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FISCHER-TROPSCH SYNTHESIS ON Pd-Co/Nb$_2$O$_5$ CATALYSTS

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1.   Introduction

Cobalt based catalysts have been widely used in the CO + H$_2$ reaction for the production of hydrocarbons [1-5]. They are among several others to produce hydrocarbons from CO hydrogenation due to their ability to hydrogenate dissociated carbon species and promote chain growth. Cobalt is a typical metal that may adsorb CO molecules dissociatively forming carbon atoms at the surface, which may be hydrogenated, and it is an appropriate catalyst for the formation of long chain hydrocarbons [5,6]. However, the main problem of the F-T synthesis is the wide range of product distribution when conventional F-T catalysts are being used. 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 supports and the addition of a second metal component.

In this study, we investigate the performance the bimetallic Pd-Co/niobia systems in CO hydrogenation reaction, in an attempt to explain the effect of a second metal on the product selectivity of Co-based catalysts compared to the Co/Nb$_2$O$_5$ systems.

2.   Experimental

The cobalt catalyst was prepared by incipient wetness impregnation with a Co(NO$_3$)$_2$. 6H$_2$O (Riedel-de Häen, 99% purity) solution. The Co content was kept constant at approximately 5% (wt.) [1, 5]. Then Pd was impregnated in sequence by wet impregnation in order to obtain 0.6 % of the metal. After impregnation, all catalysts were dried overnight at 110^{0}C followed by calcination at 2 K/min up to 400^{0}C, kept at this temperature for 3 h and stored for characterization and catalytic tests. Catalytic evaluation of the catalysts with the CO hydrogenation reaction was performed on a fixed bed. The reaction was performed at 20 atm and started after the temperature had stabilized by the CO/H$_2$/He mixture flow into the reactor at a rate of 30 ml/min to ensure

constant space velocity for all experiments. The conditions were established for isoconversion. The total reaction time was approximately 50 h. Feed gas was a mixture of 31.7% CO/64.3% H_2/4% He. Helium was used as an internal standard to calculate the total CO conversions. These gases passed through filters at room temperature to remove O_2 and water traces. Reaction products were analyzed on line by gas chromatography.

A FTIR spectrometer (Nicolet, model Nexus 470) equipped with a DRIFTS (Diffuse reflectance infrared Fourier Transform spectroscopy) cell (Spectra-Tech) chamber for high temperature treatment and ZnSe mirror assembly was used to study the $CO+H_2$ reaction at different temperatures. These experiments were carried out after *in situ* reduction with pure H_2 (99.99) at 30 mL/min at 10 K/min up to 500^0C for 6 h and then purged with He for 30 min. Subsequently the sample was cooled down to the reaction temperature. A feed mixture of $1CO:2H_2$ (32%CO: 64% H_2: 4% He) was introduced at 25 mL/min, under similar reaction conditions. Each spectrum was referenced to the spectrum of the reduced sample [5].

3.   Results and Discussion

The H_2 chemisorption measurement results for Co/Nb_2O_5 and Co-Pd/Nb_2O_5 catalysts, reduced at 500^0C, were 14.3 and 12.3 μmols/gcat, respectively, based on the irreversible adsorption at 175^0C, suggesting the presence of big cobalt particles and very small Pd particles on top of Co particles.

Figure 1 displays the selectivity with time on stream, for a space velocity $6000h^{-1}$ and isoconversion (30%); reaction temperature 270^0C and pressure 20 bar, after reduction at 500°C. The bar diagrams of Figure 1A presents product selectivities on Co/Nb_2O_5 catalyst based on mols of carbon product in the C_i range/ΣC_i formation with time on stream. Methane was very low (≈3.0%) and the diesel fraction (C_{13-18}) was very high (54-49%). Note that CH_4, C_{2-4}, C_{5-12}, C_{13-18}, and C_{19+} correspond to saturated hydrocarbons. The range C_{2-4} may also include some C_{2-4} olefins (ethene and propene), which were not resolved from the more pronounced saturated hydrocarbon chromatographic peaks. Higher molecular weight olefins (C_5-$_{12}$ and C_{13}-$_{18}$) were detected on the Co/Nb_2O_5 catalyst.

