Synthesis of Metal Nanoparticles as Catalysts in the Fischer-Tropsch Process

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Abstract

In the Fischer-Tropsch (FT) process, synthesis gas; a mixture of predominantly CO and H_2, obtained from coal, peat, biomass or natural gas is converted to a multicomponent mixture of hydrocarbons. In this study, a high intensity ultrasonic horn has been used to irradiate the organometallic precursors; Cobalt carbonyl $Co_2 (CO)_8$ and ruthenium carbonyl $Ru_3(CO)_{12}$, in low-volatility solvent, with the oxide supports; titania TiO_2, under helium flow for 5 h at 273 K, to produce nanostructured materials, as catalysts in the Fischer-Tropsch process, with high catalytic activities. The activity of catalysts are better than reference catalysts, and the activity of CoRu catalyst seems very interesting; because it begins to be active at 220 °C, it shows a CO conversion exceeding 90%, and the selectivity towards CH_4 and CO_2 is very low, which is between the objectives of the Fischer-Tropsch synthesis. SEM-EDX microscopy indicated that nanoclusters have been deposited on the surface of supports, and well dispersed on the surface, whereas, XRD spectroscopy showed that Co presents as oxide and is not bound with the support. TPR analysis indicated that the addition of small amounts of Ru facilitate the reduction of Co catalyst. This has been concluded from the lowering of the reduction temperature.

Keywords: Fischer-Tropsch; gas; hydrocarbons; catalyst; ultrasonic; nanoparticles.

1. Introduction

Coal, biomass and natural gas can be converted into synthesis gas; a mixture of CO and H_2, by either partial oxidation or steam reforming processes. The conversion of the synthesis gas to longer chain hydrocarbons, at an elevated pressure and temperature and in the presence of metal catalyst, called Fischer-Tropsch (abbreviated further in the text as FT) synthesis. The Main reactions of the FT synthesis are:

1. Paraffins $(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$

2. Olefins $2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O$

3. Water gas shift reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$

The commercial process involves three main sections, namely: synthesis gas production and purification, FT synthesis, and product grade-up. Choi *et al.* [1] gives a capital cost breakdown of these three individual process sections for a 45,000 bbl/day FT plant. The synthesis gas preparation (that is air separation plant, partial oxidation, steam reforming of natural gas, and syngas cooling) is about 66% of the total on-site capital costs. The FT synthesis section consisting of FT slurry reactors, CO_2 removal, synthesis gas compression and recycle, and recovery of hydrogen and hydrocarbons is 22% of the total costs. Finally, the upgrading and refining section of hydrocarbons is about 12%. Note that at a fixed production rate the property of catalyst directly affects the synthesis gas conversion and the selectivity, and therefor the size of the syngas generation section. Consequently, it is of utmost importance to the overall economics.

All group VIII metals have noticeable activity in the hydrogenation of carbon monoxide to hydrocarbons. Vannice *et al.* [2] showed that the molecular average weight of hydrocarbons produced by FT synthesis decreased in the following sequence:

Ru > Fe > Co > Rh > Ni > Ir > Pt > Pd. Thus, only ruthenium, iron, cobalt, and nickel have catalytic characteristics which allow considering them for commercial production. Nickel catalysts under practical conditions produce too much methane. Ruthenium is too expensive; moreover, its worldwide reserves are insufficient for large-scale industry. Both cobalt and iron catalysts are commonly used in the industry for hydrocarbon synthesis. They were proposed by Fischer and Tropsch as the first catalysts for syngas conversion. Cobalt catalysts are more expensive, but they are more resistant to deactivation, and they give higher productivity at a high synthesis gas conversion [3]. The water-gas shift reaction is more significant on iron than on cobalt catalysts. Therefore, Iron catalysts produce hydrocarbons and oxygenated compounds under different H_2/CO ratios. They seem to be more appropriate for conversion of biomass-derived syngas to hydrocarbons than cobalt systems because they can operate at lower H_2/CO ratios, whilst, cobalt catalysts are viable for natural-gas based FT processes for the production of middle distillates and high-molecular weight products. Because the resources of natural gas are very large in Libya and other Arabic countries, this work is about the synthesis of nanoparticles Cobalt-supported catalysts by sonochemistry, which as I have been found here is more effective than traditional methods.

