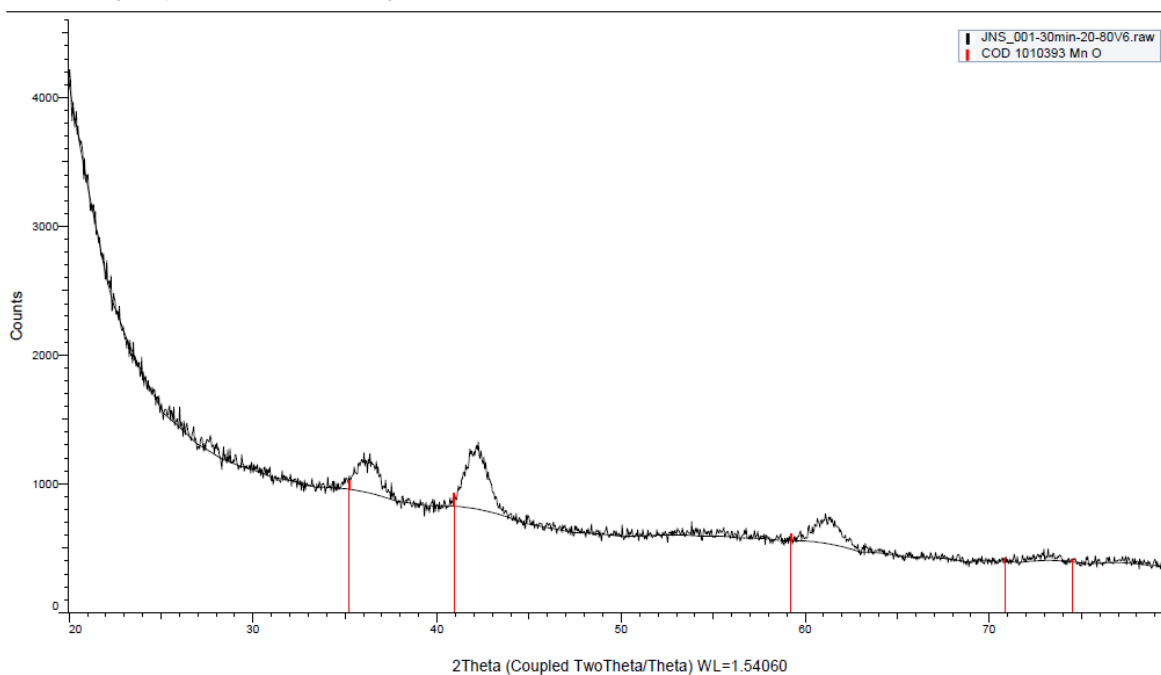


Figure 14. XRD result for MnO.

The red lines in the previously graphics mean where should be a pic if the component is presented in the sample in the XRD technique. The first graphic shows that CoO is presented in the catalyst, however MnO is not sure that is presented because the red lines are not in the middle of the pics.

FT reaction:

The catalyst was tested at 210°C before and after reduction; with a ratio H<sub>2</sub>/CO of 2:1 and 10:1; and GHSV of 0.3, 0.6 and 0.9 l/g cat/h.

Firstly, the catalyst was tested with a H<sub>2</sub>/CO ratio 2:1, 210°C, 1.85 bar.

The following figure is the conversion diagram for the catalyst before reduction:

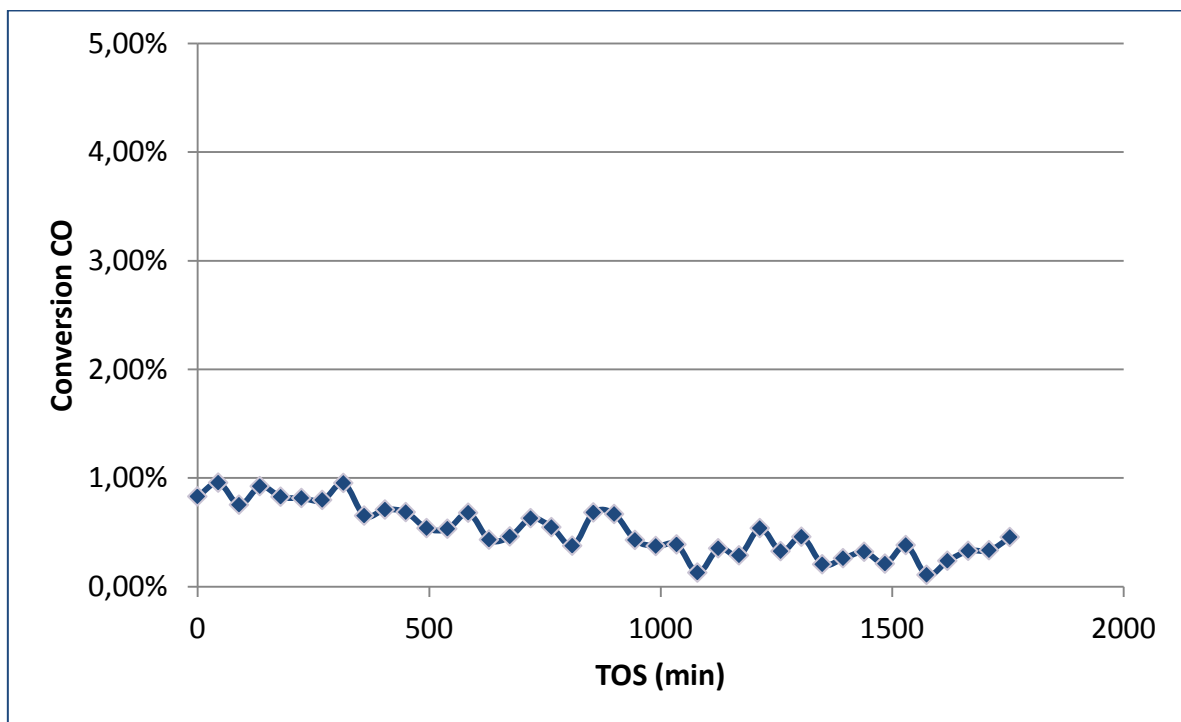


Figure 15. Conversion diagram for CAT\_J01 without reduction.

As shown the graphic above, the catalyst does not have activity at all. The conversion is between 1-0%. This result is favorable for the proposed catalyst because it may indicate that the whole Co is covered totally with MnO, a catalyst of Co coated with multi layer as it was proposed.

Secondly, this catalyst was tested again under FT conditions after reduction at 350°C showing the following results:

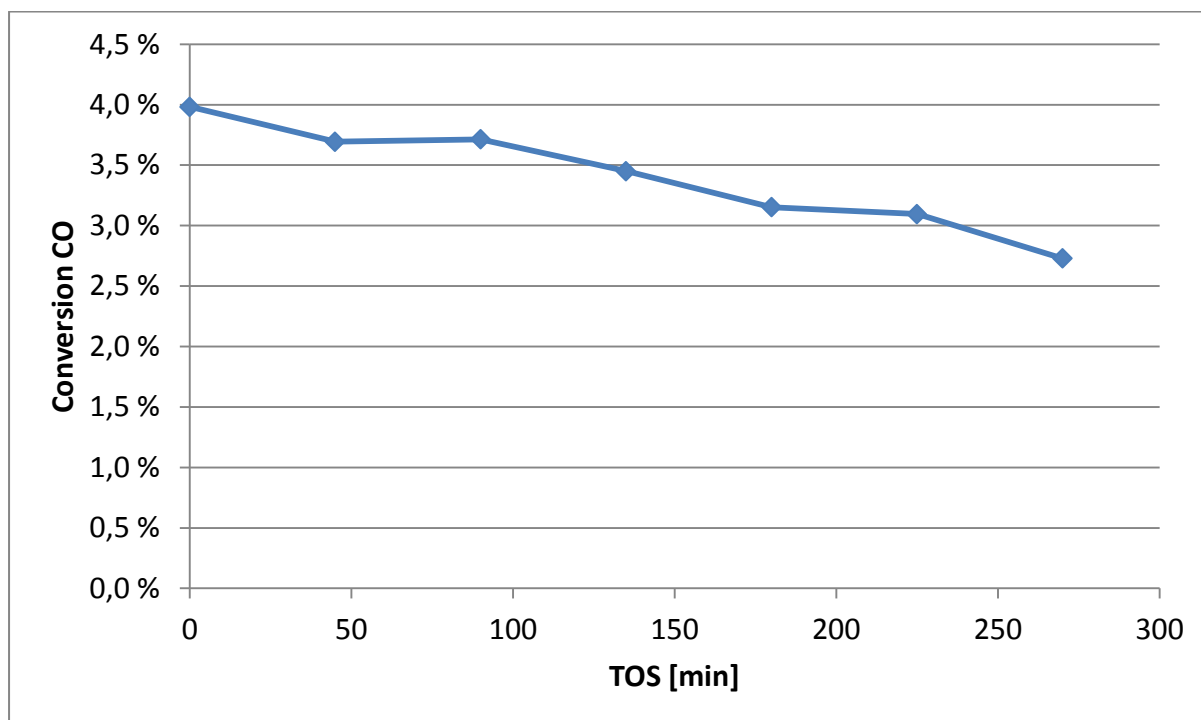


Figure 16. Conversion diagram for CAT\_J01 reduction.

As it is demonstrated, it got high activity after reduction. The results of conversion for GHSV of 0.15, 0.3, and 0.6 l/gcat/h are 10, 6, and 4, respectively. (Appendix 2.1)

The conversion decreases with the GHSV, as it will be shown in the comparing diagram at the end of this chapter.

Regarding olefin/paraffin ratio, this catalyst gives good results for ratio of C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub>.

Regarding the selectivity, it is lower for CH<sub>4</sub> so this catalyst is very favorable, and it is higher for C<sub>2</sub>, C<sub>4</sub>, C<sub>5+</sub>, C<sub>3=</sub> and C<sub>4-</sub>.

The results of most of the catalysts will be compared in at the end of this chapter for a ratio 2:1 and 10:1 to simplify the discussion of the results showing all the catalysts together.



- CAT J02: Core/shell Co/MnO: 50%

This catalyst is a core/shell of Co/MnO coating 50% of the Co surface.

This catalyst was tested by FT at the same conditions than CAT\_J01.

Conversion, O/P ratio and selectivities of this catalyst before and after reduction, with 2:1 ratio and 10:1; will be compared with all the catalysts at the end of the chapter.

Also, it was evaluated the catalyst with the variation of temperature when it is decreasing from 210°C until 180°C and when it was increasing from 210°C until 250°C.

The results are shown in the following graphics.

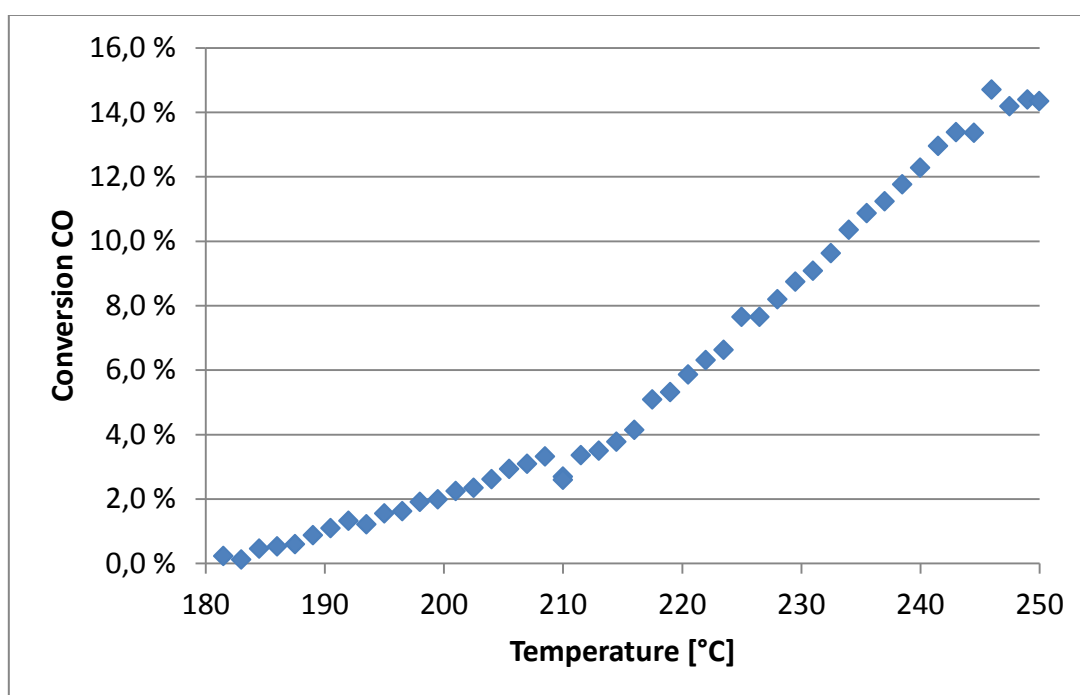


Figure 17. Conversion CO vs temperature CAT\_J02.

The conversion increases with the temperature, so it would be favorable to work at high temperature. But it is important to compare with other parameters to know the optimal conditions.

The following graphics shows the dependence of the selectivity to diverse products and O/P ratio with the temperature:

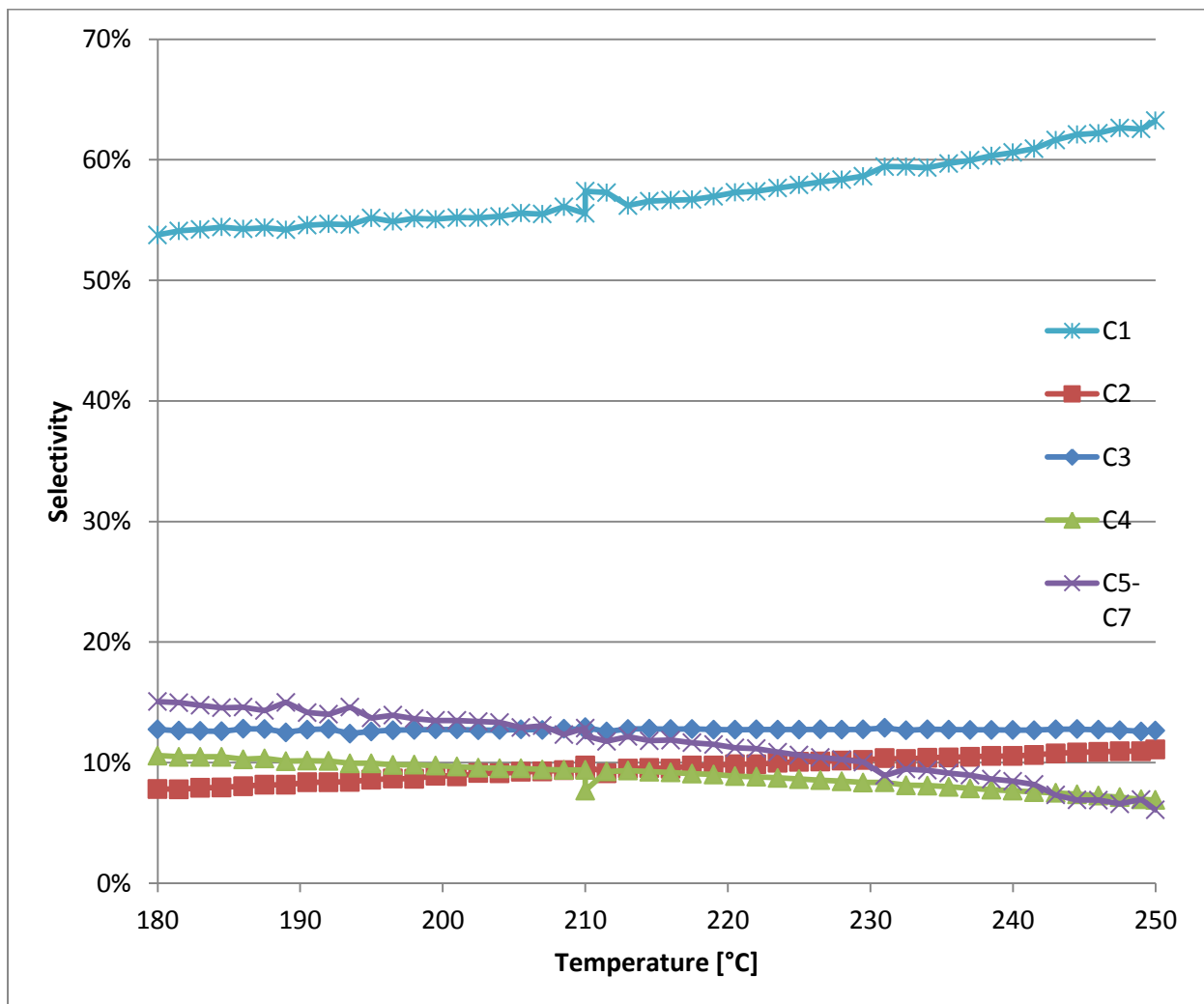


Figure 18. Selectivity vs temperature CAT\_J02.

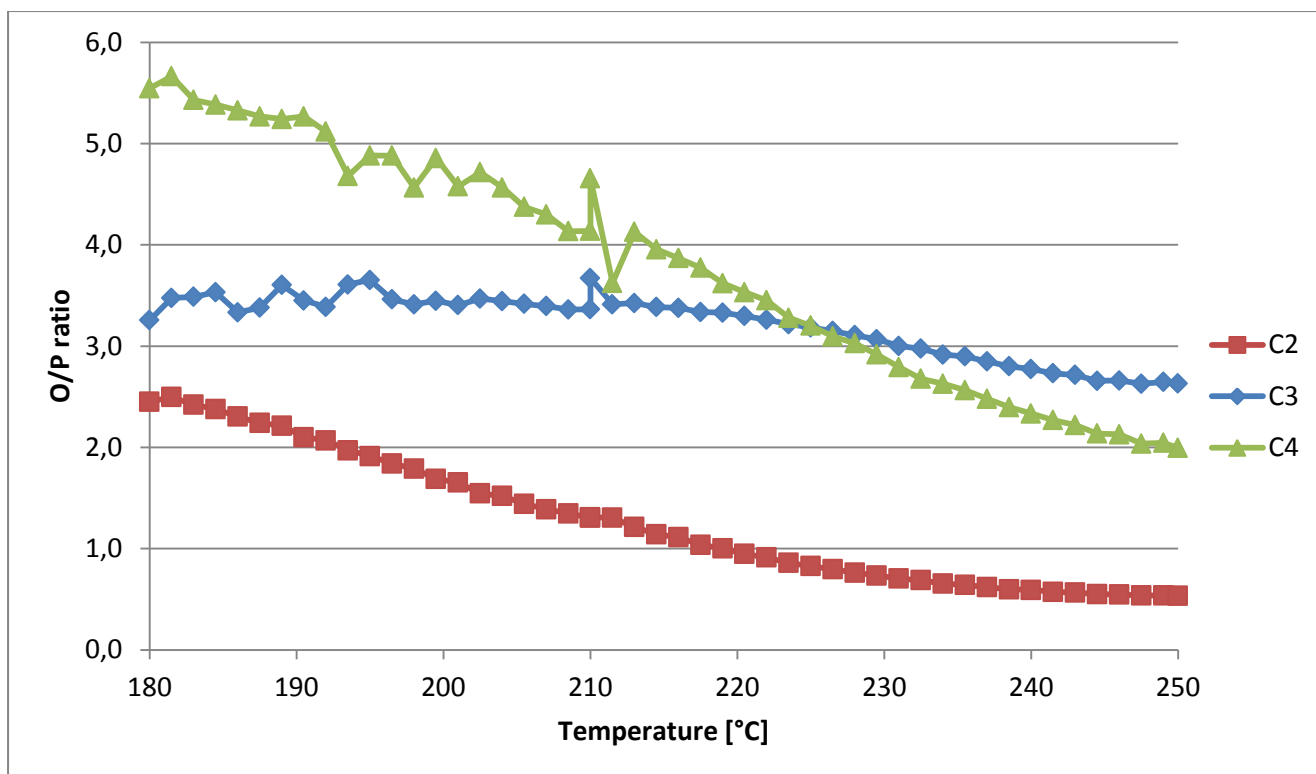


Figure 19. O/P ratio vs temperature CAT\_J02.

C<sub>3</sub> is the desire product. As shown, the selectivity and O/P ratio of C<sub>3</sub> are constants; it means that C<sub>3</sub> does not dependence with the temperature. For this reason it could be possible to work at every temperature. The problem is that the methane selectivity increases with the temperature, so at high temperature it would produce too much methane. And the problem at low temperatures is the low conversion CO. Therefore, the optimum temperature would be at medium temperature around 210°C.

- CAT J03: MnO/CoO

This catalyst is a core/shell of MnO/CoO.

TEM result:

MnO

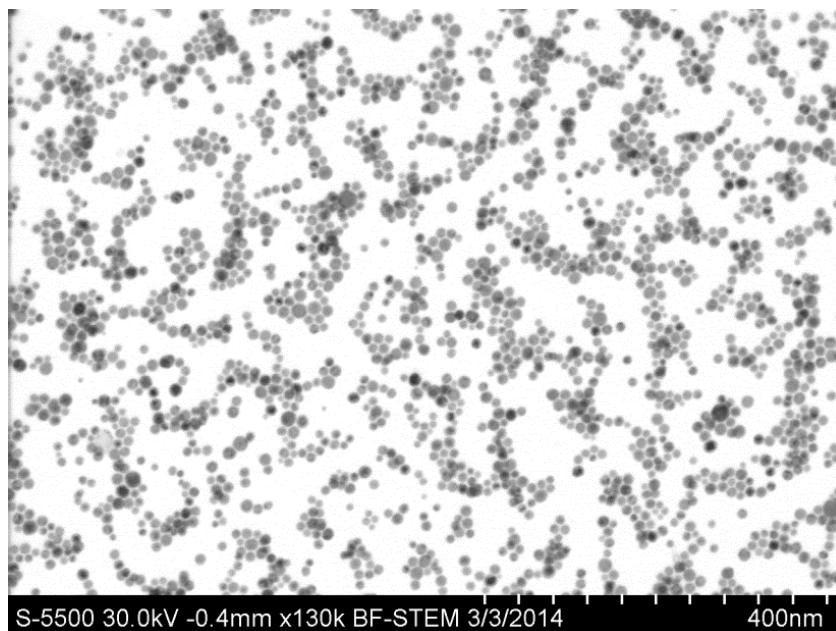


Figure 20. TEM image of MnO nanoparticles.

