

## The Promoting Effect of Ru and Re Addition to Co/Nb<sub>2</sub>O<sub>5</sub> catalyst in the Fischer-Tropsch Synthesis

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The promoting effect of Ru and Re addition to Co/Nb<sub>2</sub>O<sub>5</sub> catalyst in the Fischer-Tropsch Synthesis was studied. The catalysts were characterized by TPR, XRD and H<sub>2</sub> chemisorption. The Re and Ru addition increased both the activity and the C<sub>5</sub><sup>+</sup> selectivity by different mechanisms. Re prevented the cobalt agglomeration whereas Ru increased the Co<sup>0</sup> site density. The Ru addition to Co/Nb<sub>2</sub>O<sub>5</sub> catalyst promoted diesel selectivity in the F.T.S. while the Re addition promoted the diesel as well as the gasoline one.

### 1. Introduction

Natural gas has becoming more attractive as an energy source due to the increasing prices of oil, the huge reserves of gas and environmental problems. This situation has driven many researches to develop more economic processes of upgrading the natural gas to higher hydrocarbon fuels. The Fischer-Tropsch (FT) synthesis is an alternative route to produce liquid fuels from synthesis gas.

Cobalt based catalysts have been widely used in the CO + H<sub>2</sub> reaction for the production of hydrocarbons (1). However, the main problem of the F-T synthesis is the wide range of product distribution by the conventional FT catalyst (2). In order to overcome the selectivity limitations and to enhance the catalyst efficiency in CO hydrogenation, several approaches have been studied, such as the use of reducible support (3) and the addition of a second metal (4).

Niobia (3,4) and titania-supported (5,6) cobalt catalysts showed a high selectivity toward long chain hydrocarbons in the FT synthesis after reduction at high temperature. These results might be explained by the formation of new sites during high temperature reduction.

The addition of noble metals to supported-cobalt catalyst has also affected the activity and selectivity of CO hydrogenation. Kappor et al. (7) reported that an increase in the C<sub>5</sub><sup>+</sup> hydrocarbon selectivity was observed on the CO hydrogenation, after addition of Ru, Pd or Pt to the Co/Al<sub>2</sub>O<sub>3</sub> catalyst. Iglesia et al. (5,6) verified that Co-Ru bimetallic interactions were able to increase the reaction rate and selectivity towards C<sub>5</sub><sup>+</sup> hydrocarbons in the FT synthesis and to improve catalysts regeneration and reducibility. This synergetic effect was mainly related to an increase of the cobalt oxide reduction, providing a higher metallic site density. In the case of Co-Re bimetallic catalysts, the

addition of rhenium prevent the cobalt sinterization (6). Recently, we observed that the presence of rhodium increased the  $C_5^+$  selectivity and decreased the methane formation on Rh-Co/Nb<sub>2</sub>O<sub>5</sub> catalysts (4). This promoting effect was attributed to an intimate contact between rhodium particles spread over a thin layer of cobalt ions.

The main goal of this work is to investigate both the effect of Ru and Re addition to Co/Nb<sub>2</sub>O<sub>5</sub> catalyst and the role of niobium oxide support on the selectivity of CO hydrogenation.