The bar diagrams of Figure 1B clearly point out that the selectivity towards methane and C_{2-4} hydrocarbons for the bimetallic Co-Pd/Nb_2O_5 changed with Pd addition and with time on stream. Note that the methane formation rate for this catalyst increased. Olefins, except $C_4^=$ were not detected before on the pure Co-containing catalysts. Light products and gasoline fractions increased, while diesel fraction decreased.
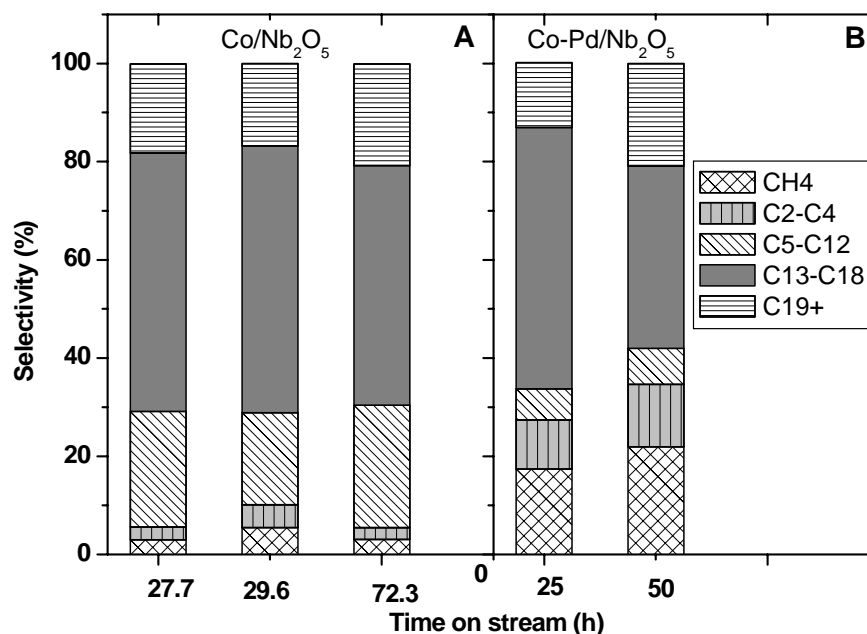
Figure 1. Catalytic Test – $H_2/CO=2$, 270°C, 20 atm, (A) Co/Nb₂O₅, (B) Co-Pd / Nb2O5

Methane was around 17-21% and the diesel fraction decreased from 53 to 37%. The addition of the second metal indicates also higher selectivity towards alkanes. Product retention and condensation are not expected to have occurred because the overall mass balance indicates that the reactor operates steady-state. Noteworthy is that during 70 hours the catalyst was stable and deviation of mass balance was around 20%. In addition, after 50 h samples were taken and coke was analysed by TG (not shown). It presents a loss of approximately 16% of carbon due to the coke deposition, which allows us to explain the deviation observed. Experiments were reproduced under similar conditions at isoconversion (around 30%).

The Anderson-Schulz-Flory equation with these experiments displayed great deviation in the C_{13}-C_{18} range. As expected, the total hydrocarbon molar compositions cannot be interpreted as an ASF distribution. Although the C_2-C_3 anomalies and the change of the chain growth probability in the range from C_3 to C_8-C_{12} range may be explained by α-olefin readsorption with secondary chain propagation and the existence of two mechanisms for chain propagation, the

increasing selectivity observed between C_8-C_{12} for all experiments cannot be explained by these mechanisms [7].

Figure 2 shows the DRIFTS measurements of the CO hydrogenation at atmospheric pressure and temperature variations, searching an explanation and understanding of surface species formation under real conditions.

Typical spectra of the samples Co/Nb_2O_5 and Co-Pd/Nb_2O_5 are displayed in Figure 2A and 2B, respectively. After *in situ* reduction with H_2 during 6 h, the $CO/H_2/He$ flow mixture was introduced at a ratio of $H_2/CO=2$. The reference spectrum was the reduced catalyst prior to gas admission. Spectra were obtained at different temperatures. Figure 2A presents the spectrum $Co/5\%Nb_2O_5$, where Nb_2O_5 was used as reference spectrum. At 200^0C it displays characteristic bands of CO in the gas phase (2174 cm^{-1}) [1,3,9], a small peak for formate species at 2900 cm^{-1} (νC-H) and 1611 cm^{-1} [4].

The catalyst also shows CO bands at different temperatures 250^0C and 270^0C (b,c) indicating linear adsorption on top of metallic Co particles (2056 cm^{-1}). On the other hand, the band at 2115 cm^{-1} is attributed to the CO adsorption on Co^+ species [3]. Zhang et al [8] suggests the presence of ionic $Co^{\delta+}$ species with less electron donation capacity. At higher temperature (250 – 270^0C) this band is shifted towards 2174cm^{-1}, suggesting an increase of reduced Co species.

Formate bands were observed around 2900 cm^{-1} and around 1305-1611cm^{-1} (νC-H), 1592 cm^{-1} (ν_{ass} C-O), 1393 cm-1 (δ_s C-H), 1371 cm-1 (ν_s C-O). [4,10] that increased with the temperature increase. Above 270^0C the band at 2350 cm^{-1}, relative to CO_2 formation was observed, which may be related to the "shift" reaction or/and the decomposition of formate species.

On the other hand, bands around 3011-2880 cm^{-1} evidence the presence of CH_x species during the reaction, suggesting also the formation of hydrocarbons [3], in particular the band at 3017 cm^{-1}, which corresponds to the axial deformation and at 1305 cm^{-1} band of the angular deformation of C-H bond of gas methane. According to Rygh et al [3] these bands are due to the formation of intermediate CH_X species.