MnO/CoO

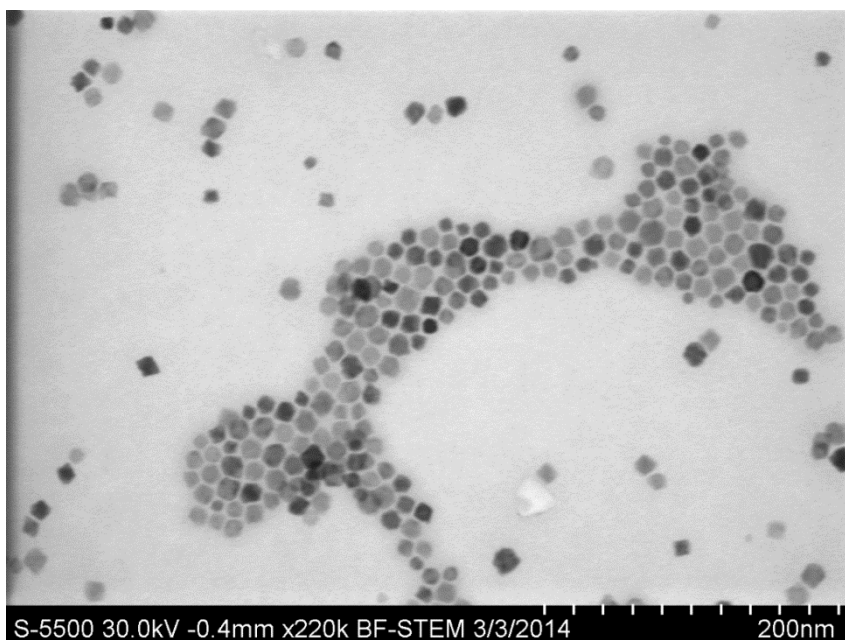


Figure 21. TEM image CAT\_J03, MnO/CoO.

It was an increment from 11.51 nm of the MnO nanoparticles until 14.51 nm when the core/shell was formed.

Regarding the activity test by FT, this catalyst did not have activity at normal conditions (210°C, 1.8 bar and flows of 20, 28, 2 mL/min for H<sub>2</sub>, Ar and CO, respectively); after reduction at 350°C the catalyst did not have activity either.

- CAT J04:

It is a core/shell catalyst of MnO coating with a layout of CoO.

This catalyst was characterized with TGA and FT for activity testing.

Results of TGA:

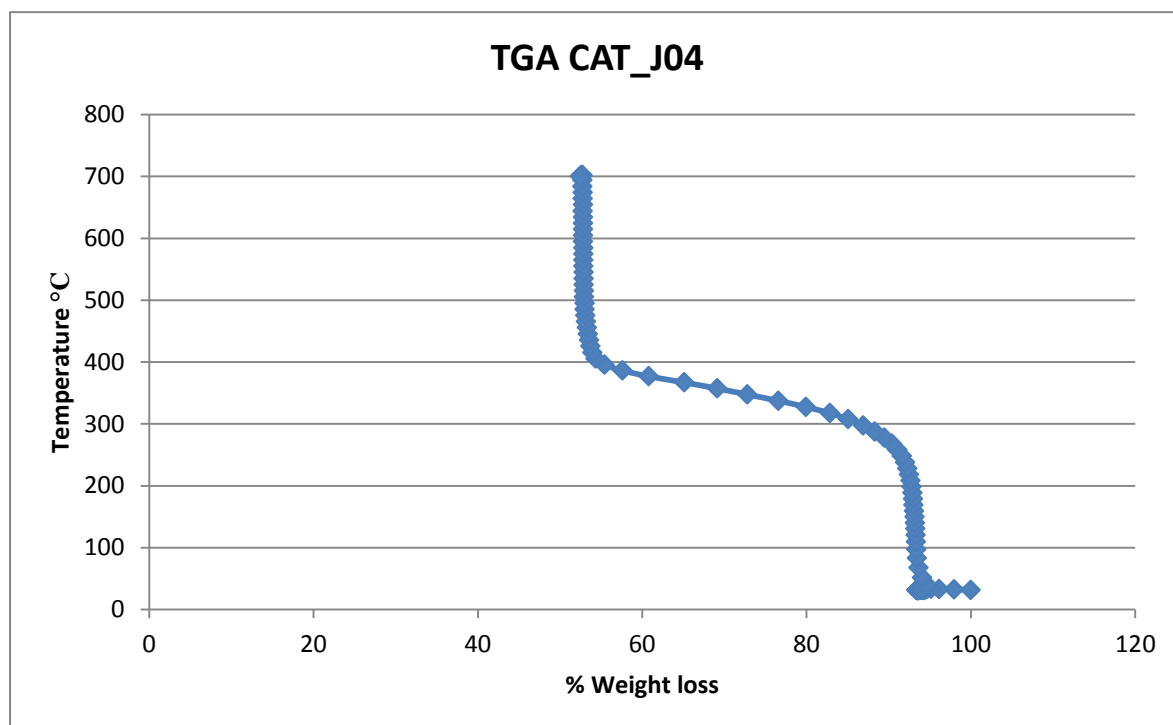


Figure 22. TGA result CAT\_J04.

As it is shown in the graphic, 50 % of the weight was lost at high temperature. It means that the catalyst was composed with a lot of organic compounds.

To obtain better results in FT the catalyst was calcined at 600°C.

The results of the activity testing by FT was unfavorable, the catalyst didn't have any activity.

- CAT J05:

Core/Shell: MnO/CoO

Results TEM. The MnO nanoparticles had a size of 11,51nm, after the synthesis of the catalyst the size was 13,74nm.

MnO nanoparticles

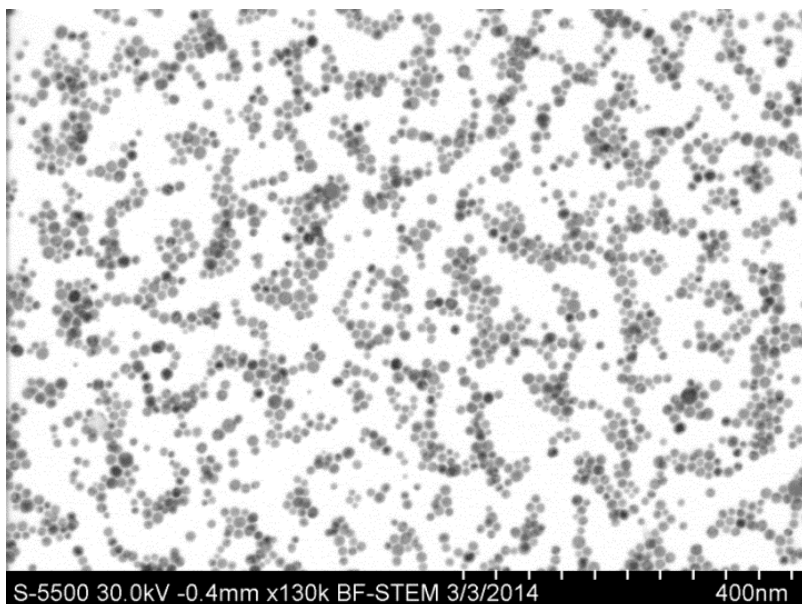


Figure 23. TEM of MnO nanoparticles.

MnO/CoO

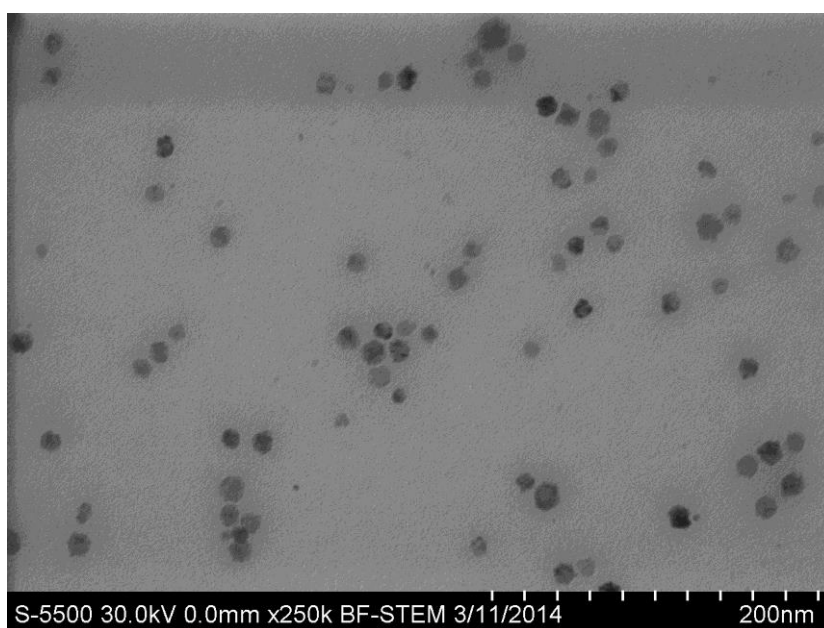


Figure 24. Figure 24 .TEM image of CAT\_J05.

The change in the size of the nanoparticles means that the core/shell has been formed.

The experiment of this catalyst formed with the presence of hexadecanediol gave worse results than without it, it was an increment of nanoparticles size of 12.19 nm, but it was difficult to get the TEM images because there was too much presence of the surfactants. This is why this catalyst was not chosen for the activity test. (Appendix 2.3)

This catalyst was reduced the whole night at 350°C, and then it was tested from 400°C to 500°C giving the following results.

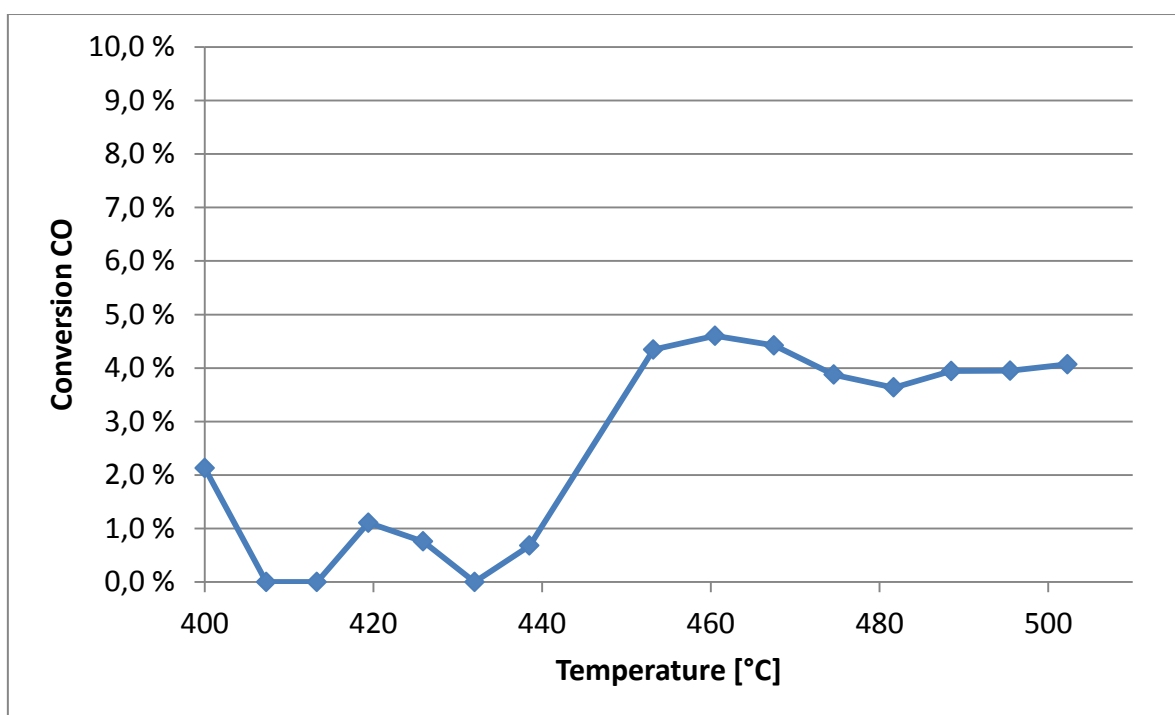


Figure 25. Conversion vs temperature CAT\_J05.

In the graphic above it is shown conversion CO vs temperature from 400-500°C. As it can be seen in the diagram, the fluctuation is big. This is because the experiment was performed with the old mass flow controllers with a too big flow range, so the values are differing a lot.

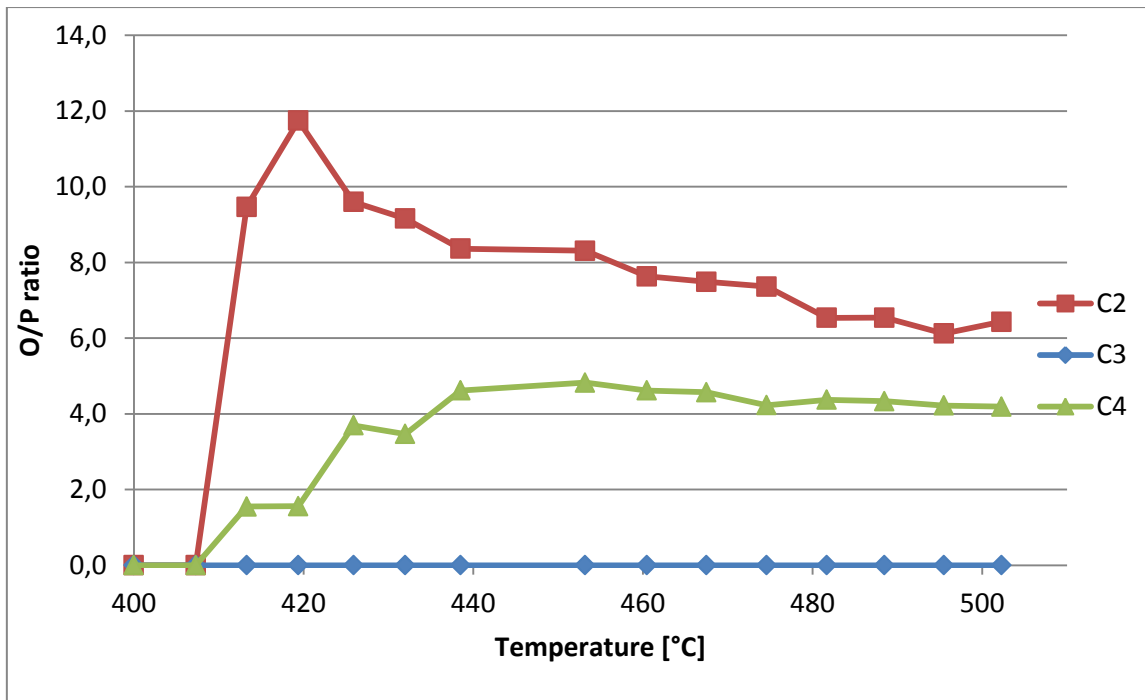


Figure 26. O/P ratio vs temperature CAT\_J05.

Regarding the O/P ratio, it is constant and equal to 0 for C<sub>3</sub>. For this desire product the temperature is not a parameter that could vary. In the cases of C<sub>2</sub> and C<sub>4</sub>, O/P ratio has a big fluctuation as conversion until 420°C. Later on, the O/P ratio decreases slightly with the temperature.

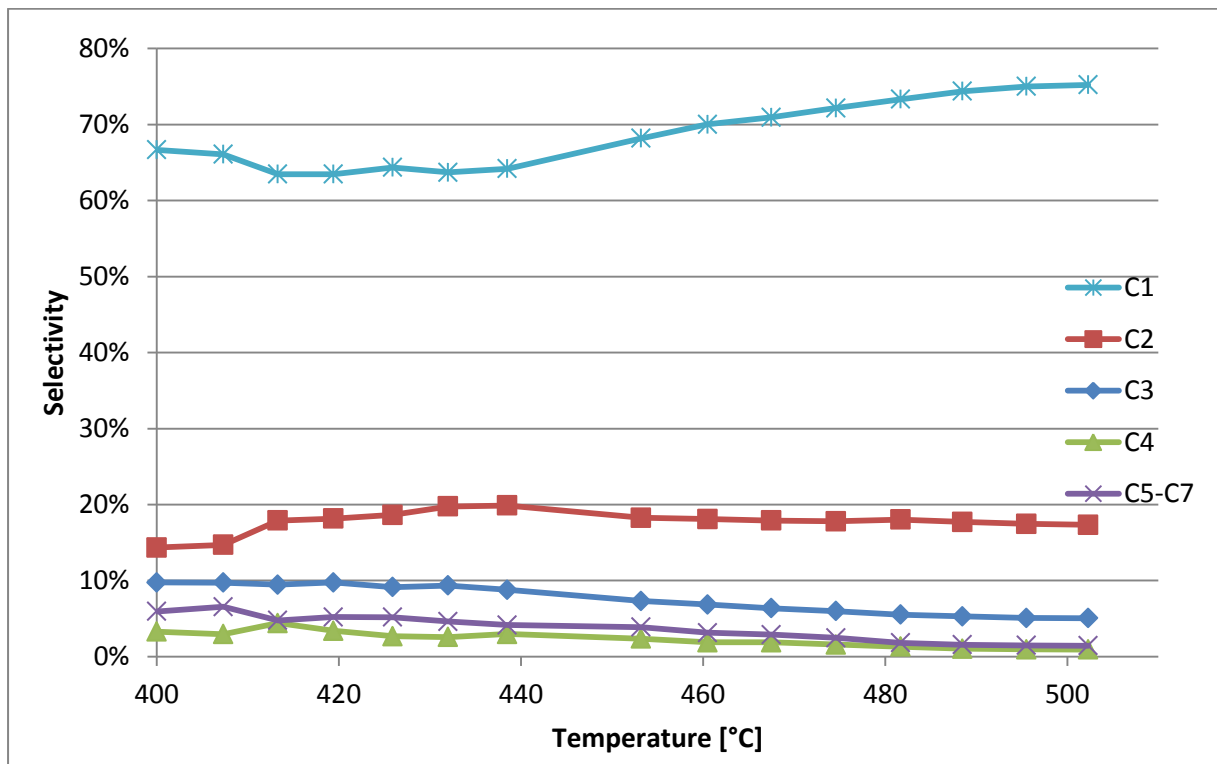


Figure 27. Selectivities vs temperature CAT\_J05.



Respecting the selectivity, there is a high methane formation. In second position, C<sub>2</sub> has a constant formation with the temperature. The selectivity to C<sub>3</sub>, C<sub>4</sub> and C<sub>5+</sub> decrease with the temperature.

- CAT J06: Core/shell CoO/MnO: 100%

This catalyst was tested by FT with H<sub>2</sub>, CO and Ar. The catalyst did not have activity at 210°C and 1.8 bar, the same conditions than the others. The temperature was increased at 250°C and there was little activity, it is possible that the surface of CoO it was not completely coated. The temperature was decreased at 210°C and the activity was tested between 210°C and 250°C with an increment of 10°C. There was not activity.

After that, the catalyst was reduced with H<sub>2</sub> and it was tested at 210°C again.

After all, this catalyst did not present activity by FT.

- CAT J07: Core/shell CoO/MnO:200%

There was not enough time to characterize and test this catalyst by FT.

- CAT J08: Core/shell CoO/MnO: 0%

This catalyst is formed by pure Cobalt. It is part of the second synthesis of Co nanoparticles. The size of Co nanoparticles is 8 nm, given by TEM characterization.

Then, the catalyst was tested by FT using the new syngas flow with a ratio of 2:1 H<sub>2</sub>/CO. It was tested at different GHSV of 0.6, 0.3, 0.15, 0.1 and 0.05 l CO/h/g. It was tested at 210°C and 1.8 bar.

Later on, the catalyst was reduced at 350°C and tested again.

Finally, the catalyst was tested with 10:1 H<sub>2</sub>/CO ratio and 0.9 lCO/h/g.

This catalyst will be compare in a general comparison with all the catalysts.

- CAT J09: Core/shell CoO/MnO: 25%

The core/shell of this catalyst is formed by Co nanoparticles with a diameter of 8nm; and coated 25% of the surface with MnO.

This catalyst was tested by FT with the same conditions than CAT\_J08; using the new syngas flow with a ratio of 2:1. It was tested at different GHSV of 0.6, 0.3, 0.15, 0.1 and 0.05 l CO/h/g. It was tested at 210°C and 1.8 bar.

Later on, the catalyst was reduced at 350°C and tested again.

This catalyst was not evaluated with 10:1 ratio H<sub>2</sub>/CO. The results for 0.05 lCO/h/g will not be discuss because they looked strange because the stabilization at this low space velocity takes a very long time.

This catalyst will be compare in a general comparison with all the catalysts.

- CAT J10: Core/shell CoO/MnO: 75%

Co nanoparticles of 8 nm were used to form this catalyst. The surface is coated 75% with MnO.

The catalyst was tested by FT with the same conditions than CAT\_J08 and CAT\_J09. It was used syngas flow with a ratio of 2:1 to produce results at 0.6, 0.3, 0.15, 0.1 and 0.05 l CO/h/g of GHSV. It was tested at 210°C and 1.8 bar.

Later on, the catalyst was reduced at 350°C and tested again, but the results after reduction were not possible to evaluate.

This catalyst was evaluated with 10:1 H<sub>2</sub>/CO ratio too.

## General comparison:

The following graphics show the results for all the catalysts together. These results will be discussed regarding the following properties: Conversion CO; O/P ratio C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub>; and selectivities CH<sub>4</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>5+</sub>, C<sub>3=</sub> and C<sub>4=</sub>.

First, it will be discuss the H<sub>2</sub>/CO ratio of 2:1.