2. Material and Methods

In sonochemistry high energy chemical reactions occur during the ultrasonic irradiation of liquids. The chemical effects of ultrasound, however, do not come from a direct interaction with molecular species. Ultrasound spans the frequencies of roughly 15 kHz to 1 GHz, with associated acoustic wavelengths of 10 to 104 cm which are not molecular dimensions. Instead, these phenomena derive principally from acoustic cavitation; the formation, growth, and implosive collapse of bubbles in liquid. Bubble collapse induced by cavitation produces intense local heating, high pressures, and very short lifetimes. The synthesis start with metal-organic compounds, during the cavitation, the bonds are broken, and the metal atoms agglomerate to form nanoclusters of amorphous metals. If the process is carried out in the presence of porous supports, such as titania, we can deposit these nanoclusters on the surface of support, and form supported heterogeneous catalysts.

Cobalt carbonyl $Co_2(CO)_8$ and ruthenium carbonyl $Ru_3(CO)_{12}$ have been used as organometallic precursors, with titania TiO_2 as the oxide support. The device used for synthesize the catalysts is produced by SONICS, VIBRA CELL series with effective power of 750 W. It is provided by a piezoelectric transducer of the mixed crystal lead zirconate titanate (PZT). The horn is of titanium alloy with replaceable tip, in titanium alloys the wavelength for 20 kHz sound is about 26 cm. The horn is a half wavelength long, so the cross-sectional area is reduced at its midpoint, where there is no vibration no stress. The cooling system is from HAAKE, F3 series. It works in the range (0 °C; 100 °C) with accuracy of 0.02 °C. The pump supplies a pressure of 300 mbar and a maximum flux of 12.5 l/min. The synthesis process was performed at 0 °C.

The catalysts have been prepared by putting Co_2 $(CO)_8$ $Ru_3(CO)_{12}$ in a bottle with 200 ml of decane and an opportune quantity of support (TiO_2). The sonication flask was hermetically sealed directly to the horn (Ti-Horn, 20 kHz) and the mixture was irradiated with a high intensity ultrasonic horn under helium flow for 5 h at 273 K; the acoustic power transferred to the liquid was of about 200 W/cm^2. After sonication the powders were filtered, washed with hexane and calcinated at 350 °C for 5 h. Final concentration of Co and Ru in the catalysts was checked using ICP analysis. Table 2.1 shows prepared samples.

Table 2.1: Prepared samples.

	Sample		Units
	S1	S2	
TiO_2	7.116	7.0268	g
$Co_2(CO)_8$	4.3417	4,8106	g
Co	1.4992	1.6611	g
Co	17.40	19.12	wt%
$Ru_3(CO)_{12}$		0.0477	
Ru		0.0226	g
Ru		0.2595	wt%

For the characterizations, SEM, XRD spectroscopy and TPR, BET have been used.

3. Results and Discussion

The Specific surface area and the pore size distribution of catalysts are displayed in Table 3.1. The BET surface area is in the expected range. The cobalt loaded catalyst shows a significantly lower

BET surface area and pore volume, and a slightly smaller average pore size (Table 3.1). This suggested that part of cobalt species have entered into the pores of the support.

Table 3.1: BET.

	BET	Pore volume	Size pore
	(m^2/g)	(m^3/g)	$(A°)$
Co/TiO$_2$	55	0.12	87
Co-Ru/TiO$_2$	13	0.04	85