This catalyst displays the symmetric stretching of -CH_2 at 2880 cm^{-1}, that evidences this intermediate species. Spectra (d) and (e) confirm these bands taken in a closed chamber.
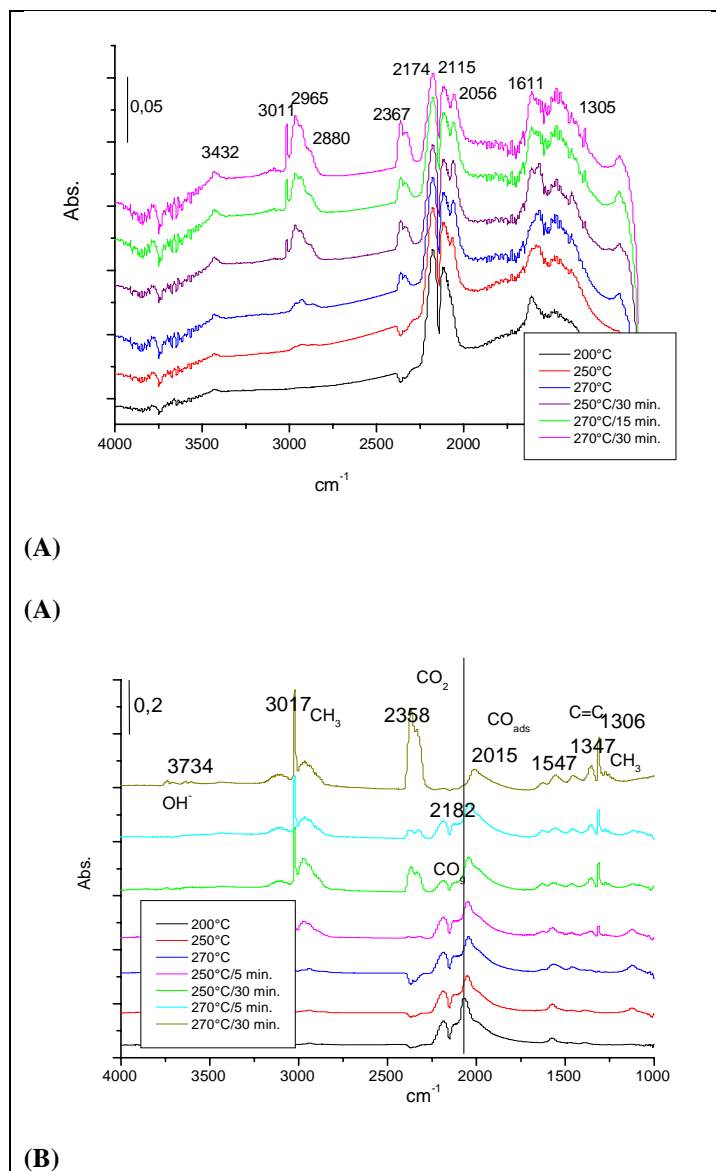
(A)

(A)

(B)

Figure 2A - Co/Nb2O5: (a) catalyst at 200^{0}C, (b) catalyst at 250^{0}C, (c) catalyst at 270^{0}C, (d) 250^{0}C closed chamber/30 min., (e) 270^{0}C closed chamber for 15 min.; (f) 270^{0}C closed chamber for 30 min.

Figure 2B Co-Pd/Nb2O5: (g) 473K, (h) 250^{0}C, (i) 270^{0}C, (j) 250^{0}C closed chamber / 15 min., (k) 250^{0}C closed chamber / 30 min.; (l) 270^{0}C closed chamber / 5 min., (m) 270^{0}C closed chamber / 30 min.

The Co-Pd/Nb_2O_5 (fig. 2B) displays a different behavior for CO adsorption on Co^+ species (~2115cm^{-1}), that changes with increasing temperature. However, significant modifications were observed between 3000-2800 cm^{-1} and 1600 cm^{-1}. The shoulder at 1547 cm^{-1} is assigned to the formation of -C=C-, suggesting the formation of olefins. One can see that the formation of CHx intermediates at 523 K, related to the bands 2951cm^{-1} (ν_s CH_2), 2928 cm^{-1} (ν_{ass} CH_2), 2963cm^{-1} (ν_{ass} CH3) and at 3017 cm^{-1} to the CH_4 gas; while at 1455cm^{-1} (δ_{ass} CH_2+CH_3) and 1375cm^{-1} (δ_s CH_3) and at 1306cm^{-1} (δ_s C-H) to methane. The band at 1605cm^{-1} (ν C=O) is due to the adsorption of bidentade carbonate species, which are responsible for the CO_2 formation.

4.   Conclusion

The Co/Nb_2O_5 showed a significant change with time on stream upon the addition of Pd. The selectivity towards heavier product range, diesel (C13-18) and C19+) increased with time on stream and was very stable up to 50 h.

DRIFTS results showed the formation of -C=C-, suggesting the formation of olefins upon addition of Pd. The results suggest likewise that the CH_xO species are the precursors for the formation of hydrocarbons. The Co-Pd/Nb_2O_5 shows CO adsorption on $Co^{\delta+}$ species The CH_x^- is thought to be formed as methyl radicals on Co^0 particles.

5.   References

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