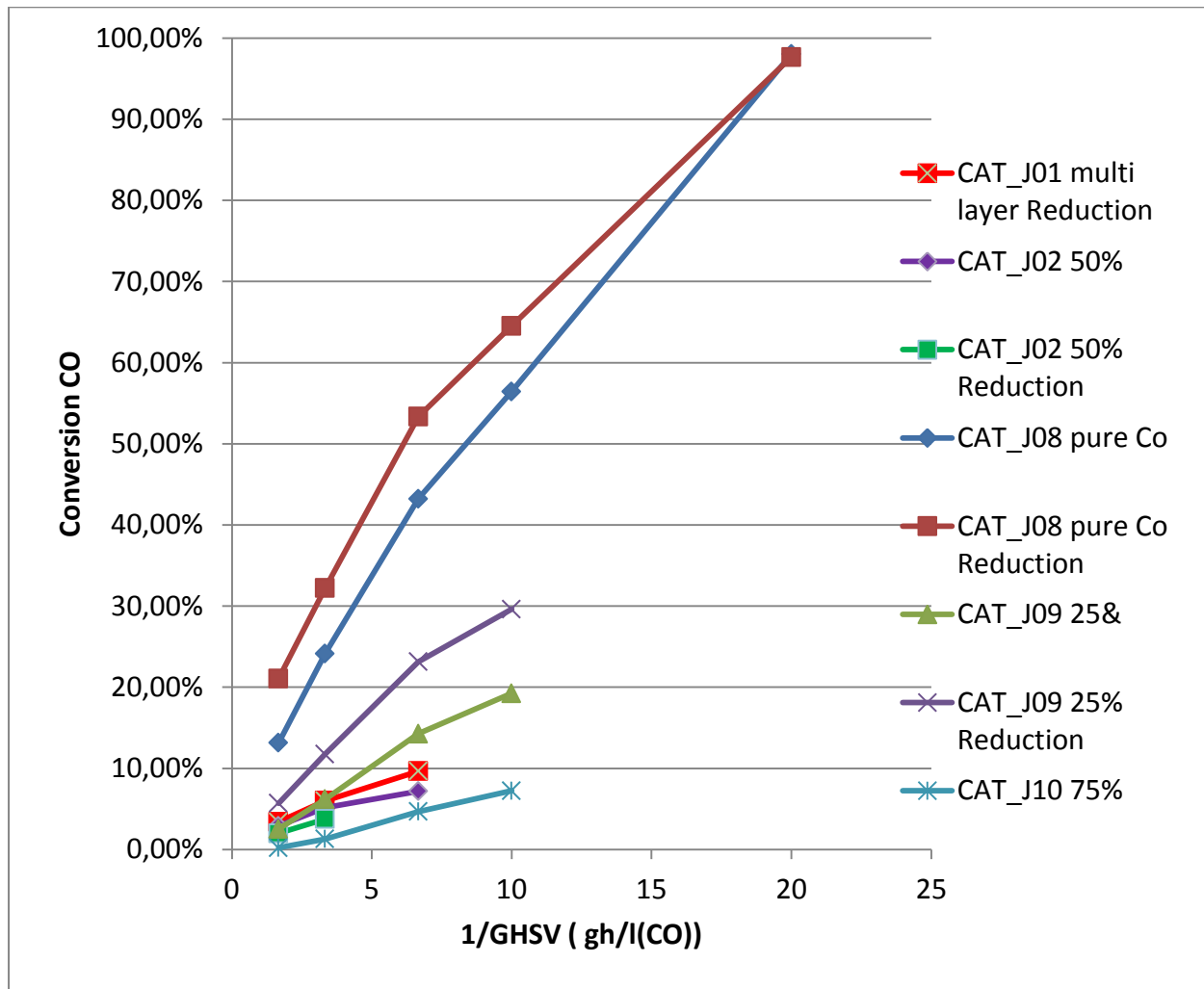


Figure 28. 2:1 Conversion CO vs residence time for all the catalysts.

As shown in the figure, conversion CO increased with the increment of residence time; or which is the same as saying that conversion CO decreased at high GHSV.

The catalyst formed with pure Co (CAT\_J08) has the highest conversions, before and after reduction for the same GHSV than the others.

Regarding the conversion, CAT\_09, coated 25% of MnO, shows good results compared with pure Co. CAT\_09 after reduction has higher conversion than before reduction.

The CAT\_J10, which surface is coated 75%, has the lowest conversions.

However, despite high conversion CO is a good point to keep in mind, the results for the O/P ratios are interesting.

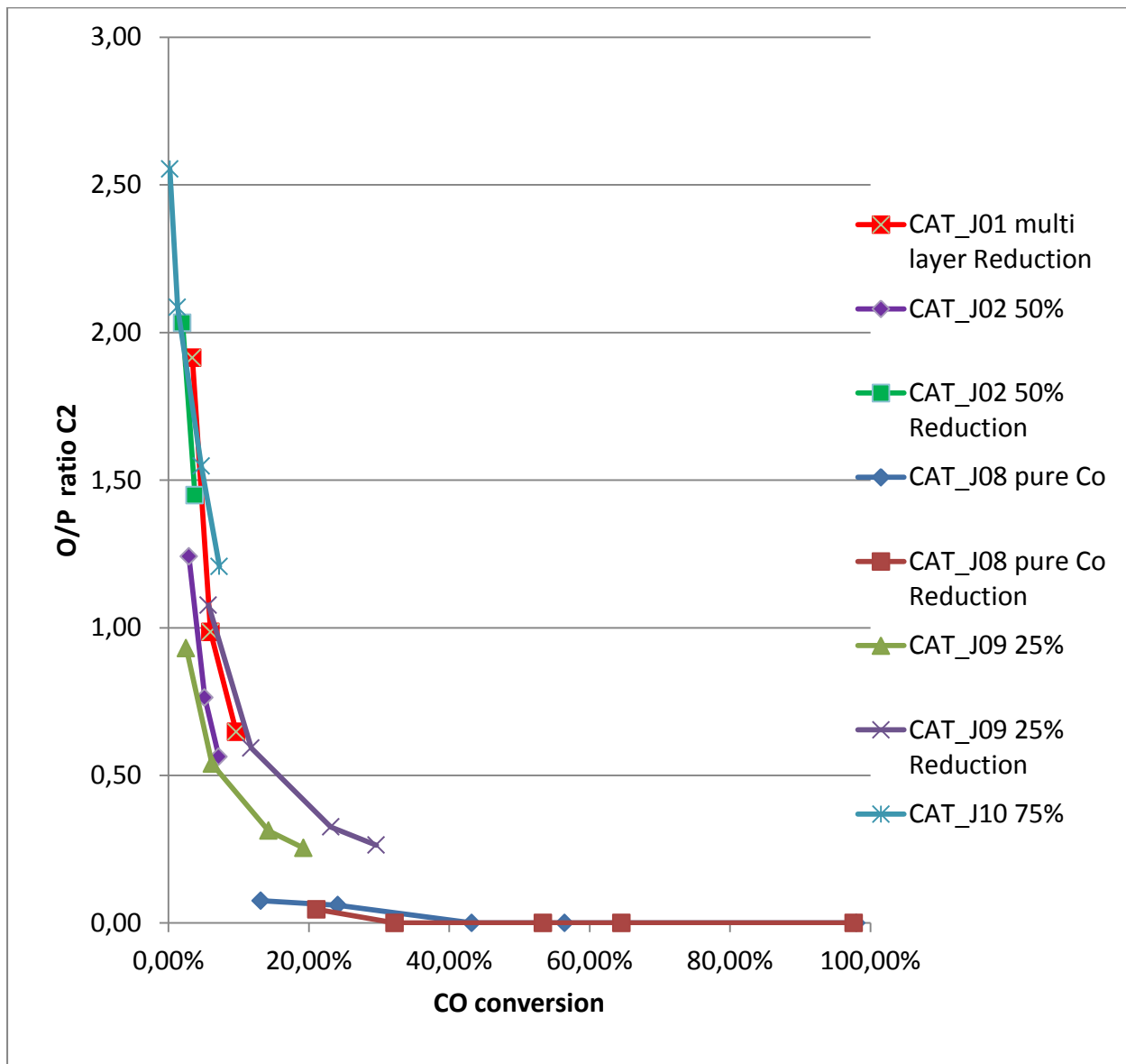


Figure 29. 2:1 O/P C<sub>2</sub> ratio vs CO conversion for all the catalysts.

Regarding O/P C<sub>2</sub>, CAT\_J10, CAT\_J02 and CAT\_J01 have high O/P C<sub>2</sub> ratio despite the low conversions.

In this case, pure Co does not show any O/P ratio C<sub>2</sub> at all.

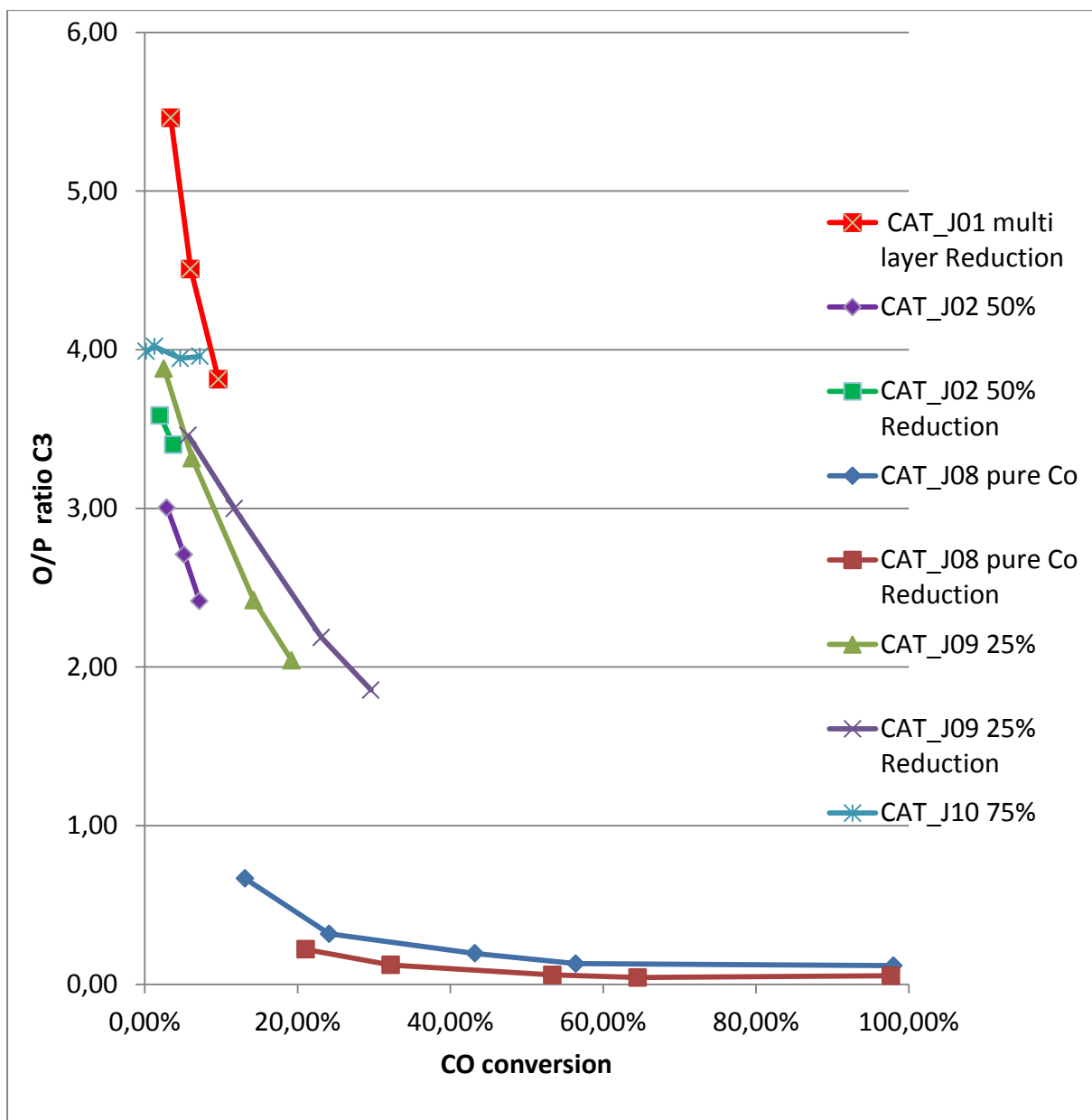


Figure 30. 2:1 O/P C<sub>3</sub> ratio vs CO conversion for all the catalysts.

As shown in the figure above, CAT\_J01, formed by multi layer of MnO, has high O/P ratio C<sub>3</sub> at low conversions. C<sub>3</sub> is a desire product and it means that this catalyst could be a good option.

Also, CAT\_J10 shows high O/P ratio C<sub>3</sub> comparing with the others.

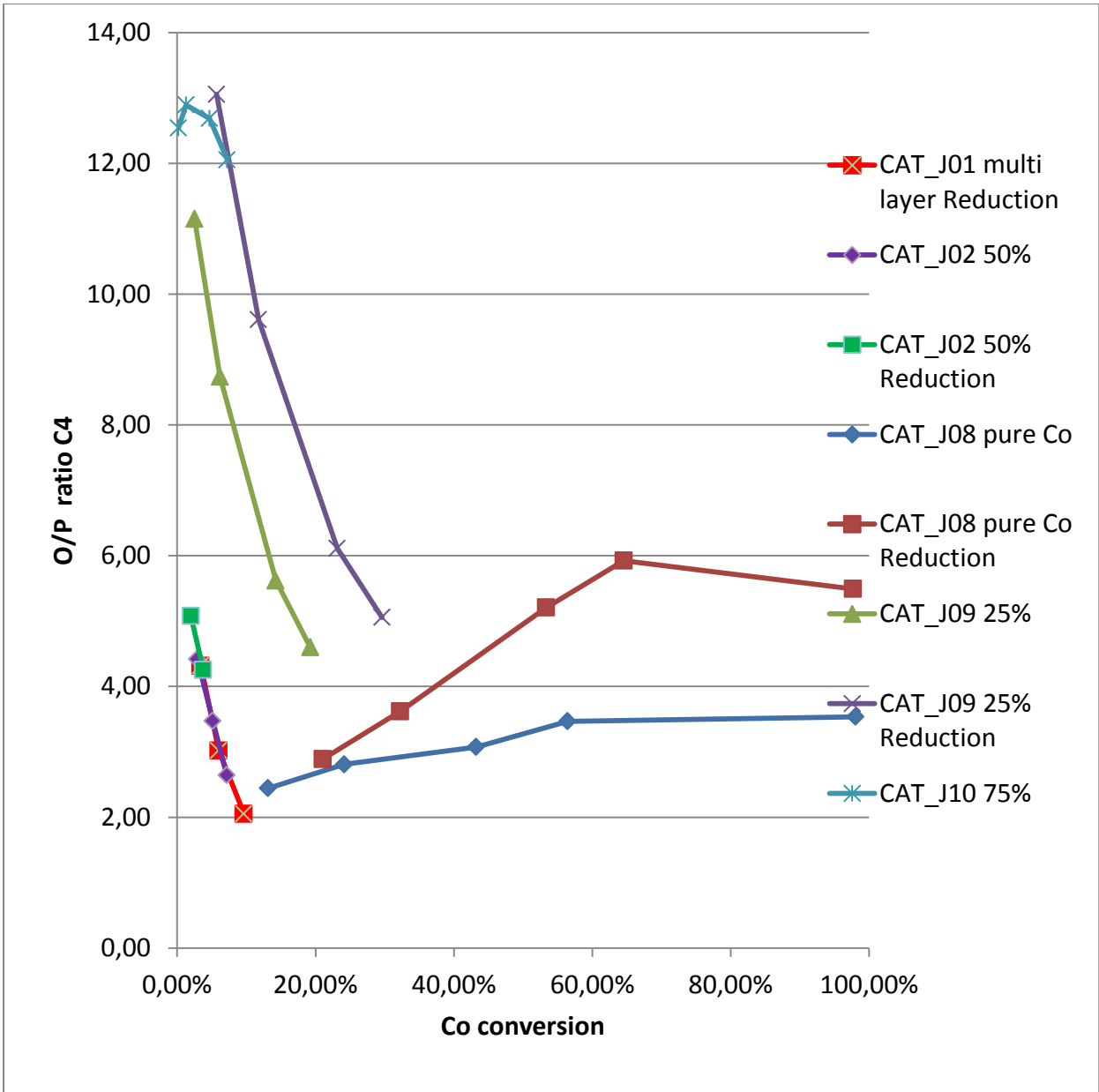


Figure 31. 2:1 O/P C<sub>4</sub> ratio vs CO conversion for all the catalysts.

CAT\_J10 gives good results for O/P ratio C<sub>4</sub> around 13, however for pure Co is around 3-6. Also, CAT\_J09 has high O/P ratio C<sub>4</sub>.

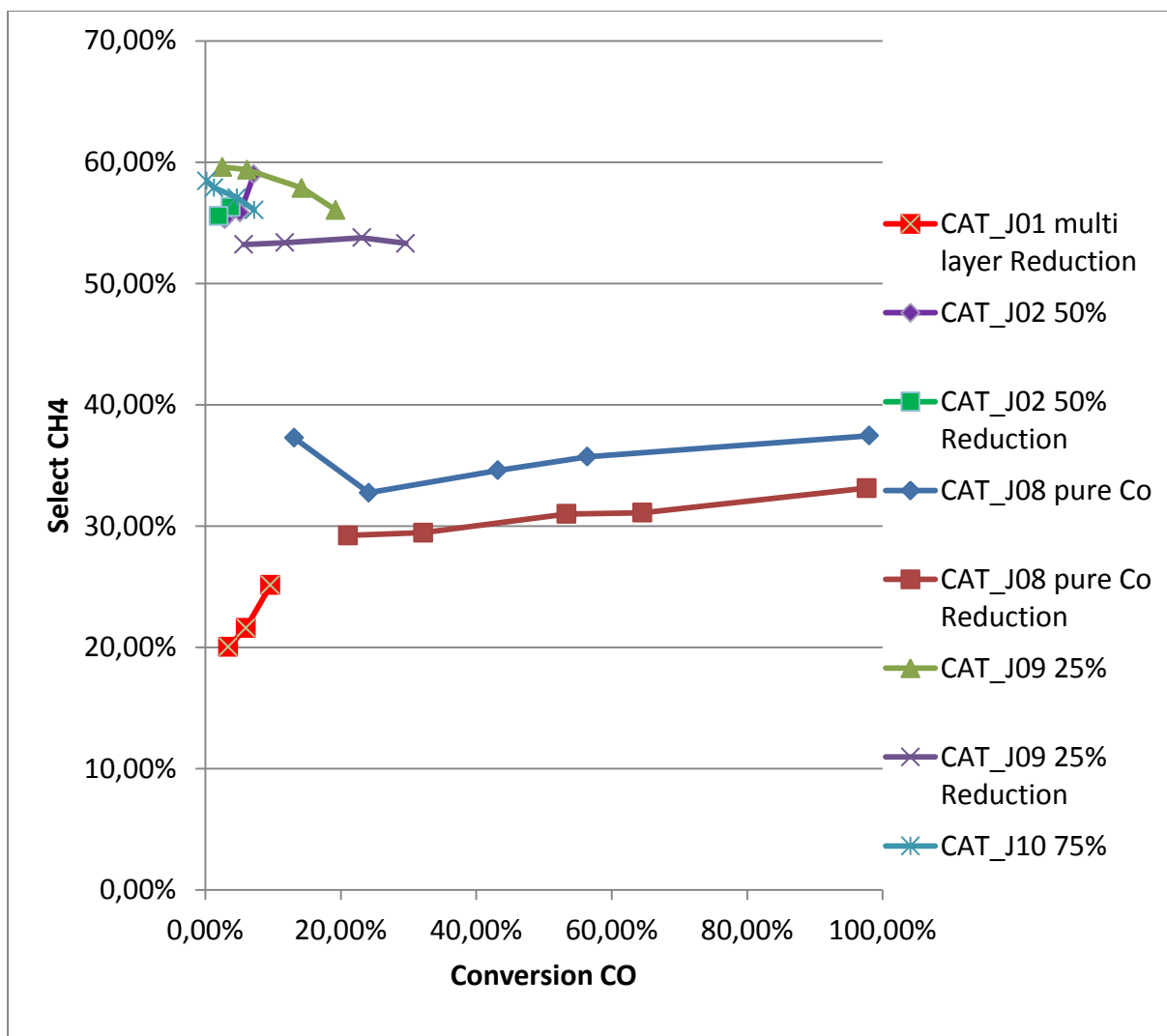


Figure 32. 2:1 Selectivity CH<sub>4</sub> vs CO conversion for all the catalysts.

CH<sub>4</sub> is an undesire product, therefore the lowest selectivity of CH<sub>4</sub> is favorable for the catalyst.

In this case, CAT\_J01 has the lowest selectivity of CH<sub>4</sub> with a value between 20-25%. It is lower than pure Co that has a selectivity between 30-40%.

The rest of the catalysts are around 50-60%.

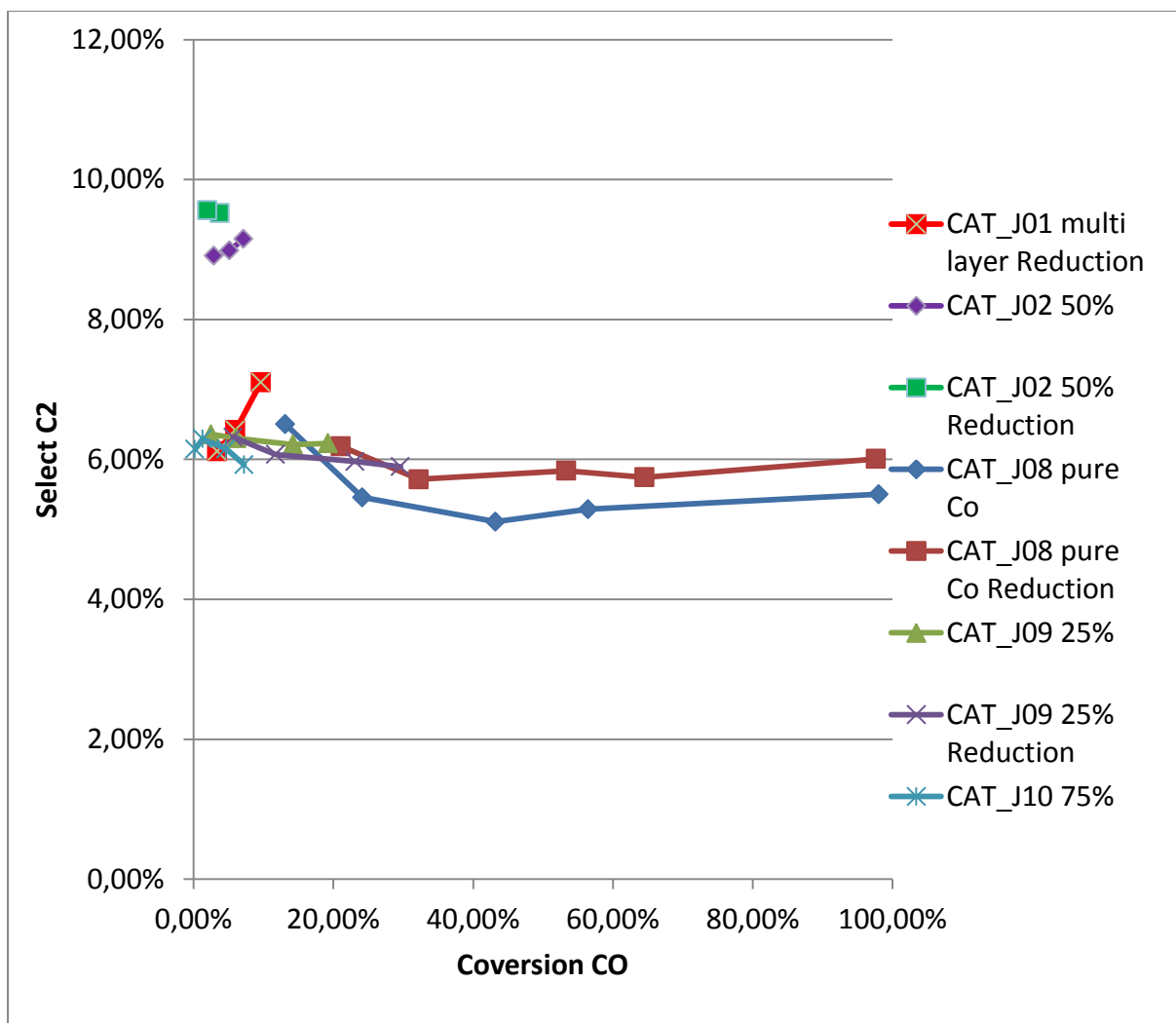


Figure 33. 2:1 Selectivity C<sub>2</sub> vs CO conversion for all the catalysts.