The X-ray diffraction (XRD) patterns of the catalysts are displayed in Figure 3.1. The evidenced diffraction peaks centred at $2\vartheta = 31.2°$, $36.8°$, $44.8°$, and $65.2°$ are indicative of the presence of Co_3O_4 on the support surface (PDF card n° 76-1802) [4, 5, 7]. From XRD analyses the vibrational bands of ruthenium oxide are not observed [6]; this is probably due to the low concentration of ruthenium oxide, and thus to the scarce sensitivity to revealing this species. Moreover, from a detailed analysis of the spectra we can deduce that no evidence of cobalt-support interaction is present.
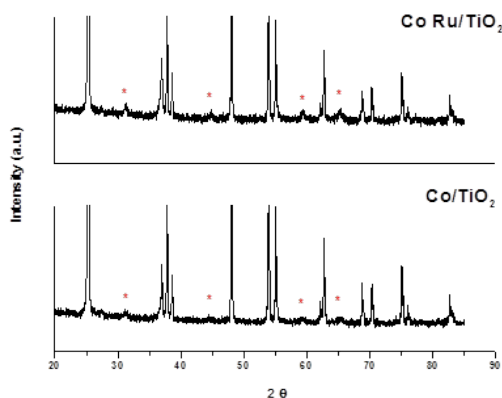

Figure 3.1: XRD spectroscopy.

In Figure 3.2, the SEM images of the catalyst are reported. In both figures, the white or light spots on the catalyst granules represent high concentration of cobalt and its compounds: about 8-10 wt.% Co (determined by EDX analysis). The darker areas of the granules, on the contrary, indicate the support with minimal % of cobalt (3-6 wt.%). The average particle size observed is 10-20 nm. From the EDX analysis a Ru local concentration of 0.1 wt.% was

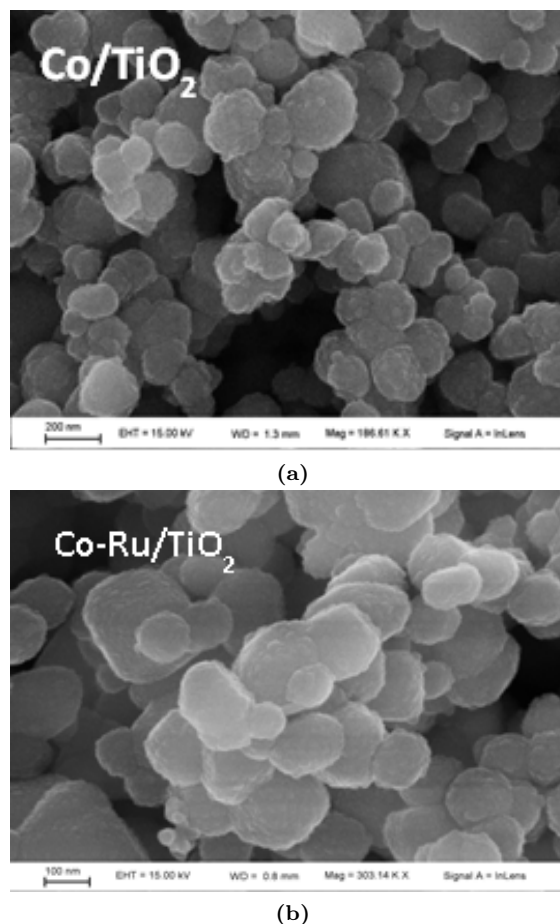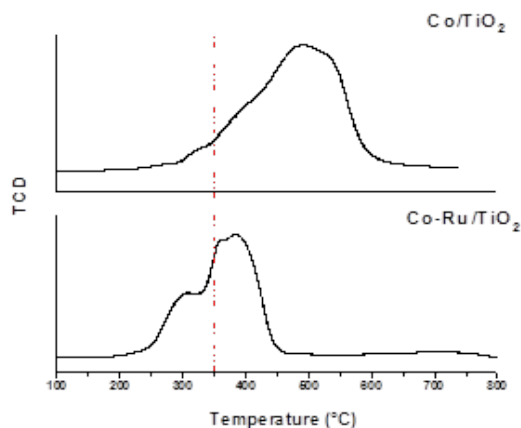determined. The EDX analysis was made on areas of a few microns squares.

(a)

(b)

Figure 3.2: SEM images.

Figure 3.3 presents the TPR profile of the catalyst, where the first peak (278 °C) is typically assigned to the reduction of Co_3O_4 to CoO. The second peak (380 °C) is mainly assigned to the second reduction step: CoO to Co^0. Both the promoted and without promotion Co catalysts reduced in two steps, but the low temperature reduction peaks for the Ru-promoted catalyst were about 100 °C lower in temperature. In addition, the broad high temperature reduction feature associated with Co species which were extremely difficult to reduce, was replaced by a peak at lower temperature in the Ru-promoted Co catalyst. This demonstrates the positive effect of ruthenium on the reducibility of cobalt oxide [8] that is very important for the activation process of the catalysts in the industrial process.