## 2. Experimental

The Nb<sub>2</sub>O<sub>5</sub> support was obtained by calcination of niobic acid (CBMM) in air at 823K, for 2h. The catalysts were prepared by incipient wetness impregnation or coimpregnation of the support with an aqueous solution of the precursor salts (cobalt nitrate, ruthenium and rhenium chloride). These catalysts contained 5 wt.% Co and 0.6 wt.% of Ru or Re. After impregnation, the samples were dried at 393K for 16h and calcined in air at 673K for 2h. TPR experiments were performed in a conventional apparatus. The samples were reduced with a mixture containing 5% H<sub>2</sub>/N<sub>2</sub> at a heating rate of 10K/min from 298 to 1273K. X-Ray diffraction (XRD) measurements were carried out in a Rigaku Dmax 2200 PC diffractometer with an attached Anton Paar XRK 900 reactor. The data for the calcined and reduced catalysts were recorded using Cu K<sub>α</sub> radiation (40 kV, 40 mA) and a secondary graphite monochromator. The X ray diffractogram was scanned with a step size of 0.05° (2θ) from 5° to 100° (2θ) and counting time of 1s per step. Crystallite sizes were estimated from the integral breadth of the Co(111) line using Scherrer equation. In order to calculate the crystallite size, the XRD pattern of the support was subtracted from the diffractogram of the reduced catalyst. Quantitative XRD phase analysis was carried out to determine the reduction degree by using the Fullprof software (8), following the procedure proposed by Hill and Howard (9). The weight fraction of each phase was calculated from the respective scale factor. The parameters refined for each phase were the scale factor, the lattice constants and the peak width parameter. Structural data for Co<sub>3</sub>O<sub>4</sub> and metallic cobalt were taken from Wyckoff (10) and for t-Nb<sub>2</sub>O<sub>5</sub> from Kato and Tamura (11). CoNb<sub>2</sub>O<sub>6</sub> was used as an isomorphous phase to FeTa<sub>2</sub>O<sub>6</sub> (PDF 83-0588) (10). The hydrogen chemisorption was measured in a volumetric adsorption system. The catalyst was reduced under H<sub>2</sub> at 773K, for 16h. Then, the samples were evacuated for 9h at reduction temperature and cooled to adsorption temperature under vacuum. Total adsorption isotherm was determined at 448K. The CO hydrogenation was carried out in a stainless steel microreactor ( $m_{cat} = 200\text{mg}$ ) at 493K and 0.1 MPa using a mixture of H<sub>2</sub> / CO = 2.0 at differential conditions. Before the reaction, the samples were reduced under hydrogen flow at 773K for 16h. The products were analyzed by on line gas chromatography (Varian 3400, FID and TCD).

## 3. Results and discussion

### 3.1. Catalyst Characterization

The TPR profiles of niobia-supported catalysts are shown in Figure 1. The reduction profile of Co/Nb<sub>2</sub>O<sub>5</sub> catalyst exhibited a shoulder at 643K and a broad peak at

754K. It has been reported the presence of  $\text{Co}_3\text{O}_4$  particles and  $\text{Co}^{2+}$  species on the niobia-supported cobalt catalysts (4). According to the literature, the shoulder around 643K could be attributed to the reduction of  $\text{Co}_3\text{O}_4$  particles, whereas the peak at 754K corresponds to the reduction of  $\text{Co}^{2+}$  either formed by reduction of  $\text{Co}_3\text{O}_4$  and  $\text{Co}^{2+}$  species interacting with niobia. DRS and XPS analyses revealed that the  $\text{Co}^{2+}$  species were represented by cobalt niobate (4). Furthermore, TPR and magnetic measurements showed that the hydrogen uptake at high temperature was also related to a partial reduction of niobia. Therefore, TPR analyses can not be used to quantify the reduction degree of niobia supported catalysts. The TPR profile of  $\text{Re}/\text{Nb}_2\text{O}_5$  catalyst exhibited a small peak around 580 K and a high hydrogen consumption above 1000K. The  $\text{Ru}/\text{Nb}_2\text{O}_5$  catalyst presented two peaks at 450 and 480 K and a  $\text{H}_2$  uptake above 1000 K, similar to that observed on  $\text{Re}/\text{Nb}_2\text{O}_5$  catalyst.

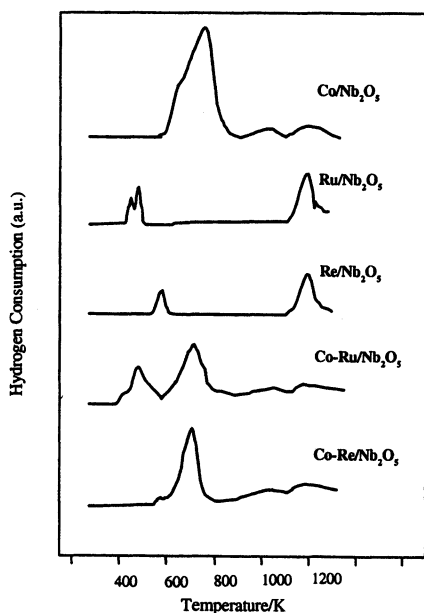


Figure 1- TPR profiles of the niobia-supported catalysts.

lines disappeared while the lines corresponding to metallic Co were detected. On the other hand, the diffraction patterns of  $\text{CoNb}_2\text{O}_6$  phase remained without any change on the  $\text{Co}/\text{Nb}_2\text{O}_5$  and  $\text{Re-Co}/\text{Nb}_2\text{O}_5$  catalysts. These results indicated that metallic cobalt is mainly formed from the reduction of  $\text{Co}_3\text{O}_4$  phase, and the  $\text{CoNb}_2\text{O}_6$  phase can not be reduced at temperatures below 773 K on these catalysts. But, the presence of ruthenium also promoted the reduction of the niobate phase. Rietveld method was used to calculate the cobalt reduction degree and the results were presented on Table 1. The rhenium