C<sub>2</sub> selectivity is mostly the same for all the catalysts around 6%, with the exception of CAT\_J02 that it is around 9%.

With these results is difficult to compare regarding the C<sub>2</sub> selectivity.



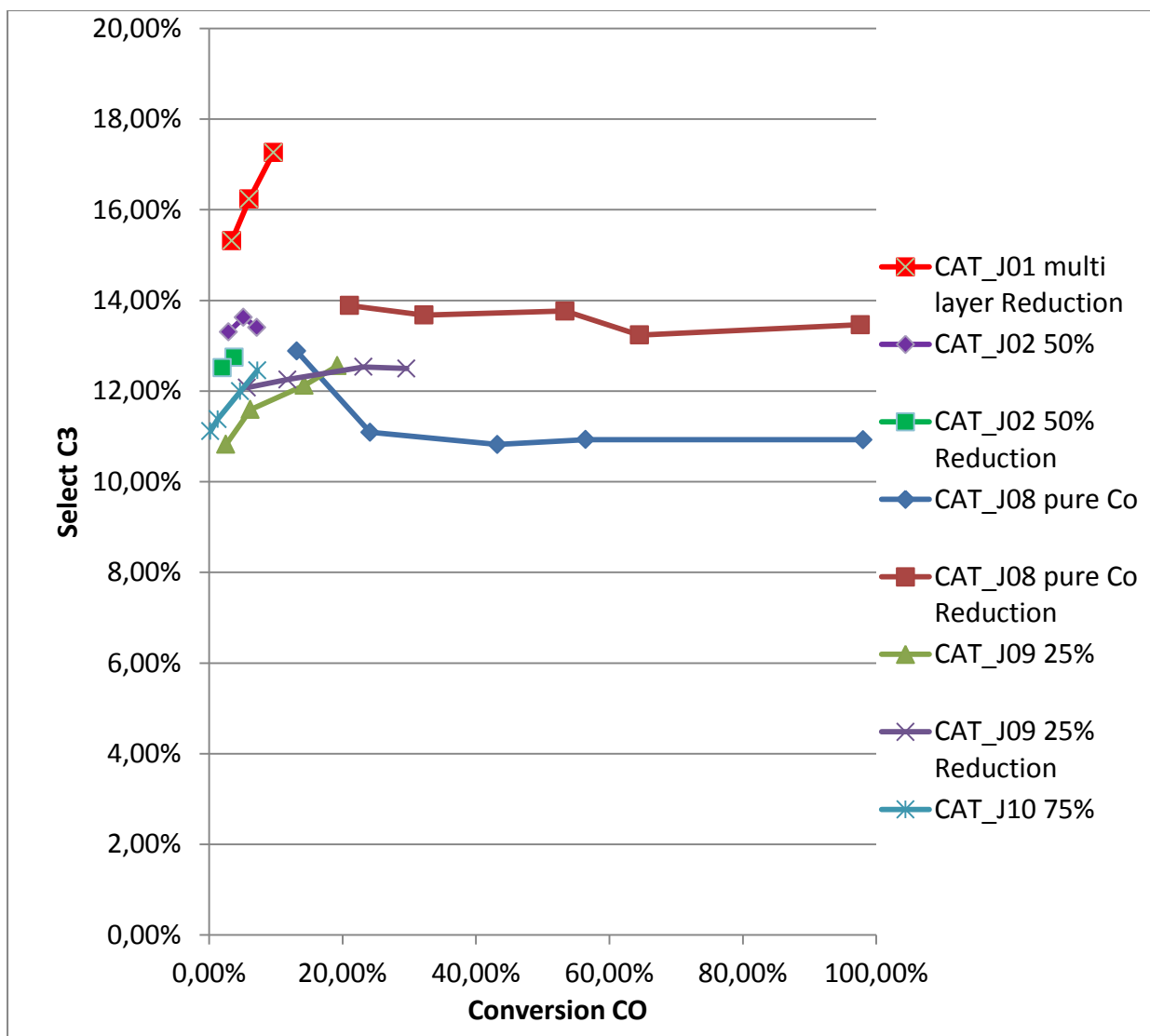


Figure 34. 2:1 Selectivity C<sub>3</sub> vs CO conversion for all the catalysts.

Regarding C<sub>3</sub> selectivity, CAT\_J01 is higher than the others around 16%. The rest of the catalysts have mostly the same values between 10-14%.

It attracts attention that for CAT\_J08, pure Co, the different selectivities do not vary so much with the increment of the conversion.

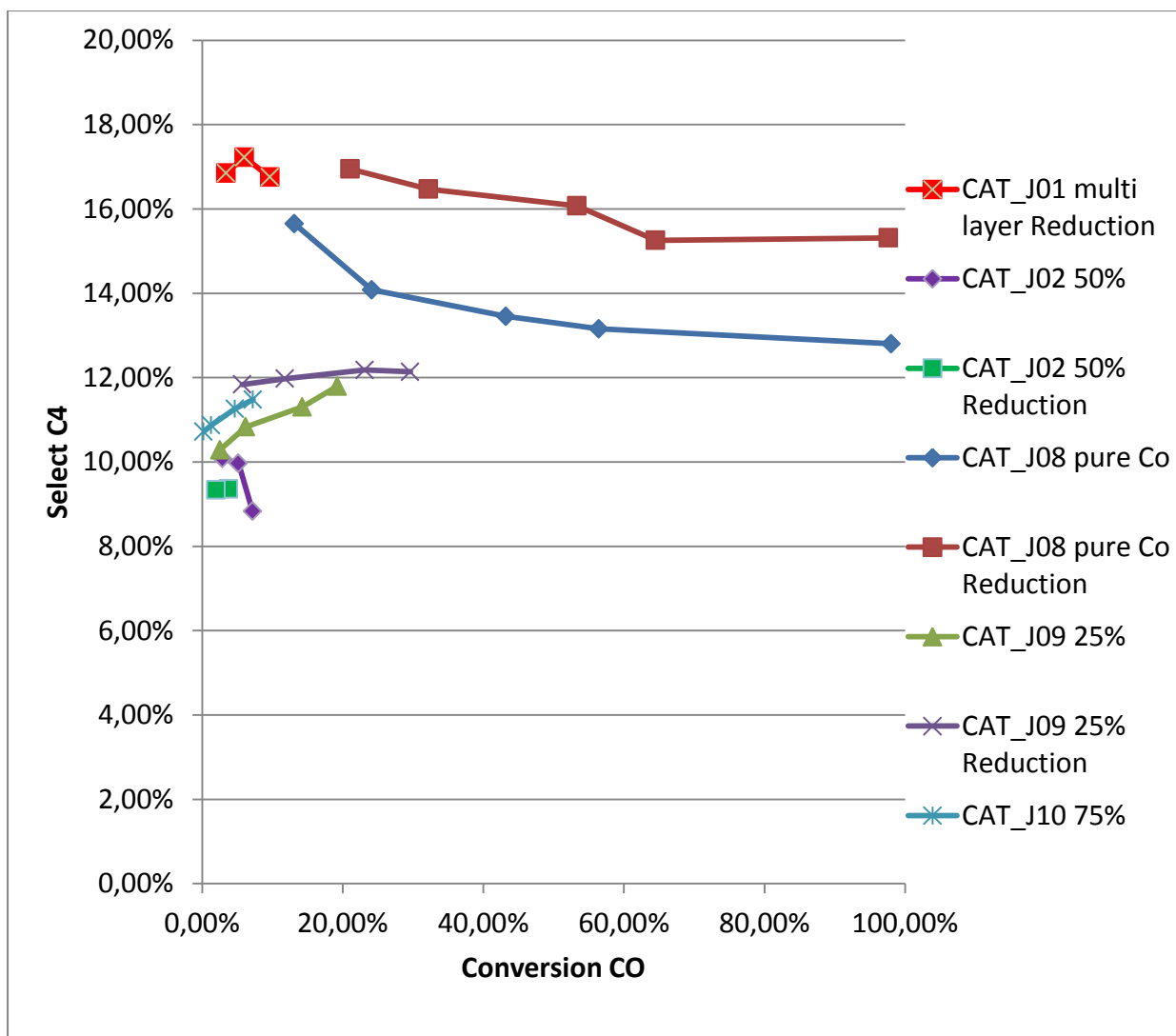


Figure 35. 2:1 Selectivity C<sub>4</sub> vs CO conversion for all the catalysts.

CAT\_J01 has higher selectivity C<sub>4</sub> than the others again. This is even higher than pure Co.

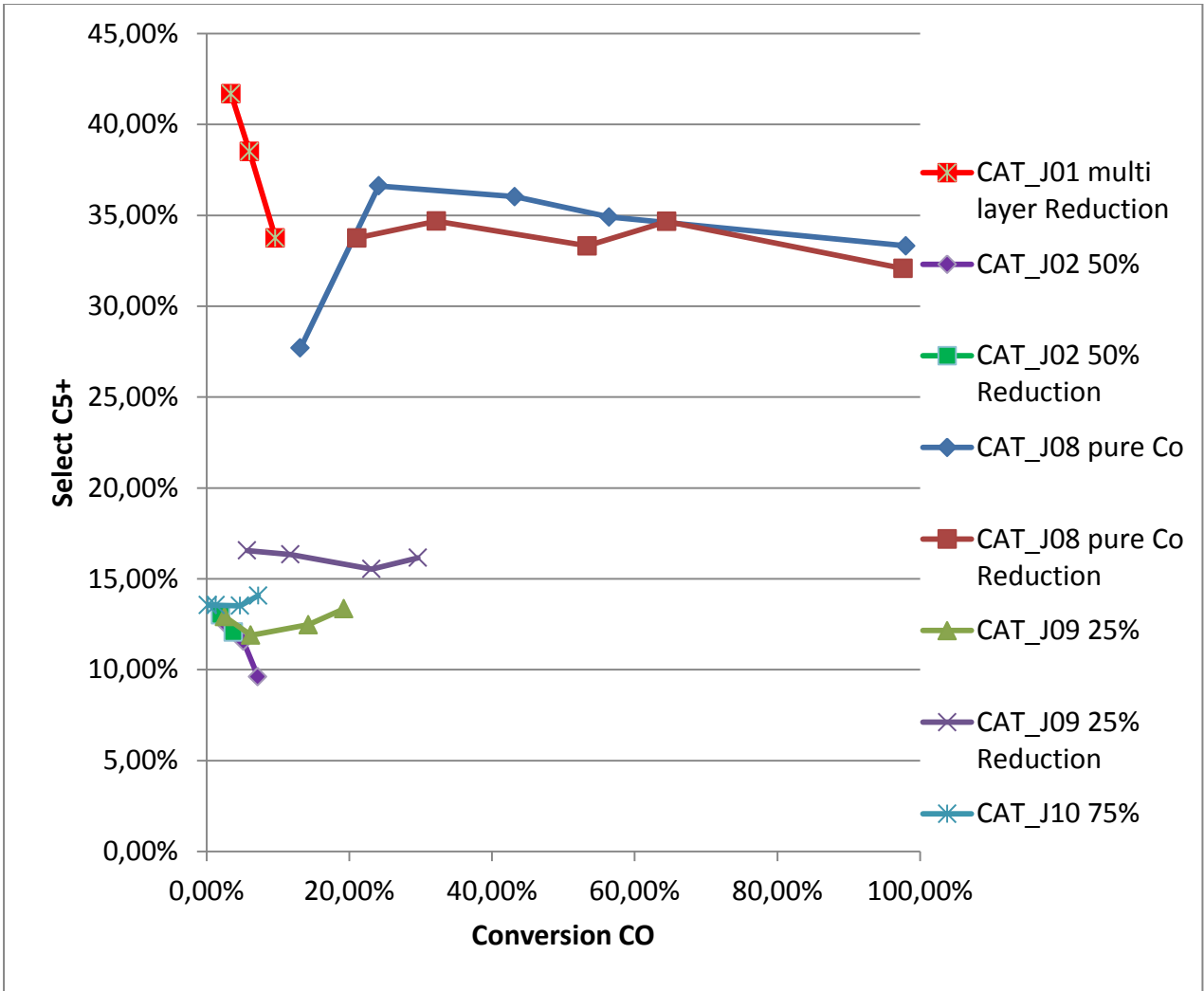


Figure 36. 2:1 Selectivity  $C_{5+}$  vs CO conversion for all the catalysts.

As shown in the figure, CAT\_J01 has a selectivity between 32-42 % for products  $C_{5+}$ . It is higher than pure Co again., but pure Co has really high selectivity too at high conversions.

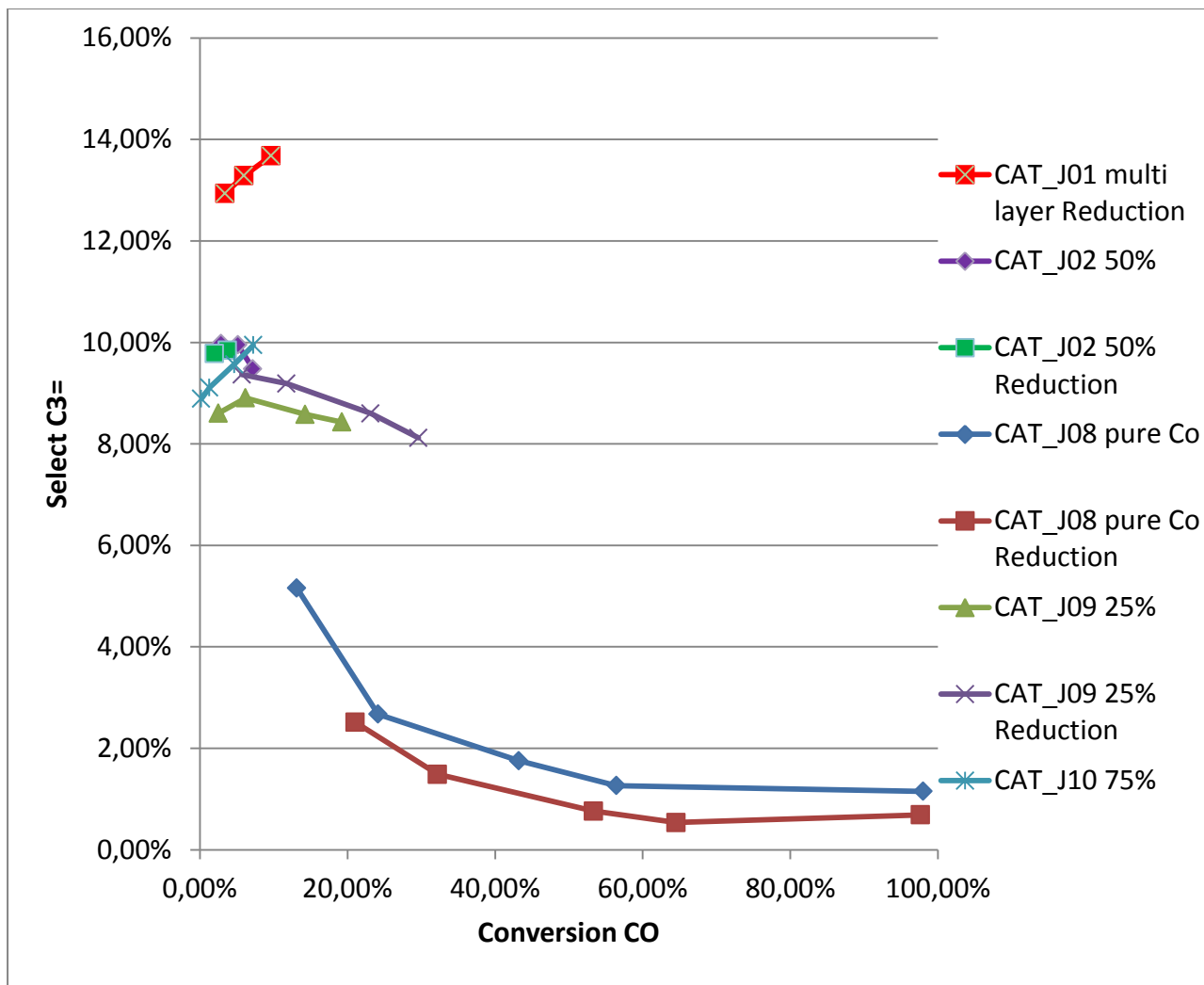


Figure 37. 2:1 Selectivity  $C_{3=}$  vs CO conversion for all the catalysts.

Anew, CAT\_J01 has a selectivity to  $C_{3=}$  much higher than the others. This time, pure Co is much lower than the rest of the catalysts.

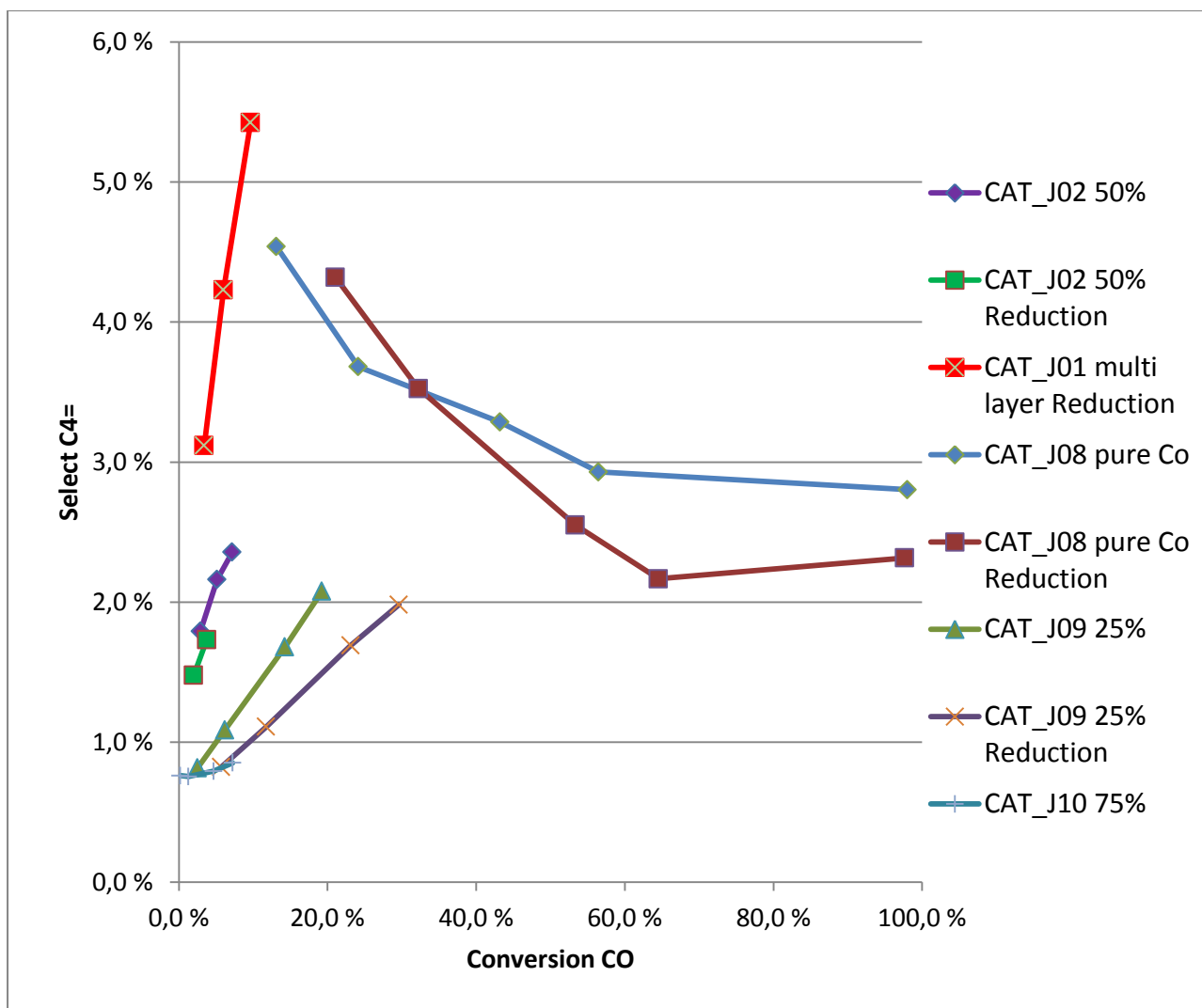


Figure 38. 2:1 Selectivity C<sub>4=</sub> vs CO conversion for all the catalysts.

Regarding selectivity C<sub>4=</sub>, CAT\_J01 is again higher than the others at low conversions. Then, CAT\_J08 has high selectivity too compared with the rest of the catalysts.

In conclusion, for a H<sub>2</sub>/CO ratio 2:1 CAT\_J01, a catalyst formed by a core/shell of Co as core and multi layer of MnO in the shell, has really good results comparing with the others giving high O/P ratio C<sub>2</sub>; high O/P ratio C<sub>3</sub>; high selectivity C<sub>3</sub>; high selectivity C<sub>4</sub>; high selectivity C<sub>5+</sub>; high selectivity C<sub>3=</sub>; high selectivity C<sub>4=</sub>; and low selectivity CH<sub>4</sub>.

CAT\_J08, formed by pure Co, as it was expected has good results too and the high conversions attract attention.

On the other hand, for H<sub>2</sub>/CO ratio of 10:1 these are the results for CAT\_J01, CAT\_J02, CAT\_J08 and CAT\_J10. All the evaluations have done at 0.9 l CO/g/h of GHSV.