Figure 3.3: TPR.

Table 3.2: Catalytic activity.

Co/TiO$_2$					
T (°C)	CO % Conv	CO$_2$	CH$_4$	< C$_7$	> C$_7$
180	1.3	0	0	15	85
210	2.3	8	5	22	65
235	7.7	10	7	35	48
245	28.2	14	5	10	71
260	50.9	11	4	7	78
Co-Ru/TiO$_2$					
T (°C)	CO % Conv	CO$_2$	CH$_4$	< C$_7$	> C$_7$
180	0.8	30	39	46	0
220	19	3	25	29	43
245	98.2	8	18	14	60

The results of the catalytic activity tests in the Fischer-Tropsch Synthesis (FTS) are reported in Table 3.2. To take of comparison two catalysts have been taken as reference, that were synthesized with different methods: impregnation to incipient wetness and sonochemistry, both with the same percentage of cobalt and without Ru added. CoRu/TiO$_2$ shows very interesting performances. It is already active at 180 °C and the conversion of CO is practically total at 245 °C, while the reference catalysts show a very lower conversion of CO at 250 °C. These results are probably connected to the positive effect of added ruthenium that helps the reduction of cobalt oxide to metal, which is the catalytically active form, during the activation treatment. The CoRu/TiO$_2$ catalyst gives a very low selectivity to methane and CO$_2$ at CO conversion level higher than 90%. The reaction products prevailingly pertain to the gasoline (C$_5$-C$_{11}$) and diesel (C$_{12}$-C$_{18}$) fractions.

4. Conclusion

The synthesis of hydrocarbons from CO hydrogenation over transition metals is perhaps the most promising source of chemicals and fuels from non-oil based raw materials such as coal, natural gas and biomass. It is currently one of the most promising topics in the energy industry for four reasons:

1. World demand for petroleum is continually increasing while the world oil production has plateaued. Thus, there is a tremendous interest in alternative methods of liquid fuels production.

2. Synthetic fuels burn cleaner than petroleum-based diesel and jet fuels, because synthetics do not have soot-forming aromatics and other non-hydrocarbon contaminants.

3. Coal, natural gas, or heavy residues can be used on sites where these are available at low costs.

4. The resources of coal and natural gas are very large.

Then, a research on the synthesis of new catalysts assumes a great importance because of the possible economic advantages [9, 10]. The possibility of using sonochemistry as a method for obtaining good performance catalysts was then experienced. In this perspective, a first type of catalyst was synthesized, characterized and tested on a laboratory reactor.

In this study, for a complete and accurate understanding of the chemical nature of the metal species on the surface of the catalysts, we used different instrumental techniques. Each technique gave us different information, but complementary each other. The XRD analyses confirmed the nature of oxides but, above all, gave us information about their crystallinity and allowed us to determine the crystallite size of Co$_3$O$_4$. The ruthenium oxide was not detected because of its very low percentage. Investigations made by SEM showed a heterogeneous distribution of oxides on the surface of the support, and afforded to estimate the percentage of metal through the EDS technique. Finally, TPR

and BET analyses gave us important information on reducibility, number of active sites per gram and nanometer size of metal clusters. From these analyses, we also obtained the more interesting result: the presence of ruthenium favors the reducibility of cobalt oxide.

The activity of CoRu catalyst seems very interesting; because it begins to be active at 220 °C it shows a CO conversion exceeding 90%. The selectivity towards CH_4 and CO_2 is very low, which is between the objectives of the Fischer-Tropsch synthesis, and even better than reference catalysts. The selectivity to hydrocarbons is very good, especially for the gasoline (C_5-C_{11}) and diesel (C_{12}-C_{18}) range. Moreover, the conversion level remains constant for several hours: 56 hours at 200 °C and 48 hours at 180 °C, without evidence of deactivation.

Acknowledgment

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