The ruthenium addition to  $\text{Co}/\text{Nb}_2\text{O}_5$  catalyst promoted the reduction of  $\text{Co}_3\text{O}_4$  particles since the hydrogen consumption at low temperature (400-600K) was higher than the one on the monometallic ruthenium catalyst. On the other hand, the hydrogen uptake attributed to cobalt oxide reduction was not shifted to lower temperature on the  $\text{Re-Co}/\text{Nb}_2\text{O}_5$  catalyst. These results were in agreement with the literature. Hoff (12) also observed that rhenium did not promote the reduction of the cobalt on  $\text{Co-Re}/\text{Al}_2\text{O}_3$ . The addition of Ru to  $\text{Co}/\text{Al}_2\text{O}_3$ ,  $\text{Co}/\text{SiO}_2$  and  $\text{Co}/\text{TiO}_2$  increased the reducibility of cobalt oxide (6).

Figures 2a and b showed the XRD patterns of the catalysts after reduction at 773 K.  $\text{Nb}_2\text{O}_5$ ,  $\text{CoNb}_2\text{O}_6$ , and metallic Co phases were presented in all catalysts. However, the amount of  $\text{CoNb}_2\text{O}_6$  phase calculated decreased in the following order:  $\text{Co}/\text{Nb}_2\text{O}_5 \approx \text{Re-Co}/\text{Nb}_2\text{O}_5 > \text{Ru-Co}/\text{Nb}_2\text{O}_5$ . After reduction, the  $\text{Co}_3\text{O}_4$

addition did not change the cobalt reduction degree whereas the amount of metallic cobalt increased on the Ru-Co/Nb<sub>2</sub>O<sub>5</sub> catalyst. These results agree well with the TPR analyses.

The position of the Co(111) line was practically the same on all catalysts (Table 1). Therefore, it was very difficult to confirm the formation of a Co-Ru alloy on the niobia-supported Co-Ru catalysts. Furthermore, the metal addition led to a decrease on the metallic cobalt crystallite size. The amount of adsorbed hydrogen was higher on the bimetallic catalysts. The dispersion and the particle size of the Co/Nb<sub>2</sub>O<sub>5</sub> and Ru-Co/Nb<sub>2</sub>O<sub>5</sub> catalysts were basically the same since the extension of reduction of the bimetallic catalyst was higher. The rhenium addition decreased the cobalt particle size. According to the literature, rhenium prevents the cobalt sinterization (6).

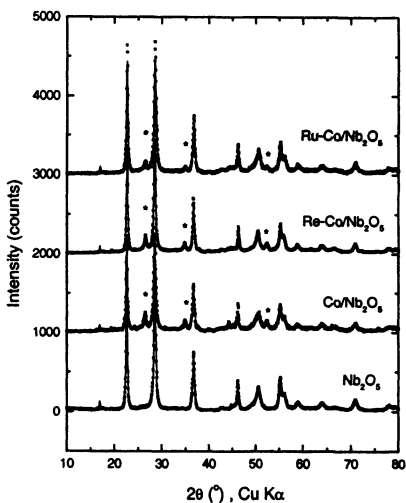


Figure 2 - XRD patterns of reduced catalysts and support.(a)  $0 < 2\theta < 100$ ; (b)  $40 < 2\theta < 60$ . The symbol \* mark angular positions of CoNb<sub>2</sub>O<sub>6</sub> peaks.

### 3.2. Catalytic Activity and Selectivity

Table 2 showed CO conversion, reaction rate, turnover frequency (TOF) and selectivities on the CO hydrogenation over the niobia-supported catalysts. The metal addition increased the TOF, which followed the order: Co/Nb<sub>2</sub>O<sub>5</sub> < Re-Co/Nb<sub>2</sub>O<sub>5</sub> < Ru-Co/Nb<sub>2</sub>O<sub>5</sub>. The higher turnover rate of the Re-Co/Nb<sub>2</sub>O<sub>5</sub> catalyst could be attributed to the presence of smaller Co particle size (6). However, Ru-Co/Nb<sub>2</sub>O<sub>5</sub> catalyst exhibited approximately the same particle size than Co/Nb<sub>2</sub>O<sub>5</sub> catalyst. As it was observed on the TPR analyses, ruthenium addition increased the cobalt oxide reducibility. Then, the presence of Ru enhanced the activity due to the increase of the Co site density. The same behavior was observed on Co/TiO<sub>2</sub> and Ru-Co/TiO<sub>2</sub> catalysts (5).