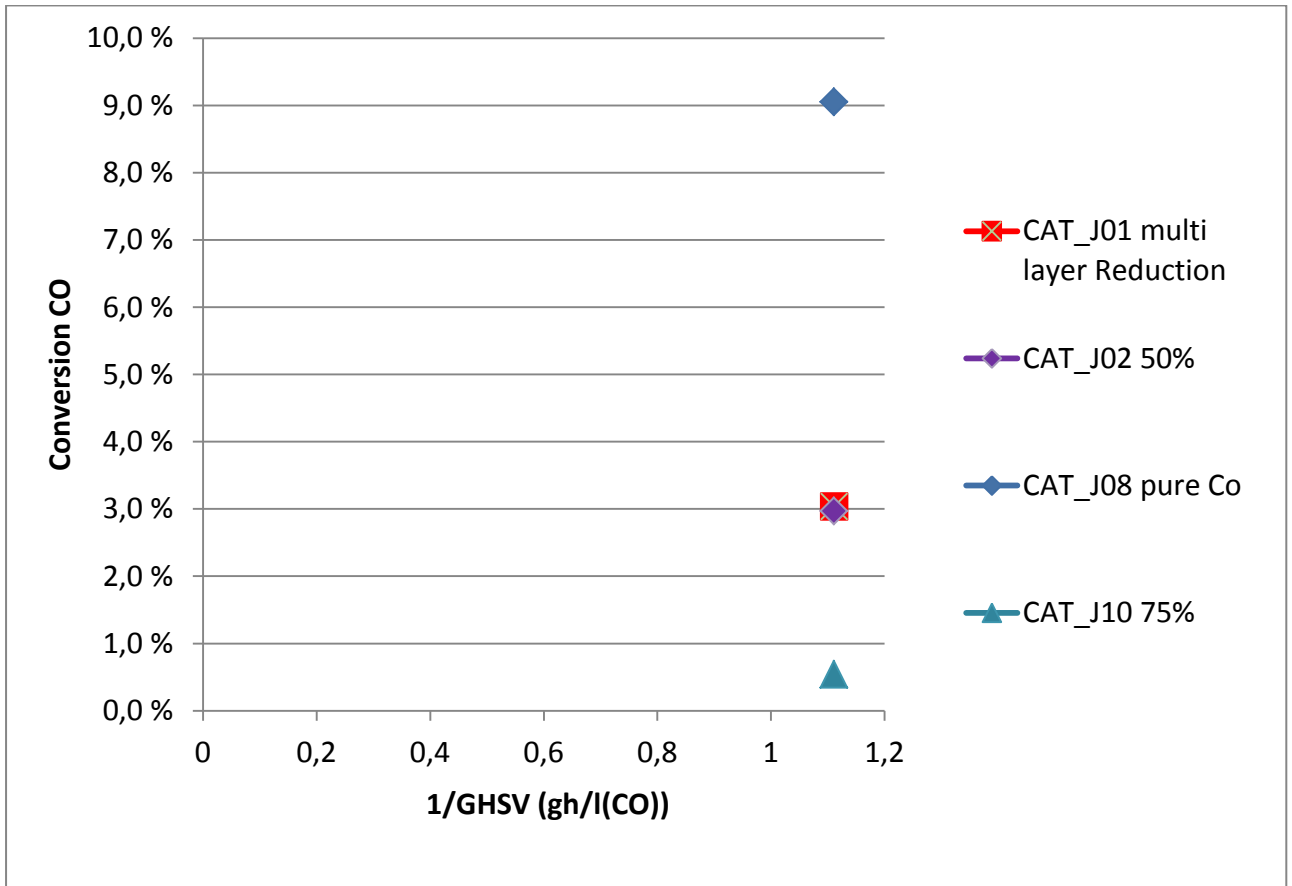


Figure 39. 10:1 Conversion CO vs residence time for all the catalysts.

Regarding the conversion CO, CAT\_J08 has the highest conversion of 9% at the same conditions than the other catalysts. CAT\_J01 and CAT\_J02 have a conversion CO of 3%, while CAT\_J10 has the lowest conversion.

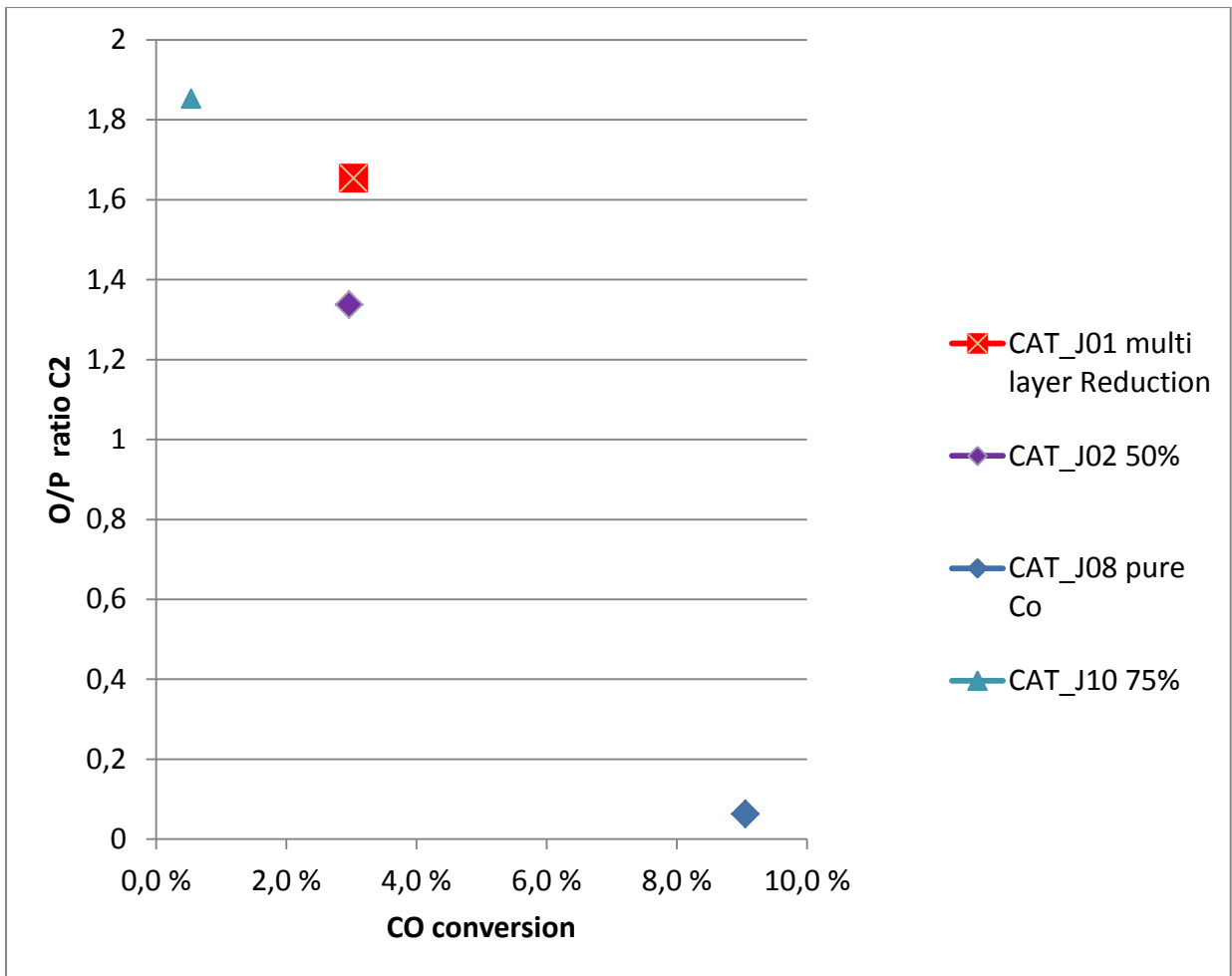


Figure 40. 10:1 O/P C<sub>2</sub> ratio vs CO conversion for all the catalysts.

About O/P ratio C<sub>2</sub>, CAT\_J10 has the highest selectivity as it was shown before for a ratio H<sub>2</sub>/CO 2:1. Also CAT\_J01 has a higher selectivity.

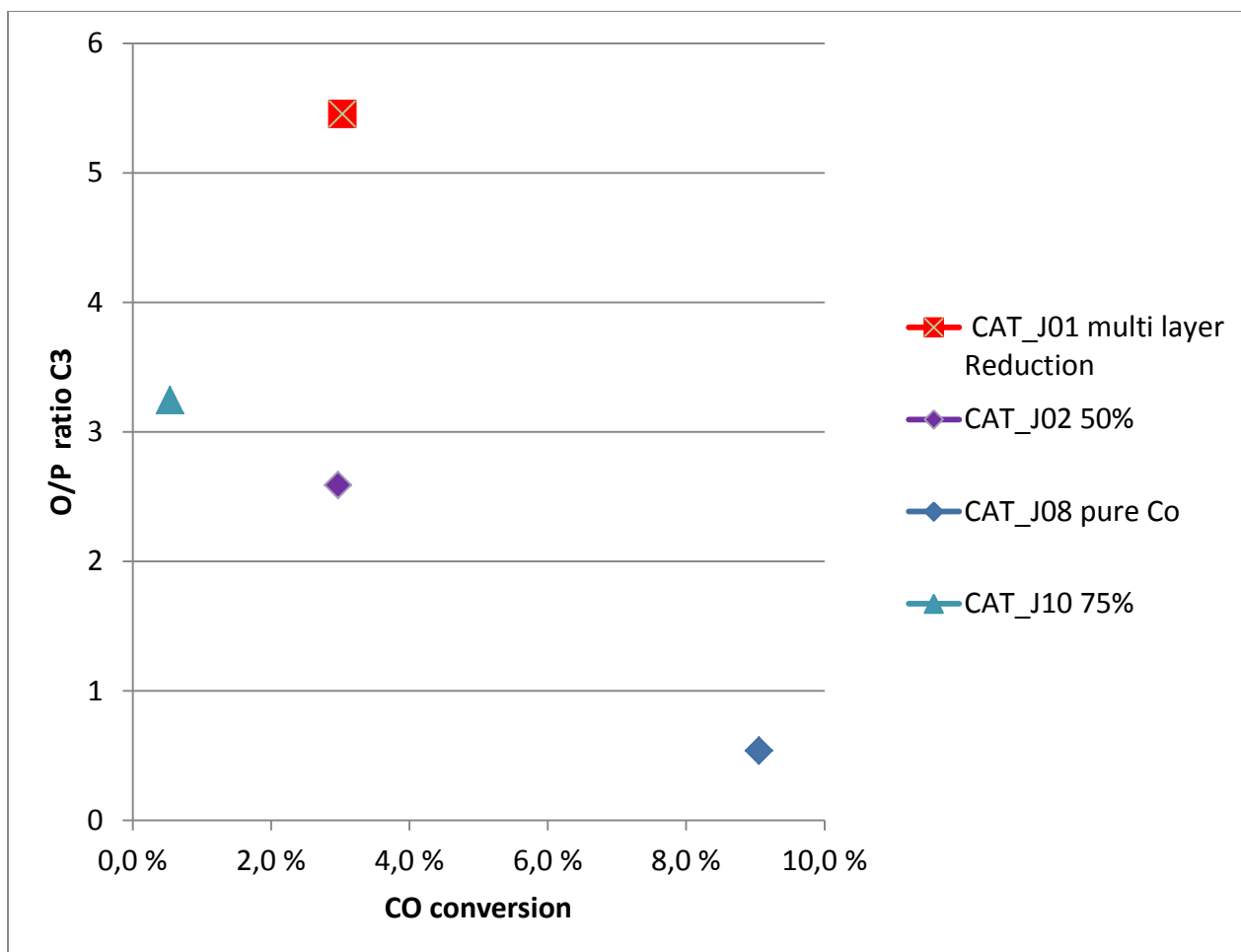


Figure 41. 10:1 O/P C<sub>3</sub> ratio vs CO conversion for all the catalysts.

CAT\_J01 has good results concerning O/P ratio C<sub>3</sub>, followed by CAT\_J10 and CAT\_J02.

CAT\_J08, pure Co, has low O/P ratio C<sub>2</sub> and C<sub>3</sub> as using a ratio H<sub>2</sub>/CO 2:1.



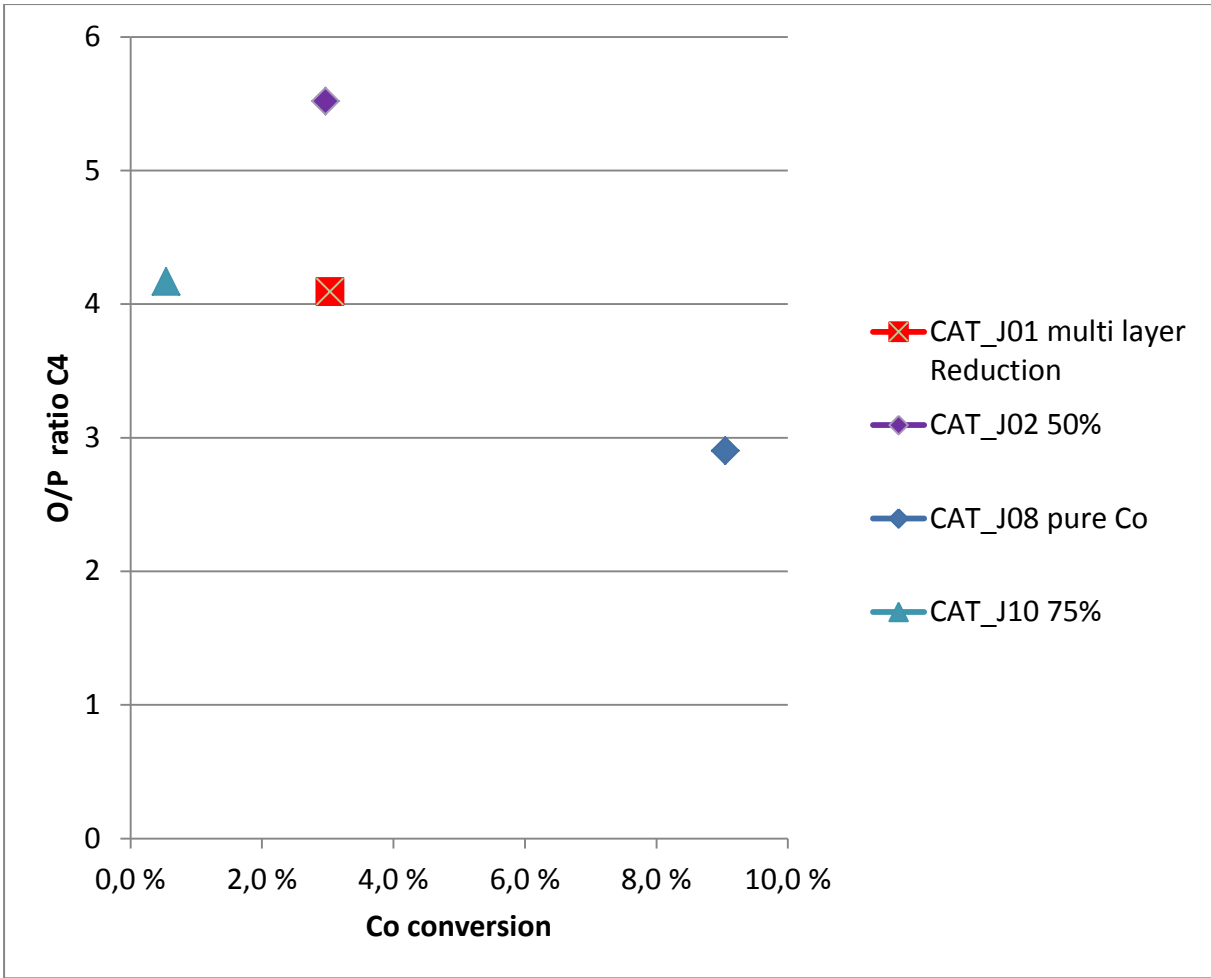


Figure 42. 10:1 O/P C<sub>4</sub> ratio vs CO conversion for all the catalysts.

Regarding O/P ratio C<sub>4</sub>, CAT\_J02 has highest results. CAT\_J10 and CAT\_J01 have also high results compared with CAT\_J08.

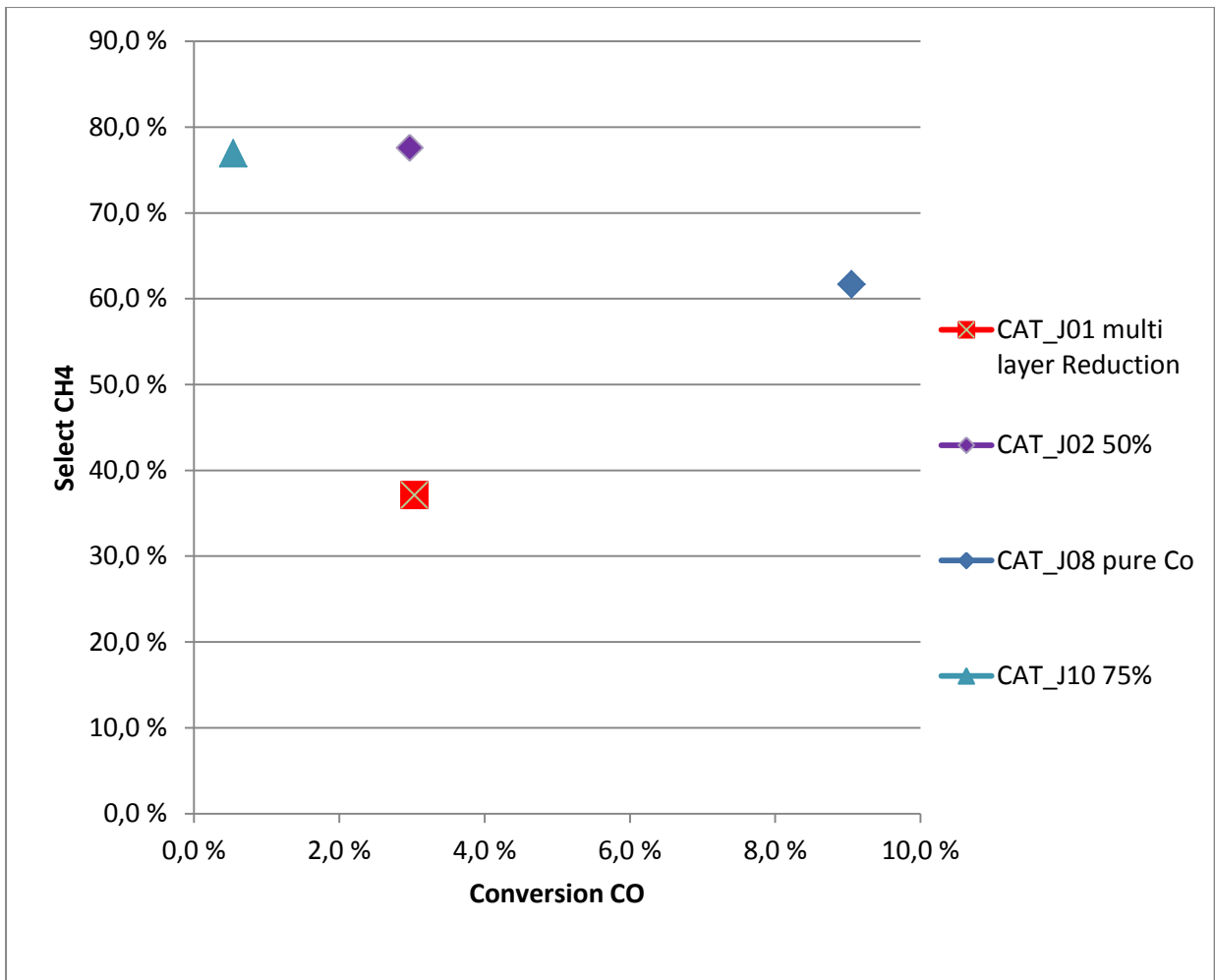


Figure 43. 10:1 Selectivity CH<sub>4</sub> vs CO conversion for all the catalysts.

About the methane selectivity, CAT\_J01 has the lowest. This is a favorable factor in a catalyst. This catalyst has low methane selectivity with a 2:1 H<sub>2</sub>/CO ratio too.

On the other hand, CAT\_J02 and CAT\_J10 have high methane formation.

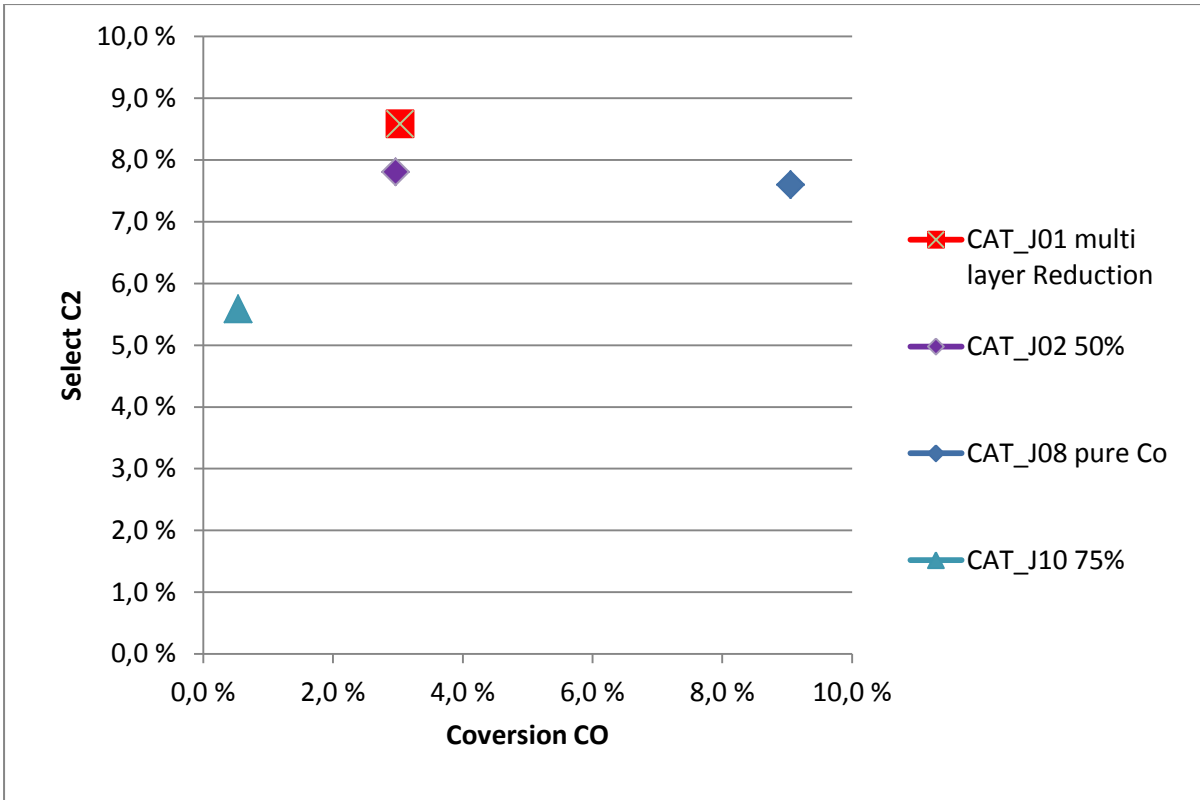


Figure 44. 10:1 Selectivity C<sub>2</sub> vs CO conversion for all the catalysts.

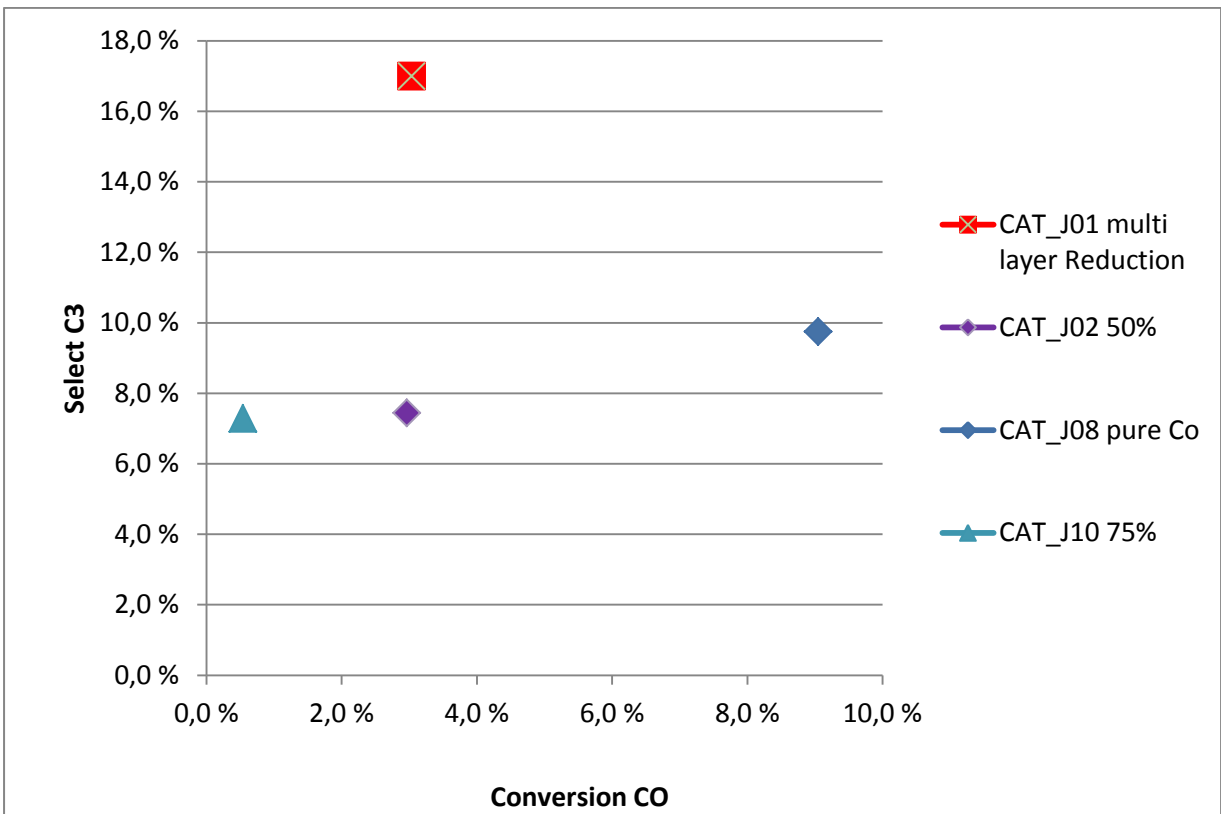


Figure 45. 10:1 Selectivity C<sub>3</sub> vs CO conversion for all the catalysts.

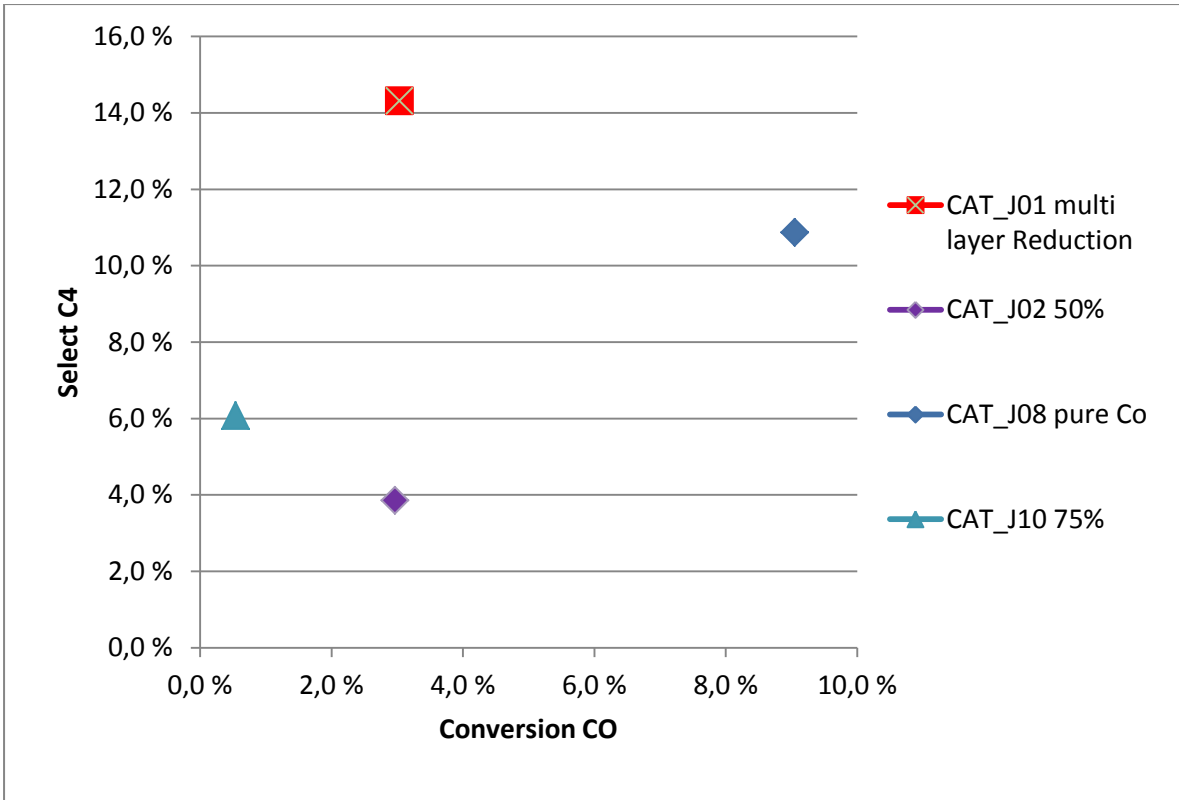


Figure 46. 10:1 Selectivity C<sub>4</sub> vs CO conversion for all the catalysts.

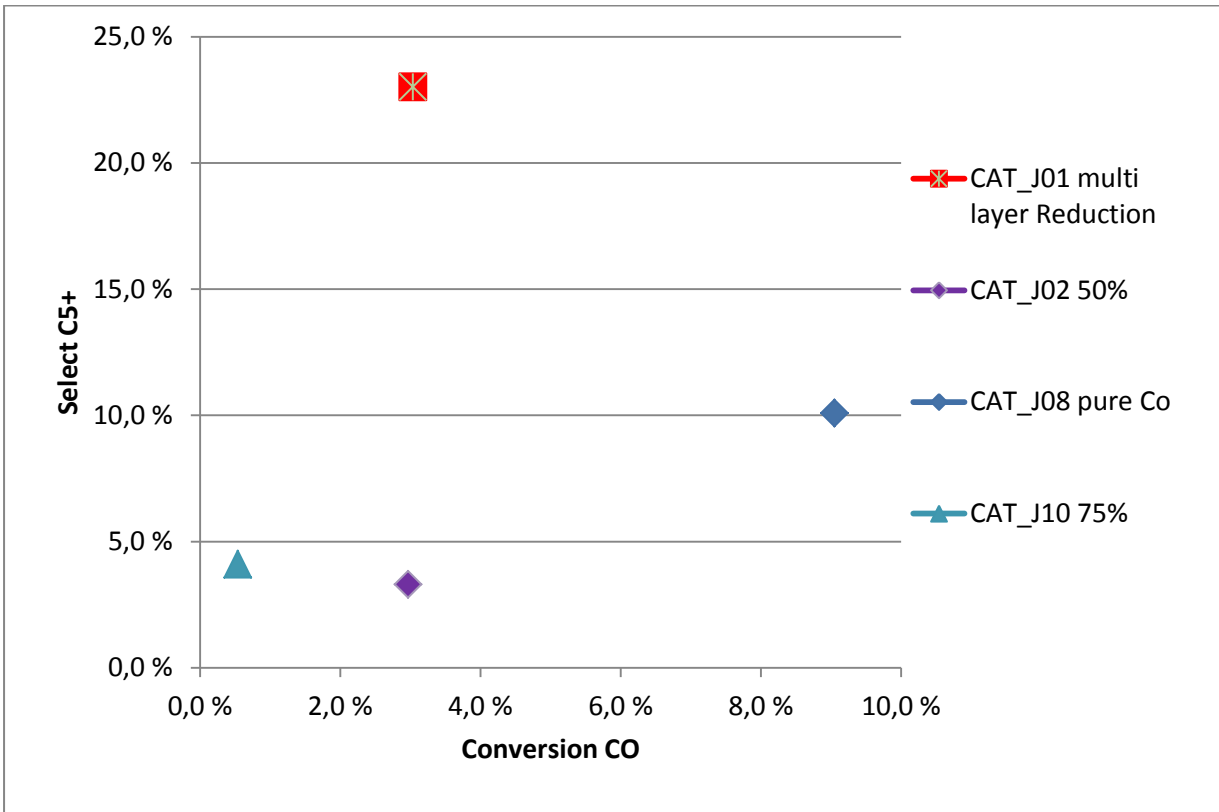


Figure 47. 10:1 Selectivity C<sub>5+</sub> vs CO conversion for all the catalysts.

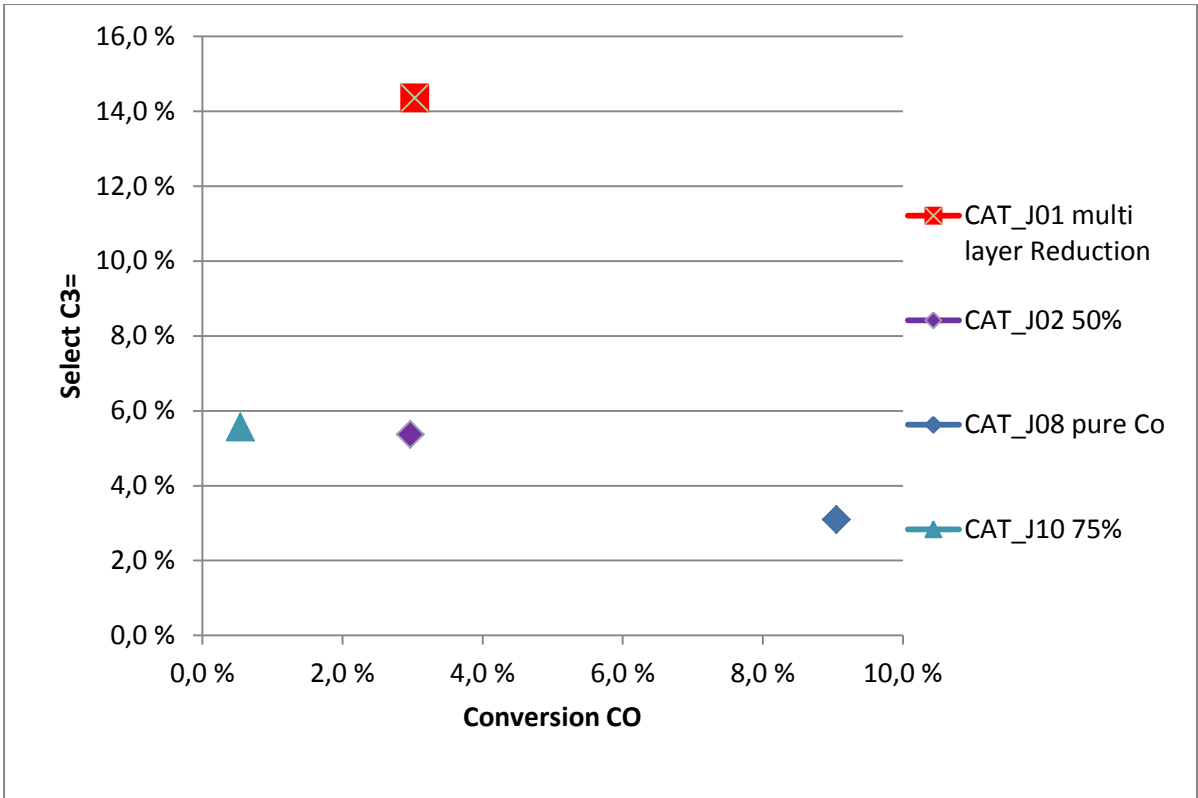


Figure 48. 10:1 Selectivity C<sub>3=</sub> vs CO conversion for all the catalysts.

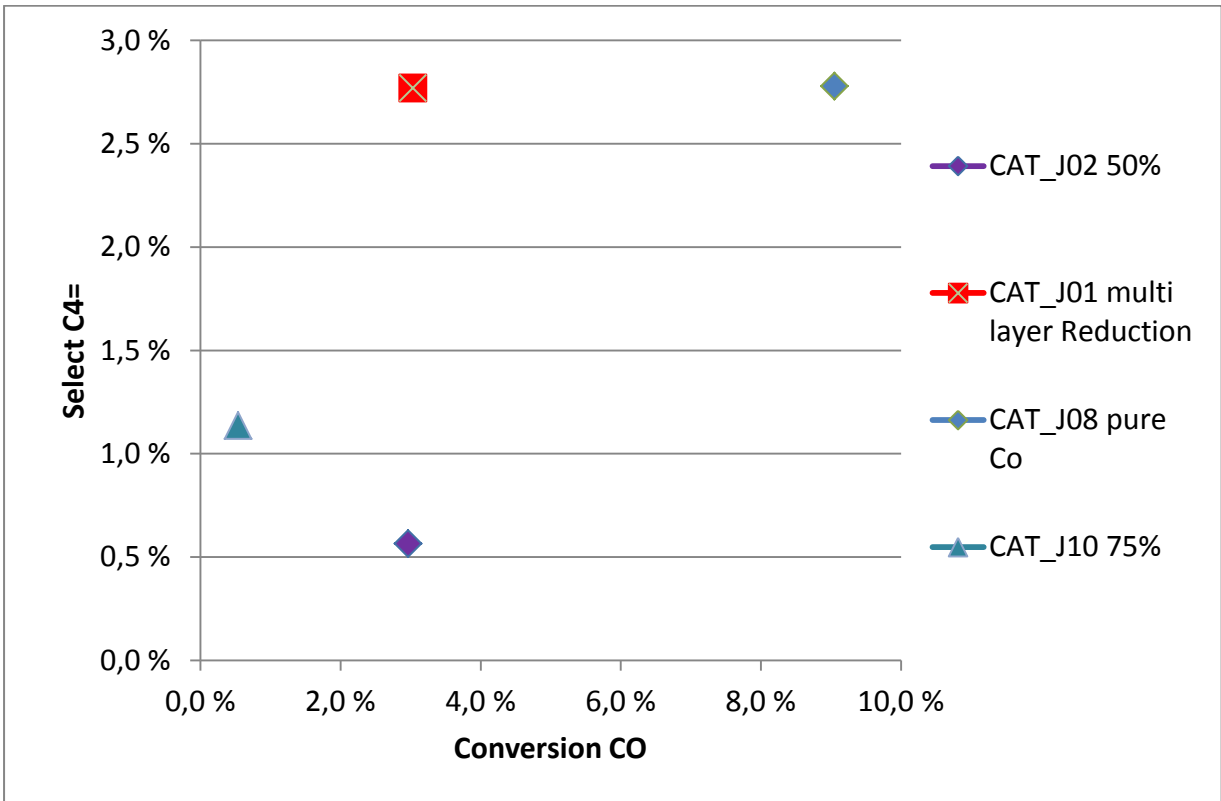


Figure 49. 10:1 Selectivity C<sub>4=</sub> vs CO conversion for all the catalysts.

CAT\_J01 has the highest selectivities of C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>5+</sub>, C<sub>3=</sub> for a H<sub>2</sub>/CO ratio 10:1. Regarding C<sub>4=</sub> selectivity, CAT\_J01 and CAT\_J08 have both the same value.

Also, CAT\_J01 has a low methane selectivity using a ratio 10:1 of H<sub>2</sub>/CO ratio.

In conclusion, regarding the CO conversion, CAT\_J08, formed by pure Co, has the highest conversion. However, as it was looked for in these experiments with the model of different catalysts using MnO as shell is a good option for a catalyst. It is possible with a multi layer of MnO in the shell, CAT\_J01, to get a low methane formation and at the same time high selectivities for the rest of the products compared with pure Co.

### 4.3 Results $\text{La}_2\text{O}_3$

Oleic acid was the first precursor used to form  $\text{La}_2\text{O}_3$  from La oleate.

The nanoparticles were characterized with TEM and XRD techniques.

Result TEM:

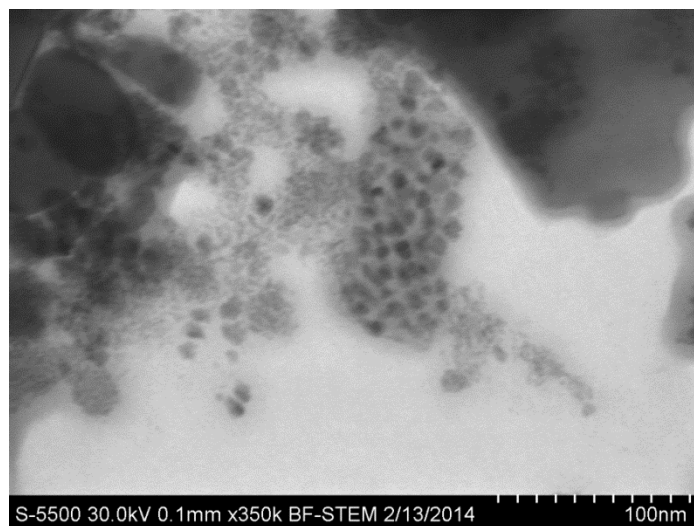


Figure 50. TEM  $\text{La}_2\text{O}_3$  nanoparticles.

The size of the nanoparticles are around 10-13 nm. The image was difficult to take because the nanoparticles were dirty with Teflon. The Teflon melted during the reaction because of the high temperature.

As it was mentioned in the previous chapter, it was proposed different precursors for the formation of  $\text{La}_2\text{O}_3$ , because it was necessary find a precursor with a lower reaction temperature required.

The comparison of precursors for the synthesis of Lanthanum oxide was carried out with the TGA technique to know the decomposition temperature for each precursor.

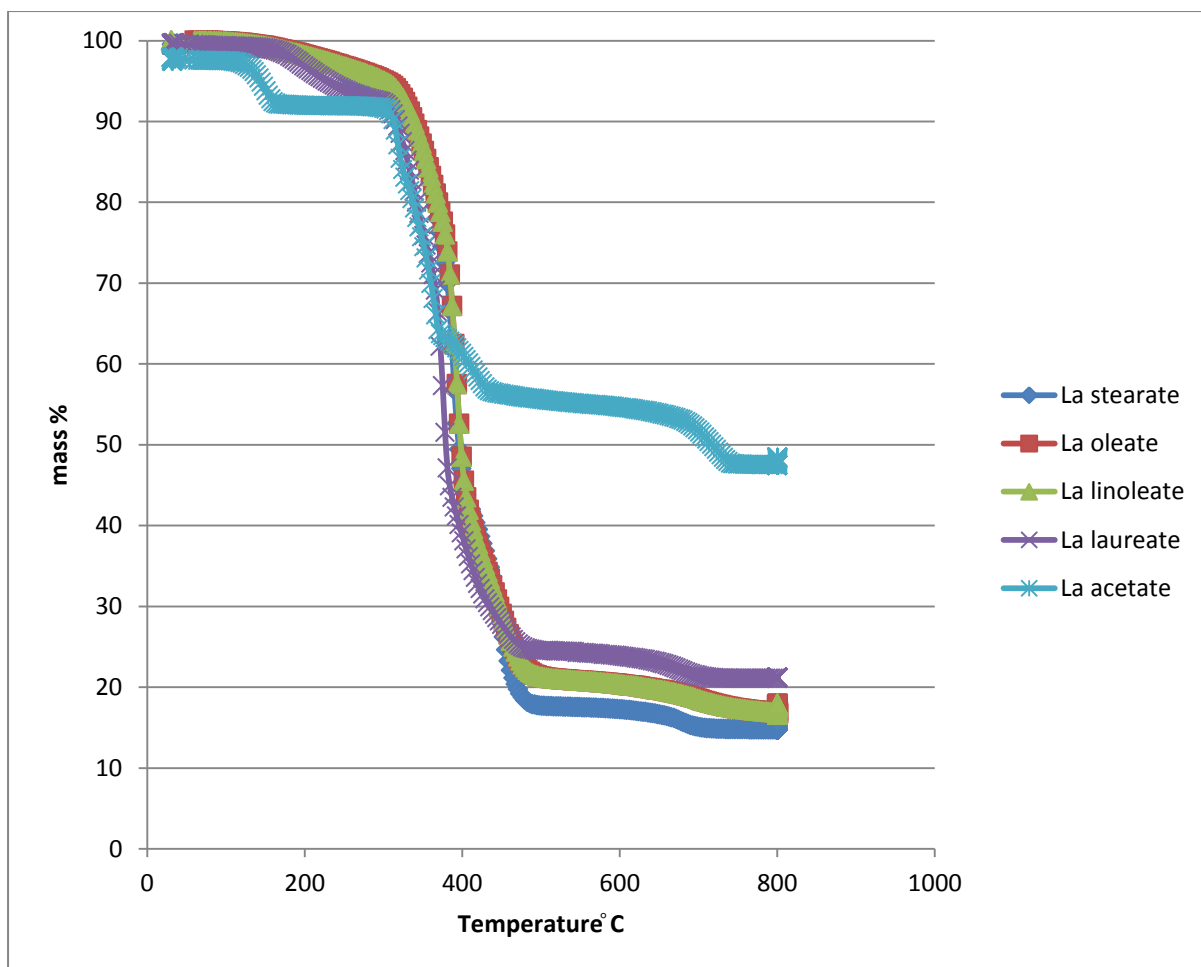


Figure 51. Comparison TGA of precursors for  $\text{La}_2\text{O}_3$ .

The results of the TGA give that Lanthanum laureate decomposes at lower temperature, it means that the reaction could be done at lower temperature and it would make easier to carry out the reaction with the heater system and the material of the stir.



## 5. Conclusions

In this chapter will be concluded the results for all the catalysts synthesized.

It has been synthesized 10 core/shell catalysts.

Catalysts number 3, 4 and 5 are core/shells of MnO/CoO, formed by Co acetate as precursor to form the shell. These three catalysts were formed using a solution of MnO nanoparticles with 11.52 nm of size.