Co/Nb<sub>2</sub>O<sub>5</sub> catalyst exhibited a very low methanation activity and a high selectivity towards long chain hydrocarbons. Silva et al. (3) compared the catalytic behavior of

Co/Al<sub>2</sub>O<sub>3</sub> and Co/Nb<sub>2</sub>O<sub>5</sub> catalysts reduced at 573 and 773K on the FT reaction. After reduction at 573K, Co/Al<sub>2</sub>O<sub>3</sub> and Co/Nb<sub>2</sub>O<sub>5</sub> catalysts presented both high methanation

Table 1- Reduction degree, angular position of Co(111) line and estimated crystallite sizes (dp) of the metallic cobalt particles obtained from XRD analyses and the amount of hydrogen chemisorbed.

Catalyst	Reduction degree (%) <sup>a</sup>	Co (111) (°)	d <sub>p</sub> (nm) <sup>b</sup>	H <sub>2</sub> adsorbed (μmoles H <sub>2</sub> /g <sub>cat</sub> ) <sup>c</sup>	D (%) <sup>d</sup>	d <sub>p</sub> (nm) <sup>e</sup>
Co/Nb <sub>2</sub> O <sub>5</sub>	48	44.27	25±2	16.2	7.9	12
Ru-Co/Nb <sub>2</sub> O <sub>5</sub>	68	44.33	14±2	20.7	7.2	13
Re-Co/Nb <sub>2</sub> O <sub>5</sub>	48	44.28	10±2	25.4	12.5	8

<sup>a</sup> Reduction degree of cobalt calculated using the Rietveld method

<sup>b</sup> Estimated from XRD

<sup>c</sup> Amount of hydrogen adsorbed measured by H<sub>2</sub> chemisorption

<sup>d</sup> Cobalt metal dispersion calculated from hydrogen adsorption

<sup>e</sup> Cobalt particle size calculated by using the formula :  $D = 96/d$  (  $d = \text{nm}$  )

Table 2- CO conversion (X) and selectivity for methane (CH<sub>4</sub>), light hydrocarbons (C<sub>2</sub>-C<sub>4</sub>), gasoline (C<sub>5</sub>-C<sub>11</sub>), diesel (C<sub>12</sub>-C<sub>18</sub>), hydrocarbons containing more than 19 carbons atoms (C<sub>19</sub><sup>+</sup>) and alcohol, after reduction at 773K.

Catalyst	X(%)	Rate μmol/g.s	TOF s <sup>-1</sup> .10 <sup>3</sup>	CH <sub>4</sub>	C <sub>2</sub> -C <sub>4</sub>	Gasol	Diesel	C <sub>19</sub> <sup>+</sup>	Alcohol	C <sub>5</sub> <sup>+</sup>
Co/Nb <sub>2</sub> O <sub>5</sub>	6.7	0.050	1.54	10.3	29.0	33.8	18.8	2.3	5.8	55.0
Re/Nb <sub>2</sub> O <sub>5</sub>	0.9	0.011	--	4.3	5.2	8.3	59.0	22.8	0.3	90.1
Ru/Nb <sub>2</sub> O <sub>5</sub>	4.6	0.053	--	54.3	22.7	13.5	5.9	0.0	3.6	19.4
Re-Co/Nb <sub>2</sub> O <sub>5</sub>	7.4	0.130	2.56	9.4	8.7	49.4	26.0	5.6	0.8	81.0
Ru-Co/Nb <sub>2</sub> O <sub>5</sub>	6.8	0.160	3.86	3.5	32.4	28.7	29.3	1.8	4.2	59.8