When CAT\_J03 was formed, there was an increment of the nanoparticles until 14.51 nm, however this catalyst does not have activity.

CAT\_J04 was tested by TGA and it lost 50% of the weight at high temperature because it was formed with a lot of organic compounds. It was calcined before tested by FT, but it did not present activity either.

Regarding CAT\_J05, there was an increment of the nanoparticles until 13.74 nm. This catalyst was tested after reduction between 400-500°C and it has high methane formation at higher temperatures and low selectivities for C<sub>4</sub>, C<sub>3</sub> and C<sub>5+</sub>.

On the other hand, the rest of the catalysts are a core/shell of Co/MnO, with the exception of CAT\_J08 that it is pure Co. Co nanoparticles were synthesized using Dicobalt octacarbonyl and the size of the nanoparticles were 5 and 8 nm. For catalysts number 1, 2, 6, and 7 were used Co nanoparticles of 5 nm; and 8nm Co nanoparticles were used for catalysts number 8, 9, and 10.

CAT\_J01 is a catalyst of Co coated with multi layer of MnO. It was tested by XRD and CoO was presented in the catalyst. With the TEM images, it is possible to size the nanoparticles giving an increment from 5 nm to 6.3 nm. This catalyst did not have activity before reduction, but after reduction the results were completely different. Comparing this catalyst with the others coated by different percents (0%, 25%, 50%, and 75%) of MnO in the surface of the core of Co, it is the catalyst with better results for the objective of this thesis. The catalysts were tested at 2:1 and 10:1 H<sub>2</sub>/CO ratio. Both ratios have similar results for the catalysts tested.

The highest conversion of the catalyst belongs to CAT\_J08, formed by pure Co. However, this catalyst has low O/P ratios of C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> and low selectivities for the desire products.

CAT\_J01 has high O/P ratio C<sub>2</sub> and C<sub>3</sub>, and also for selectivities C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>5+</sub>, C<sub>3=</sub> and C<sub>4=</sub>. Also, the methane, undesired product, formation is very low compared with the rest of the catalysts.

CAT\_J10, catalyst of Co coated 75% of the surface with MnO, has high O/P ratio C<sub>2</sub> and C<sub>4</sub> too. However the methane selectivity is too high.

It was proposed different precursors for the formation of Lanthanum oxide, La<sub>2</sub>O<sub>3</sub>, the precursors were: Lanthanum oleate; Lanthanum linoleate; Lanthanum laureate; and Lanthanum stearate. The first synthesization of Lanthanum oxide was done with La oleate, but it required a high temperature to react. Therefore, all the precursors proposed were characterized by TGA to know which one decompose at lower temperature. In conclusion, La laureate is the precursor that decomposes at lower temperature and it would be the optimal precursor.

## 6. Literature

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## 7. Attachments

### 7.1 Calculations

1) Co nanoparticles:

-First synthesis:

$$m_{Co} = m_{Co_2(CO)_8} \cdot 2 \text{ mol Co in } Co_2(CO)_8 \cdot \frac{M_{Co}}{M_{Co_2(CO)_8}}$$

$$m_{Co} = \frac{1,08 \text{ g}_{Co_2(CO)_8}}{341 \frac{\text{g}_{Co_2(CO)_8}}{\text{mol}}} \cdot 58 \frac{\text{g}_{Co}}{\text{mol}} \cdot 2 \text{ mol} = 0,372 \text{ g Co}$$

$$\text{Concentration Co nanoparticles 1} = \frac{372 \text{ mg Co}}{30 \text{ mL}} = 12,4 \frac{\text{mg Co}}{\text{mL}}$$

-Second synthesis:

$$m_{Co_2(CO)_8} = 1,08 \cdot 3 = 3,24 \text{ g } Co_2(CO)_8$$

$$\begin{aligned} m_{Co} &= m_{Co_2(CO)_8} \cdot 2 \text{ mol Co in } Co_2(CO)_8 \cdot \frac{M_{Co}}{M_{Co_2(CO)_8}} \\ &= 3,24 \text{ g } Co_2(CO)_8 \cdot 2 \text{ mol Co} \cdot 58,9 \frac{\text{g}_{Co}}{\text{mol}} \cdot \frac{1}{341 \frac{\text{g}_{Co_2(CO)_8}}{\text{mol}}} = 1,11 \text{ g Co} \end{aligned}$$

$$m_{Co \text{ total}} = 1,11 \text{ g} - 0,14 \text{ g (used in CAT_J08)} = 0,97 \text{ g Co}$$

$$\text{Concentration Co nanoparticles 2} = \frac{970 \text{ mg}_{Co}}{100 \text{ mL}_{OD}} = 9,7 \frac{\text{mg Co}}{\text{mL}}$$

2) Synthesis Mn Oleate:

-Manganese acetate:

$$V_{Co \text{ nanoparticles 1}} = 2,5 \text{ mL}; m_{Co} = 0,372 \text{ g Co} \cdot \frac{2,5 \text{ mL}}{30 \text{ mL}} = 0,031 \text{ g Co}$$

$$m_{MnO} = 2 \cdot 0,031 \text{ g} = 0,062 \text{ g};$$

$$n_{MnO} = \frac{0,062 \text{ g}}{70,9 \frac{\text{g}}{\text{mol}}} = 0,00874 \text{ mol}$$

$$m_{\text{Manganese acetate}} = 0,00874 \text{ mol} \cdot 173 \frac{\text{g}}{\text{mol}} = 0,1512 \text{ g};$$

-Oleic acid:

$$n_{OA} = 2 \cdot 0,00874 \text{ mol MnO} = 0,001749 \text{ mol}$$

(Mnoleate is formed of 1 mol of Mn and 2 mol of OA)

$$V_{OA} = \frac{n_{OA} \cdot M_{OA}}{\rho_{OA}} = 0,001749 \text{ mol} \cdot 282,46 \frac{\text{g}}{\text{mol}} \cdot \frac{0,494006 \text{ g}}{0,895 \frac{\text{g}}{\text{mol}}} = 0,551962 \text{ mL}$$

3) CAT\_J01:

-Co:

2,5mL of the solution of Co nanoparticles 1 in 2,5 mL 1-Octadecene.

$$m_{Co} = \frac{2,5 \text{ mL}}{30 \text{ mL}} \cdot 0,372 \text{ g} = 0,031 \text{ g}$$

-Manganese acetate:

$$m_{MnO} = 2 \cdot 0,031 \text{ g} = 0,062 \text{ g}; n_{MnO} = \frac{0,062 \text{ g}}{70,9 \frac{\text{g}}{\text{mol}}} = 0,00874 \text{ mol}$$

$$m_{Mn \text{ acetate}} = 0,00874 \text{ g MnO} \cdot 173 \frac{\text{g}}{\text{mol}} = 0,1512 \text{ g};$$

-OA:

$$n_{OA} = 2 \cdot 0,00874 \text{ mol} = 0,001749 \text{ mol};$$

$$V_{OA} = n_{OA} \cdot M_{OA} \cdot \frac{1}{\rho_{OA}} = 0,001749 \text{ mol} \cdot 282,46 \frac{\text{g}}{\text{mol}} \cdot \frac{1}{0,895 \frac{\text{g}}{\text{mL}}} = 0,5519 \text{ mL}$$

-1-Octadecene: 5mL

-Support: 12% Loading.

$$\text{Formula for calculation support mass: } m_{\text{support}} = \frac{m_{Co}}{\text{loading}} - m_{Co}$$

$$m_{Co} = \frac{5 \text{ mL of solution } \frac{Co}{MnO}}{10 \text{ mL total}} \cdot 0,031 \text{ g Co} = 0,0155 \text{ g Co}$$

$$m_{\text{support}} = \frac{0,0155 \text{ g}}{0,12} - 0,0155 \text{ g} = 0,1137 \text{ g MCF} - 26$$

4) CAT\_J02:

-Co:

2,5mL of the solution of Conanoparticles  $1.m_{Co} = 0,031g$ ;

-Manganese salt:

$$V_{Co} = \frac{0,031g}{8,89\frac{g}{cm^3}} = 0,003487cm^3;$$

Particles properties: Size Co nanoparticles =5 nm

$$V = \pi \cdot \frac{4}{3} \cdot \left(\frac{5nm}{2} \cdot 10^{-7}\frac{cm}{nm}\right)^3 = 6,5449 \cdot 10^{-20}cm^3;$$

$$Total\ number = \frac{0,003487cm^3}{6,54498 \cdot 10^{-20}cm^3} = 5,3278 \cdot 10^{16};$$

$$Total\ surface = 4 \cdot \pi \cdot \left(\frac{5}{2}\right)^2 \cdot 5,3278 \cdot 10^{16} = 4,1844 \cdot 10^{18}nm^2;$$

Coating: Surface to be covered= 50%

$$Total\ surface\ to\ be\ covered = 4,1844 \cdot 10^{18}nm^2 \cdot 50\% = 2,0922 \cdot 10^{18}nm^2;$$

$$CrossectionMnO = \pi \cdot r_{Mn}^2 + \pi \cdot r_O^2 = \pi \cdot 0,127^2nm + \pi \cdot 0,152^2nm = 0,1232nm^2;$$

$$Total\ number\ of\ MnO = \frac{2,0922 \cdot 10^{18}nm^2}{0,1232nm^2} = 1,697 \cdot 10^{19};$$

$$n_{Mn} = \frac{1,697 \cdot 10^{19}}{6,022 \cdot 10^{23}} = 2,8188 \cdot 10^{-5}mol$$

$$Amount\ MnOleate = n_{Mn} \cdot M_{MnOleate} = 2,8188 \cdot 10^{-5}mol \cdot 617,84\frac{g}{mol} = 0,01741g ;$$

$$Amount\ solution = \frac{m_{MnOleate}}{concentration\ solution} = \frac{0,01741g}{0,127\ g/L} = 0,1371L;$$

-1-Octadecene: 5mL

-Support:

$$m_{Co} = \frac{8,5mL\ of\ solution\ \frac{Co}{MnO}}{10mL\ total} \cdot 0,031gCo = 0,02635\ gCo$$

$$m_{support} = \frac{0,02635g}{0,12} - 0,02635g = 0,1932\ gMCF - 26$$

Total:

0,01741 g Mn oleate + 5 mL OD +2,5 mL Co nanoparticles + 193,2 mg MCF-26

5) MnO:

The amounts were half of the publication.[19]

$$m_{Mn\ acetate} = \frac{0,004\ mol}{2} \cdot 173,027 \frac{g}{mol} = 0,34605\ g ;$$

$$V_{1-octadecene} = \frac{15mL}{2} = 7,5\ mL ;$$

$$V_{OA} = \frac{3g}{0,895 \frac{g}{mL} \cdot 2} = 1,6759\ mL$$

6) CAT\_J03

-MnO:

$$V_{MnO} = 2mL; m_{MnO} = 2\ mL \cdot 0,0156 \frac{g}{mL} = 0,0312\ g ;$$

-Co acetate:

$$n_{Co} = \frac{0,0312g}{58,93 \frac{g}{mol}} = 0,000529\ mol$$

$$m_{Co\ acetate} = 0,000529\ mol \cdot 249,08 \frac{g}{mol} = 0,1318\ g$$

-OA:

$$V_{OA} = 2 \cdot 0,000529\ mol \cdot 282,46 \frac{g}{mol} \cdot \frac{1}{0,895 \frac{g}{mL}} = 0,3341\ mL ,\ OA\ in\ excess\ 0,0663\ mL$$

$$V_{OA} = 0,4\ mL$$

-1-Octadecene: 15 mL

-Support:

$$m_{Co} = \frac{0,0312gCoO}{74,93g\ CoO/mol} \cdot 58,93\ gCo/mol = 0,0247\ gCo$$

$$m_{support} = \frac{0,0247g}{0,12} - 0,0247g = 0,1811\ gMCF - 26$$

7) CAT\_J04

-MnO:

$$V_{MnO} = 2 \text{ mL};$$

$$m_{MnO} = V_{MnO} \cdot C_{MnO} = 2 \text{ mL} \cdot 15,69 \frac{\text{mg}}{\text{mL}} = 0,03138 \text{ g}$$

-Co:

$$d_{MnO} = 1,478 \cdot 10^{-8} \text{ m}; \rho_{MnO} = 5400000 \text{ g/m}^3;$$

$$V_{MnO} = \frac{0,03138 \text{ g}}{5400000 \text{ g/m}^3} = 5,811119 \cdot 10^{-9} \text{ m}^3$$

$$V_{\text{single particle MnO}} = \frac{4}{3} \cdot \pi \cdot r^2 = \frac{4}{3} \cdot \pi \cdot \left(\frac{d}{2}\right)^2 = \frac{4}{3} \cdot \pi \cdot \left(\frac{1,478 \cdot 10^{-8} \text{ m}}{2}\right)^2$$
$$= 1,69053 \cdot 10^{-24} \text{ m}^3$$

$$n^\circ(\text{MnO}) = \frac{V_{MnO}}{V_{\text{single particle MnO}}} = \frac{5,811119 \cdot 10^{-9} \text{ m}^3}{1,69053 \cdot 10^{-24} \text{ m}^3} = 3,43746 \cdot 10^{15}$$

$$V_{\text{total}} = 3,43746 \cdot 10^{15} \cdot 1,69053 \cdot 10^{-24} \text{ m}^3 = 5,811119 \cdot 10^{-9} \text{ m}^3;$$

$$\rho_{Co} = 8900000 \text{ g/m}^3$$

$$m_{Co} = V_{\text{total}} \cdot \rho_{Co} = 5,811119 \cdot 10^{-9} \text{ m}^3 \cdot 8900000 \frac{\text{g}}{\text{m}^3} = 0,051718889 \text{ g}$$

$$m_{Co \text{ acetate}} = \frac{m_{Co}}{M_{Co}} \cdot M_{Co \text{ acetate}} = \frac{0,051718889 \text{ g}}{58,93} \cdot 249,08 = 0,218 \text{ g}$$

-Oleic acid: 0,4 mL

-1-Octadecene: 15mL

-Support:

$$m_{\text{support}} = \frac{0,0517 \text{ g}}{0,12} - 0,0517 \text{ g} = 0,3791 \text{ gMCF} - 26$$



8) CAT\_J05

-MnO:

$$V_{MnO} = 1 \text{ mL};$$

$$m_{MnO} = V_{MnO} \cdot C_{MnO} = 1 \text{ mL} \cdot 15,69 \frac{\text{mg}}{\text{mL}} = 0,01569 \text{ g}$$

-Co acetate:  $(\text{CH}_3\text{COO})_2\text{Co} \cdot 4\text{H}_2\text{O}$  (tetrahydrate)

$$m_{Co} = 15,69 \text{ mg}; n_{Co} = \frac{0,01569 \text{ g}}{58,93 \frac{\text{g}}{\text{mol}}} = 0,000266 \text{ mol} = n_{Co \text{ acetate}}$$

$$m_{Co \text{ acetate}} = n_{Co \text{ acetate}} \cdot M_{Co \text{ acetate}} = 0,000266 \text{ mol} \cdot 249,08 \frac{\text{g}}{\text{mol}} = 0,0662 \text{ g}$$

-Oleicacid:

$$V_{OA} = n_{OA} \cdot M_{OA} \cdot \frac{1}{\rho_{OA}} = 0,000266 \text{ mol} \cdot \frac{1}{2} \cdot 282,46 \frac{\text{g}}{\text{mol}} \cdot \frac{1}{0,895 \frac{\text{g}}{\text{mL}}} = 0,042 \text{ mL}$$

-Oleylamine(OAm):

$$V_{OAm} = n_{OAm} \cdot M_{OAm} \cdot \frac{1}{\rho_{OAm}} = 0,000266 \text{ mol} \cdot \frac{3}{2} \cdot 267,49 \frac{\text{g}}{\text{mol}} \cdot \frac{1}{0,813 \frac{\text{g}}{\text{mL}}} = 0,1314 \text{ mL}$$

-1,2 hexadecanediol:

$$V_{hdiol} = n_{hdiol} \cdot M_{hdiol} \cdot \frac{1}{\rho_{hdiol}} = 0,000266 \text{ mol} \cdot \frac{3}{2} \cdot 258,44 \frac{\text{g}}{\text{mol}} = 0,1031 \text{ g}$$

-Support:

The amount of Co used in the support calculation is calculated in a theoretical way.

$$m_{support} = \frac{0,0353 \text{ g}}{0,12} - 0,0353 \text{ g} = 0,2589 \text{ gMCF} - 26$$

9) CAT\_J06

-Co:

2,5 mL Co nanoparticles 1 in hexane.

-MnOleate:

$$m_{Co} = 0,031 \text{ g}; V_{Co} = \frac{0,031 \text{ g}}{8,89 \frac{\text{g}}{\text{cm}^3}} = 0,003487 \text{ cm}^3;$$

Particles properties: Size=5 nm

$$V = \pi \cdot \frac{4}{3} \cdot \left( \frac{5 \text{ nm}}{2} \cdot 10^{-7} \frac{\text{cm}}{\text{nm}} \right)^3 = 6,5449 \cdot 10^{-20} \text{ cm}^3;$$

$$\text{Total number} = \frac{0,003487 \text{ cm}^3}{6,54498 \cdot 10^{-20} \text{ cm}^3} = 5,3278 \cdot 10^{16};$$

$$\text{Total surface} = 4 \cdot \pi \cdot \left( \frac{5}{2} \right)^2 \cdot 5,3278 \cdot 10^{16} = 4,1844 \cdot 10^{18} \text{ nm}^2;$$

Copper coating: Surface to be covered= 100%

$$\text{Total surface to be covered} = 4,1844 \cdot 10^{18} \text{ nm}^2 \cdot 100\% = 4,1844 \cdot 10^{18} \text{ nm}^2;$$

$$\text{Crosssection MnO} = \pi \cdot r_{\text{Mn}}^2 + \pi \cdot r_{\text{O}}^2 = \pi \cdot 0,127^2 \text{ nm} + \pi \cdot 0,152^2 \text{ nm} = 0,1232 \text{ nm}^2;$$

$$\text{Total number of MnO} = \frac{4,1844 \cdot 10^{18} \text{ nm}^2}{0,1232 \text{ nm}^2} = 3,395 \cdot 10^{19};$$

$$n_{\text{Mn}} = \frac{3,395 \cdot 10^{19}}{6,022 \cdot 10^{23}} = 5,6376 \cdot 10^{-5} \text{ mol}$$

$$\text{Amount MnOleate} = n_{\text{Mn}} \cdot M_{\text{MnOleate}} = 5,6376 \cdot 10^{-5} \text{ mol} \cdot 617,84 \frac{\text{g}}{\text{mol}} = 0,0348 \text{ g};$$

$$\text{Amount solution} = \frac{m_{\text{MnOleate}}}{\text{concentration solution}} = \frac{0,0348 \text{ g}}{0,127 \text{ g/L}} = 0,2742 \text{ L}$$

-7,5mL 1-Octadecene

-Support:

$$m_{\text{support}} = \frac{0,031 \text{ g}}{0,12} - 0,031 \text{ g} = 0,2273 \text{ gMCF} - 26$$

10) CAT\_J07

-Solution:

2,5 mL Co nanoparticles1 in hexane.

-MnOleate:

$$m_{\text{Co}} = 0,031 \text{ g}; V_{\text{Co}} = \frac{0,031 \text{ g}}{8,89 \frac{\text{g}}{\text{cm}^3}} = 0,003487 \text{ cm}^3;$$

Particles properties: Size=5 nm

$$V = \pi \cdot \frac{4}{3} \cdot \left( \frac{5 \text{ nm}}{2} \cdot 10^{-7} \frac{\text{cm}}{\text{nm}} \right)^3 = 6,5449 \cdot 10^{-20} \text{ cm}^3;$$

$$\text{Total number} = \frac{0,003487 \text{ cm}^3}{6,54498 \cdot 10^{-20} \text{ cm}^3} = 5,3278 \cdot 10^{16};$$

$$\text{Total surface} = 4 \cdot \pi \cdot \left( \frac{5}{2} \right)^2 \cdot 5,3278 \cdot 10^{16} = 4,1844 \cdot 10^{18} \text{ nm}^2;$$

Coating: Surface to be covered= 200%

$$\text{Total surface to be covered} = 4,1844 \cdot 10^{18} \text{nm}^2 \cdot 200\% = 8,3689 \cdot 10^{18} \text{nm}^2;$$

$$\text{CrosssectionMnO} = \pi \cdot r_{\text{Mn}}^2 + \pi \cdot r_{\text{O}}^2 = \pi \cdot 0,127^2 \text{nm} + \pi \cdot 0,152^2 \text{nm} = 0,1232 \text{nm}^2;$$

$$\text{Total number of MnO} = \frac{8,3689 \cdot 10^{18} \text{nm}^2}{0,1232 \text{nm}^2} = 6,79 \cdot 10^{19};$$

$$n_{\text{Mn}} = \frac{6,79 \cdot 10^{19}}{6,022 \cdot 10^{23}} = 11,27 \cdot 10^{-5} \text{mol}$$

$$\text{Amount MnOleate} = n_{\text{Mn}} \cdot M_{\text{MnOleate}} = 11,27 \cdot 10^{-5} \text{mol} \cdot 617,84 \frac{\text{g}}{\text{mol}} = 0,0696 \text{g};$$

$$\text{Amount solution} = \frac{m_{\text{MnOleate}}}{\text{concentration solution}} = \frac{0,0696 \text{g}}{0,127 \text{g/L}} = 0,5485 \text{L};$$

-7,5mL 1-Octadecene

-Support:

$$m_{\text{support}} = \frac{0,031 \text{g}}{0,12} - 0,031 \text{g} = 0,2273 \text{gMCF} - 26$$

11) CAT\_J08

-Co: 11,05mL Co nanoparticles2

-Support: 1g MCF-26

12) CAT\_J09

-Solution:

For using the same amount of support than in CAT\_J08:

$$m_{\text{Co}} = \frac{m_{\text{support}} \cdot \text{loading}}{1 - \text{loading}} = \frac{1 \text{g} \cdot 0,12}{1 - 0,12} = 0,1364 \text{gCo}$$

$$V = \frac{136,4 \text{mg}}{9,7 \frac{\text{mgCo}}{\text{mL}}} = 14 \text{mL of the solution of Conanoparticles2.}$$

-Manganese salt:

$$m_{\text{Co}} = 0,1364 \text{g}; V_{\text{Co}} = \frac{0,1364 \text{g}}{8,89 \frac{\text{g}}{\text{cm}^3}} = 0,01534 \text{cm}^3;$$

Particles properties: Size=8,06 nm

$$V = \pi \cdot \frac{4}{3} \cdot \left( \frac{8,06 \text{nm}}{2} \cdot 10^{-7} \frac{\text{cm}}{\text{nm}} \right)^3 = 2,7416 \cdot 10^{-19} \text{cm}^3;$$

$$\text{Total number} = \frac{0,01534 \text{cm}^3}{2,7416 \cdot 10^{-19} \text{cm}^3} = 5,5964 \cdot 10^{16};$$

$$\text{Total surface} = 4 \cdot \pi \cdot \left(\frac{8,06}{2}\right)^2 \cdot 5,5964 \cdot 10^{16} = 1,1421 \cdot 10^{19} \text{nm}^2;$$

Coating: Surface to be covered= 25%

$$\text{Total surface to be covered} = 1,1421 \cdot 10^{19} \text{nm}^2 \cdot 25\% = 2,8554 \cdot 10^{18} \text{nm}^2;$$

$$\text{CrossectionMnO} = \pi \cdot r_{Mn}^2 + \pi \cdot r_O^2 = \pi \cdot 0,127^2 \text{nm} + \pi \cdot 0,152^2 \text{nm} = 0,1232 \text{nm}^2;$$

$$\text{Total number of MnO} = \frac{2,8554 \cdot 10^{18} \text{nm}^2}{0,1232 \text{nm}^2} = 2,3166 \cdot 10^{19};$$

$$n_{Mn} = \frac{2,3166 \cdot 10^{19}}{6,022 \cdot 10^{23}} = 3,847 \cdot 10^{-5} \text{mol}$$

$$m_{Mn \text{ acetate}} = n_{Mn} \cdot M_{Mn \text{ acetate}} = 3,847 \cdot 10^{-5} \text{mol} \cdot 172,02 \frac{\text{g}}{\text{mol}} = 0,006617 \text{g};$$

-Oleicacid

$$V_{OA} = \frac{0,00661 \text{gMnacetate}}{173 \frac{\text{gMnacetate}}{\text{mol}}} \cdot 2 \text{mol} \cdot 282 \frac{\text{gOA}}{\text{mol}} \cdot \frac{1}{0,895 \frac{\text{g}}{\text{mL}}} = 0,025 \text{mL};$$

-1-Octadecene: 6 mL

-Support: 1g MCF-26

### 13) CAT\_J10

-Solution:

$$V = \frac{136,4 \text{mg}}{9,7 \frac{\text{mgCo}}{\text{mL}}} = 14 \text{mL of the solution of Conanoparticles2.}$$

-Manganese salt:

$$m_{Co} = 0,1364 \text{g}; V_{Co} = \frac{0,1364 \text{g}}{8,89 \frac{\text{g}}{\text{cm}^3}} = 0,01534 \text{cm}^3;$$

Particles properties: Size=8,06 nm

$$V = \pi \cdot \frac{4}{3} \cdot \left(\frac{8,06 \text{nm}}{2} \cdot 10^{-7} \frac{\text{cm}}{\text{nm}}\right)^3 = 2,7416 \cdot 10^{-19} \text{cm}^3;$$

$$\text{Total number} = \frac{0,01534 \text{cm}^3}{2,7416 \cdot 10^{-19} \text{cm}^3} = 5,5964 \cdot 10^{16};$$

$$\text{Total surface} = 4 \cdot \pi \cdot \left(\frac{8,06}{2}\right)^2 \cdot 5,5964 \cdot 10^{16} = 1,1421 \cdot 10^{19} \text{nm}^2;$$

Coating: Surface to be covered= 75%

$$\text{Total surface to be covered} = 1,1421 \cdot 10^{19} \text{nm}^2 \cdot 75\% = 8,56624 \cdot 10^{18} \text{nm}^2;$$

$$\text{CrossectionMnO} = \pi \cdot r_{Mn}^2 + \pi \cdot r_O^2 = \pi \cdot 0,127^2 \text{nm} + \pi \cdot 0,152^2 \text{nm} = 0,1232 \text{nm}^2;$$

$$\text{Total number of MnO} = \frac{8,56624 \cdot 10^{18} \text{nm}^2}{0,1232 \text{nm}^2} = 6,95 \cdot 10^{19};$$

$$n_{Mn} = \frac{6,95 \cdot 10^{19}}{6,022 \cdot 10^{23}} = 11,541 \cdot 10^{-5} \text{ mol}$$

$$\text{Amount manganese salt} = n_{Mn} \cdot M_{Mnacetate} = 11,541 \cdot 10^{-5} \text{ mol} \cdot 172,02 \frac{\text{g}}{\text{mol}} = 0,0198 \text{ g};$$

-Oleicacid

$$V_{OA} = \frac{0,0198 \text{ g Mnacetate}}{173 \frac{\text{g Mnacetate}}{\text{mol}}} \cdot 2 \text{ mol} \cdot 282 \frac{\text{g OA}}{\text{mol}} \cdot \frac{1}{0,895 \frac{\text{g}}{\text{mL}}} = 0,072 \text{ mL};$$

-1-Octadecene: 6 mL

-Support: 1g MCF-26

14) Precursor La<sub>2</sub>O<sub>3</sub>:

La oleate:

$$n_{LaOleate} = \frac{m_{LaOleate}}{M_{LaOleate}} = \frac{0,5g}{983,26 \frac{g}{mol}} = 5,09 \cdot 10^{-4} mol;$$

$$m_{La\ acetate} = n \cdot M_{La\ acetate} = 5,085 \cdot 10^{-4} mol \cdot 316,05 \frac{g}{mol} = 0,16071 g ;$$

$$V_{OA} = n_{OA} \cdot \frac{M_{OA}}{\rho_{OA}} = 3 \cdot 5,09 \cdot 10^{-4} mol \cdot 282,46 \frac{g}{mol} \cdot \frac{1}{0,895 \frac{g}{mL}} = 0,4814 mL$$

It was synthesized 1.5 g of La oleate so the amounts required were: 0.6 g of La acetate and 1.7 mL of OA.

La linoleic:

$$n_{La} = m_{Lacetate} \cdot \frac{1}{M_{Laacetate}} \cdot 3 = 0,3 g \cdot \frac{1}{334,05 \frac{g}{mol}} \cdot 3 = 0,000898 mol;$$

$$m_{Linoleicacid} = 0,000898 mol \cdot 280,45 \frac{g}{mol} = 0,7556 g; V_{Linoleicacid} = \frac{0,7556 g}{0,9 g/mL} = 0,839545 mL$$

Lalaureate:

$$n_{La} = m_{La\ cetate} \cdot \frac{1}{M_{La\ acetate}} \cdot 3 = 0,5 g \cdot \frac{1}{316,05 \frac{g}{mol}} \cdot 3 = 0,00474 mol;$$

$$m_{Lauric\ acid} = 0,00474 mol \cdot 200,317 \frac{g}{mol} = 0,9507 g$$

La stearate:

$$n_{La} = m_{Lacetate} \cdot \frac{1}{M_{Laacetate}} \cdot 3 = 0,5 g \cdot \frac{1}{316,05 \frac{g}{mol}} \cdot 3 = 0,00474 mol;$$

$$m_{Stearicacid} = 0,00474 mol \cdot 284,48 \frac{g}{mol} = 1,3484 g$$

## 7.2 Tables

### 1) CAT\_J01

Table 4. CAT\_J01 Reduction, ratio 2:1.

<b>GHSV (l CO/h/g)</b>	0,15	0,3	0,6
<b>SCH4</b>	25,14%	21,61%	20,0 %
<b>SC2</b>	7,10%	6,42%	6,1 %
<b>SC3</b>	17,26%	16,24%	15,3 %
<b>SC4</b>	16,75%	17,23%	16,8 %
<b>SC5?</b>	15,94%	17,08%	17,7 %
<b>SC6?</b>	9,15%	11,20%	11,4 %
<b>SC7?</b>	8,66%	10,23%	12,5 %
<b>O/P C2</b>	0,65	0,99	1,9
<b>O/P C3</b>	3,81	4,51	5,5
<b>O/P C4</b>	2,05	3,02	4,3
<b>SC5+</b>	33,74%	38,51%	41,7 %
<b>XCO</b>	9,65%	6,00%	3,4 %
<b>XH2</b>	7,31%	7,00%	6,3 %
<b>SC3-</b>	3,59%	2,95%	2,4 %
<b>SC3=</b>	13,68%	13,29%	12,9 %
<b>SC4-</b>	11,12%	12,76%	13,4 %
<b>SC4=</b>	5,42%	4,23%	3,1 %

Table 5. CAT\_J01 Reduction, ratio 10:1, GHSV: 0,9 l/g/h.

<b>SCH4</b>	37,1 %
<b>SC2</b>	8,6 %
<b>SC3</b>	17,0 %
<b>SC4</b>	14,3 %
<b>SC5?</b>	11,1 %
<b>SC6?</b>	5,5 %
<b>SC7?</b>	6,4 %
<b>O/P C2</b>	1,653
<b>O/P C3</b>	5,453
<b>O/P C4</b>	4,092
	1
<b>SC5+</b>	23,0 %
<b>XCO</b>	3,0 %
<b>XH2</b>	-0,5 %
<b>SC3-</b>	2,6 %
<b>SC3=</b>	14,4 %
<b>SC4-</b>	11,3 %
<b>SC4=</b>	2,8 %

2) CAT\_J02

Table 6. CAT\_J02, ratio 2:1.

<b>GHSV (l CO/h/g)</b>	0,15	0,3	0,6
<b>SCH4</b>	59,0 %	55,9 %	55,3 %
<b>SC2</b>	9,2 %	9,0 %	8,9 %
<b>SC3</b>	13,4 %	13,6 %	13,3 %
<b>SC4</b>	8,8 %	10,0 %	10,1 %
<b>SC5?</b>	5,2 %	6,4 %	6,5 %
<b>SC6?</b>	2,7 %	3,4 %	3,6 %
<b>SC7?</b>	1,7 %	1,8 %	2,4 %
<b>O/P C2</b>	0,5627	0,763	1,241
<b>O/P C3</b>	2,415	2,709	3,004
<b>O/P C4</b>	2,641	3,472	4,418
<b>SC5+</b>	9,6 %	11,6 %	12,4 %
<b>XCO</b>	7,2 %	5,2 %	2,9 %
<b>XH2</b>	6,7 %	5,7 %	5,2 %
<b>SC3-</b>	3,9 %	3,7 %	3,3 %
<b>SC3=</b>	9,5 %	10,0 %	10,0 %
<b>SC4-</b>	6,2 %	7,5 %	7,9 %
<b>SC4=</b>	2,4 %	2,2 %	1,8 %

Table 7. CAT\_J02 Reduction, ratio 2:1.

<b>GHSV (l CO/h/g)</b>	0,3	0,6
<b>SCH4</b>	56,3 %	55,6 %
<b>SC2</b>	9,5 %	9,6 %
<b>SC3</b>	12,7 %	12,5 %
<b>SC4</b>	9,4 %	9,3 %
<b>SC5?</b>	6,1 %	6,2 %
<b>SC6?</b>	3,4 %	3,6 %
<b>SC7?</b>	2,5 %	3,2 %
<b>O/P C2</b>	1,45	2,03
<b>O/P C3</b>	3,40	3,58
<b>O/P C4</b>	4,26	5,07
<b>SC5+</b>	12,1 %	13,0 %
<b>XCO</b>	3,8 %	2,0 %
<b>XH2</b>	1,6 %	1,9 %
<b>SC3-</b>	2,9 %	2,7 %
<b>SC3=</b>	9,8 %	9,8 %
<b>SC4-</b>	7,3 %	7,5 %
<b>SC4=</b>	1,7 %	1,5 %



Table 8. CAT\_J02, ratio 10:1.

<b>SCH4</b>	77,6 %
<b>SC2</b>	7,8 %
<b>SC3</b>	7,4 %
<b>SC4</b>	3,9 %
<b>SC5?</b>	1,6 %
<b>SC6?</b>	0,6 %
<b>SC7?</b>	1,1 %
<b>O/P C2</b>	1,337
<b>O/P C3</b>	2,589
<b>O/P C4</b>	5,519
	1
<b>SC5+</b>	3,3 %
<b>XCO</b>	3,0 %
<b>XH2</b>	-1,9 %
<b>SC3-</b>	2,1 %
<b>SC3=</b>	5,4 %
<b>SC4-</b>	3,1 %
<b>SC4=</b>	0,6 %

3) CAT\_J05

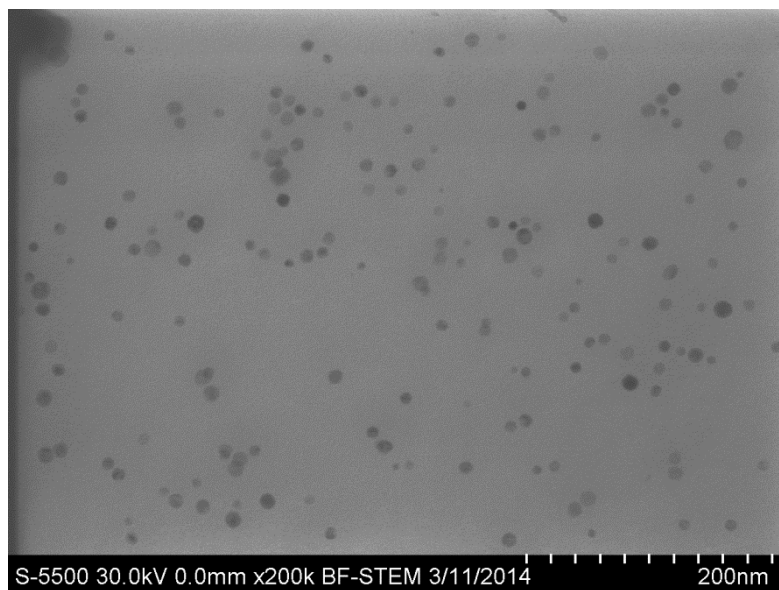


Figure 52. TEM result MnO/CoO with hexadecanediol.

4) CAT\_J08

Table 9. CAT\_J08, ratio 2:1.

<b>GHSV (l CO/h/g)</b>	0.6	0.3	0.15	0.1	0.05
<b>SCH4</b>	37,27%	32,75%	34,59%	35,72%	37,45%
<b>SC2</b>	6,50%	5,46%	5,11%	5,29%	5,50%
<b>SC3</b>	12,88%	11,09%	10,82%	10,93%	10,93%
<b>SC4</b>	15,65%	14,08%	13,45%	13,16%	12,80%
<b>SC5?</b>	16,37%	16,37%	16,21%	15,72%	14,68%
<b>SC6?</b>	5,76%	10,16%	12,18%	13,29%	9,71%
<b>SC7?</b>	5,56%	10,08%	7,63%	5,90%	8,92%
<b>O/P C2</b>	0,0753	0,0602	0,0000	0,0000	0,0000
<b>O/P C3</b>	0,6674	0,3177	0,1953	0,1307	0,1179
<b>O/P C4</b>	2,4434	2,8092	3,0748	3,4685	3,5372
	100,00%	100,00%	100,00%	100,00%	100,00%
<b>SC5+</b>	27,70%	36,62%	36,02%	34,91%	33,32%
<b>XCO</b>	13,14%	24,14%	43,22%	56,44%	98,03%
<b>XH2</b>	10,72%	24,81%	46,79%	63,12%	86,51%
<b>SC3-</b>	7,73%	8,42%	9,07%	9,67%	9,77%
<b>SC3=</b>	5,16%	2,67%	1,75%	1,26%	1,15%
<b>SC4-</b>	11,06%	10,34%	10,10%	10,14%	9,91%
<b>SC4=</b>	4,54%	3,68%	3,29%	2,93%	2,80%

Table 10. CAT\_J08 Reduction, ratio 2:1.

<b>GHSV (l CO/h/g)</b>	0.6	0.3	0.15	0.1	0.05
<b>SCH4</b>	29,23%	29,46%	31,00%	31,10%	33,14%
<b>SC2</b>	6,19%	5,72%	5,84%	5,74%	6,01%
<b>SC3</b>	13,89%	13,68%	13,77%	13,24%	13,47%
<b>SC4</b>	16,95%	16,47%	16,07%	15,26%	15,31%
<b>SC5?</b>	16,74%	17,03%	16,20%	15,41%	15,37%
<b>SC6?</b>	10,79%	10,37%	12,54%	7,88%	9,39%
<b>SC7?</b>	6,22%	7,28%	4,58%	11,38%	7,32%
<b>O/P C2</b>	0,0461	0,0000	0,0000	0,0000	0,0000
<b>O/P C3</b>	0,2209	0,1221	0,0590	0,0424	0,0539
<b>O/P C4</b>	2,8920	3,6190	5,2075	5,9239	5,4927
<b>SC5+</b>	33,75%	34,68%	33,32%	34,66%	32,08%
<b>XCO</b>	21,07%	32,22%	53,35%	64,53%	97,66%
<b>XH2</b>	18,95%	33,53%	58,43%	71,78%	86,50%
<b>SC3-</b>	11,37%	12,19%	13,00%	12,70%	12,78%
<b>SC3=</b>	2,51%	1,49%	0,76%	0,54%	0,69%
<b>SC4-</b>	12,49%	12,76%	13,28%	12,83%	12,70%
<b>SC4=</b>	4,32%	3,53%	2,55%	2,17%	2,32%

Table 11. CAT\_J08, ratio 10:1.

<b>SCH4</b>	61,68%
<b>SC2</b>	7,60%
<b>SC3</b>	9,75%
<b>SC4</b>	10,87%
<b>SC5?</b>	6,42%
<b>SC6?</b>	1,85%
<b>SC7?</b>	1,82%
<b>O/P C2</b>	0,0633
<b>O/P C3</b>	0,5392
<b>O/P C4</b>	2,9026
<b>SC5+</b>	10,09%
<b>XCO</b>	9,05%
<b>XH2</b>	6,76%
<b>SC3-</b>	6,65%
<b>SC3=</b>	3,10%
<b>SC4-</b>	8,02%
<b>SC4=</b>	2,78%

5) CAT\_J09

Table 12. CAT\_J09, ratio 2:1.

<b>GHSV (l CO/h/g)</b>	0.6	0.3	0.15	0.1
<b>SCH4</b>	59,60%	59,38%	57,88%	56,05%
<b>SC2</b>	6,36%	6,30%	6,21%	6,23%
<b>SC3</b>	10,82%	11,59%	12,13%	12,56%
<b>SC4</b>	10,29%	10,83%	11,31%	11,80%
<b>SC5?</b>	7,91%	8,42%	9,10%	9,69%
<b>SC6?</b>	2,25%	1,90%	1,67%	1,84%
<b>SC7?</b>	2,77%	1,57%	1,71%	1,82%
<b>O/P C2</b>	0,931	0,539	0,312	0,253
<b>O/P C3</b>	3,881	3,315	2,421	2,041
<b>O/P C4</b>	11,149	8,737	5,619	4,598
<b>SC5+</b>	12,93%	11,89%	12,48%	13,36%
<b>XCO</b>	2,52%	6,19%	14,26%	19,25%
<b>XH2</b>	-3,28%	2,99%	13,36%	20,40%
<b>SC3-</b>	2,22%	2,69%	3,54%	4,13%
<b>SC3=</b>	8,61%	8,91%	8,58%	8,43%
<b>SC4-</b>	9,11%	9,49%	9,44%	9,55%
<b>SC4=</b>	0,82%	1,09%	1,68%	2,08%

Table 13. CAT\_J09 Reduction, ratio 2:1.

<b>GHSV (l CO/h/g)</b>	0.6	0.3	0.15	0.1
<b>SCH4</b>	53,21%	53,37%	53,77%	53,31%
<b>SC2</b>	6,32%	6,07%	5,97%	5,90%
<b>SC3</b>	12,08%	12,25%	12,53%	12,50%
<b>SC4</b>	11,84%	11,97%	12,18%	12,14%
<b>SC5?</b>	9,67%	10,07%	10,27%	10,26%
<b>SC6?</b>	4,61%	4,05%	3,57%	3,79%
<b>SC7?</b>	2,28%	2,22%	1,70%	2,10%
<b>O/P C2</b>	1,0764	0,5927	0,3250	0,2635
<b>O/P C3</b>	3,4589	2,9985	2,1851	1,8543
<b>O/P C4</b>	13,0555	9,6083	6,1112	5,0565
<b>SC5+</b>	16,56%	16,34%	15,54%	16,16%
<b>XCO</b>	5,69%	11,76%	23,14%	29,61%
<b>XH2</b>	-0,65%	8,74%	23,62%	33,05%
<b>SC3-</b>	2,71%	3,06%	3,94%	4,38%
<b>SC3=</b>	9,37%	9,19%	8,60%	8,12%
<b>SC4-</b>	10,74%	10,67%	10,33%	10,02%
<b>SC4=</b>	0,82%	1,11%	1,69%	1,98%

## 6) CAT\_J10

Table 14. CAT\_J10, ratio 2:1.

<b>GHSV (l CO/h/g)</b>	0.6	0.3	0.15	0.1
<b>SCH4</b>	58,46%	57,90%	57,08%	56,06%
<b>SC2</b>	6,14%	6,29%	6,15%	5,93%
<b>SC3</b>	11,12%	11,38%	11,99%	12,46%
<b>SC4</b>	10,72%	10,88%	11,26%	11,48%
<b>SC5?</b>	7,70%	7,77%	8,16%	6,10%
<b>SC6?</b>	3,12%	3,07%	2,96%	6,11%
<b>SC7?</b>	2,74%	2,71%	2,40%	1,87%
<b>O/P C2</b>	2,5532	2,0851	1,5477	1,2072
<b>O/P C3</b>	3,9908	4,0207	3,9448	3,9588
<b>O/P C4</b>	12,5416	12,8943	12,6867	12,0537
<b>SC5+</b>	13,56%	13,56%	13,52%	14,08%
<b>XCO</b>	0,20%	1,29%	4,68%	7,24%
<b>XH2</b>	-7,78%	-3,80%	4,80%	32,13%
<b>SC3-</b>	2,23%	2,27%	2,43%	2,51%
<b>SC3=</b>	8,89%	9,11%	9,57%	9,94%
<b>SC4-</b>	9,54%	9,72%	10,06%	10,27%
<b>SC4=</b>	0,76%	0,75%	0,79%	0,85%

Table 15. CAT\_J10, ratio 10:1.

<b>SCH4</b>	76,94%
<b>SC2</b>	5,59%
<b>SC3</b>	7,28%
<b>SC4</b>	6,08%
<b>SC5?</b>	2,94%
<b>SC6?</b>	0,76%
<b>SC7?</b>	0,41%
<b>O/P C2</b>	1,8526
<b>O/P C3</b>	3,2448
<b>O/P C4</b>	4,1694
<b>SC5+</b>	4,10%
<b>XCO</b>	0,54%
<b>XH2</b>	-0,10%
<b>SC3-</b>	1,72%
<b>SC3=</b>	5,57%
<b>SC4-</b>	4,73%
<b>SC4=</b>	1,14%