activity and low C<sub>5</sub><sup>+</sup> formation. The reduction of the Co/Nb<sub>2</sub>O<sub>5</sub> catalyst at high temperature led to a strong decrease in the CH<sub>4</sub> production and an increase of the C<sub>5</sub><sup>+</sup> selectivity. On the other hand, the Co/Al<sub>2</sub>O<sub>3</sub> catalyst reduced at 773K showed the same product distribution as observed after reduction at 573K. These results were attributed to the decoration of cobalt particles by partially reduced niobium oxides species (NbO<sub>x</sub>) which influences the cobalt adsorption properties. The rhenium addition to Co/Nb<sub>2</sub>O<sub>5</sub> catalyst changed markedly the product distribution. The C<sub>5</sub><sup>+</sup> selectivity and, particularly, the selectivity to gasoline and diesel increased whereas the C<sub>2</sub>-C<sub>4</sub> fraction decreased. These results could not be explained by the presence of isolated Re particles since the activity of Re-Co/Nb<sub>2</sub>O<sub>5</sub> catalyst was much lower than the one of the Co/Nb<sub>2</sub>O<sub>5</sub> catalyst. Furthermore, the selectivity towards gasoline on the Re-Co/Nb<sub>2</sub>O<sub>5</sub> catalyst was higher than that observed on the monometallic catalyst. A similar increase in C<sub>5</sub><sup>+</sup> selectivity was verified increasing the cobalt dispersion on Co/TiO<sub>2</sub> catalysts (6). This behavior has already been observed by other authors and was related to the probability of increasing the olefin readsorption, leading to longer chain formation of saturated hydrocarbons (5,6). Although the increase of C<sub>5</sub><sup>+</sup> selectivity was less

important on the Ru-Co/Nb<sub>2</sub>O<sub>5</sub> catalyst, the Ru addition led to both strong reduction of methanation and an increase of diesel production. Kappor et al (7) studied the catalytic properties of Ru-Co/Al<sub>2</sub>O<sub>3</sub> catalyst in the FT process. The addition of noble metals increased the yield of liquid hydrocarbons. Co-Ru catalysts were found highly selective towards C<sub>5</sub><sup>+</sup> hydrocarbons. According to TPR results, the addition of noble metals increased the reducibility of these catalysts. The authors suggested that the presence of a higher amount of metallic cobalt was responsible for the changes in selectivity. The same explanation was proposed by Iglesia (5,6) for alumina and silica supported Ru-Co bimetallic catalyst. Based on EXAFS analysis that revealed the presence of bimetallic Co-Ru particles (4), and on XRD results after reduction in situ, probably beside the bimetallic formation the observation of a higher density of metallic cobalt. TPR analysis showed that ruthenium addition promoted the cobalt oxide reduction, however any Ru-Co alloy was observed. It also shows that the presence of Ru and Re facilitated the interaction of niobium oxide species with cobalt that would explain the promoting effect of these metals to the formation of interfacial sites, which could explain the synergistic effects. Therefore, the increase of the C<sub>5</sub><sup>+</sup> selectivity on Ru-Co bimetallic catalysts could be explained by the promotion of the interfacial site of Co-NbO<sub>x</sub> sites. This behavior has already been observed by other authors and was related to the probability of increasing the olefin readsorption, leading to longer chain formation of saturated hydrocarbons (5,6,8,9). Undoubtedly, the nature of these sites at the interface of the Co- Nb<sub>2</sub>O<sub>x</sub> , as well as the formation of higher density of metallic cobalt, promoted by Re and Ru caused the markedly growth chain toward higher C<sub>5</sub><sup>+</sup> fractions. Further in situ measurements are needed to explain the nature of these interfacial sites.

It is important to stress that the high C<sub>5</sub><sup>+</sup> selectivity on the niobia-supported catalyst was obtained performing the reaction at atmospheric pressure and low CO conversion (<10%). Under these reaction conditions, the formation of long chain hydrocarbons should not be favored. These results revealed the important role of the niobia support on the selectivity of FT reaction.

#### 4. Conclusion

The Re and Ru addition promoted the Co<sub>3</sub>O<sub>4</sub> reduction and led to an interaction of Co with niobium species at the surface. The XRD and TPR results reinforce the formation of Co-NbO<sub>x</sub> interfacial sites. The niobate Co<sub>2</sub>Nb<sub>5</sub>O<sub>14</sub> bulk phase was observed on all catalysts and was not reducible at temperatures below to 773 K. The rhenium addition decreased the cobalt particle size. Ruthenium promoted the cobalt oxide reduction. The Re and Ru addition increased both the activity and the C<sub>5</sub><sup>+</sup> selectivity of Co/Nb<sub>2</sub>O<sub>5</sub> catalyst. Particularly, the selectivity to diesel increased. The high selectivity to C<sub>5</sub><sup>+</sup> products emphasizes the role of the niobia support on the reaction..

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