

Fischer–Tropsch Synthesis on Anchored Co/Nb₂O₅/Al₂O₃ Catalysts: The Nature of the Surface and the Effect on Chain Growth

F. M. T. Mendes,[†] C. A. C. Perez,[†] F. B. Noronha,[‡] C. D. D. Souza,[†] D. V. Cesar,[†]
H. J. Freund,[§] and M. Schmal^{*,†}

Federal University of Rio de Janeiro—NUCAT-PEQ-COPPE, 128 Centro de Tecnologia Bl. G, Cidade Universitária, Rio de Janeiro, Brazil, Instituto Nacional de Tecnologia, Av. Venezuela 2, CEP 20081-310, Brazil, and Fritz-Haber Institut, Max Planck G., Faradayweg 4–6, Berlin, Germany

Received: January 10, 2006; In Final Form: March 10, 2006

A series of Co/*x*%Nb₂O₅/Al₂O₃ catalysts were prepared by anchoring niobia on an Al₂O₃ support at different niobia concentrations. Characterization of the structure and nature of surface active sites was attempted in order to correlate the CO hydrogenation activity of these systems with those of the Co/Al₂O₃ and Co/Nb₂O₅ catalysts. The effect of the reduction temperature on the CO hydrogenation activity and selectivity was studied, showing that interaction of cobalt and niobia surface species favored the selectivity for hydrocarbon chain growth. However, this effect is less pronounced on the niobia-promoted Co/Al₂O₃ compared to Co/Nb₂O₅ catalysts. X-ray photoelectron spectroscopy (XPS) and diffuse reflectance spectroscopy (DRS) results on Co/*x*%Nb₂O₅/Al₂O₃ showed prevailing amounts of Co²⁺ and Co³⁺ after calcination and reduction at 573 K, while, after reduction at 773 K, besides metallic cobalt, the Co²⁺ species still remains in contact with alumina, even for higher niobia loading. It seems that during this process formation and destruction of new interfaces involving Co⁰–NbO_x sites takes place. Results suggest that Co⁰, Co⁰–Co²⁺, and Co⁰–NbO_x are the active sites at the surface. The relative abundance of Co²⁺ species affects greatly the performance of the catalysts. DRIFTS and selectivity results suggest that these sites might be responsible for the reaction chain growth and therefore for the drastic change in the selectivity of CH₄ and C₅⁺ hydrocarbons mainly on the Co/Nb₂O₅ catalyst. DRIFTS results on Co/Nb₂O₅/Al₂O₃ showed the formation of –C=C– and –CH₃– besides CH_xO species. With increasing reduction temperature, the –C=C– species disappear while –CH₃– fragments increased markedly, suggesting the formation of increasing amounts of hydrocarbons with higher chain length.

1. Introduction

Natural gas is 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 researchers to develop more economic processes of upgrading natural gas to higher hydrocarbon fuels. The Fischer–Tropsch (F–T) synthesis is an alternative route to produce liquid fuels from synthesis gas.

Cobalt based catalysts have been widely used in the CO + H₂ reaction for the production of hydrocarbons.^{1–7} They were 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.^{8–12} However, the main problem of the F–T synthesis is the wide range of product distribution when conventional F–T catalysts are being used.¹³ 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^{14,15} and the addition of a second metal component.^{16–21}

In principle, the presence of a reducible oxide allows changes in the electronic or geometric structure, arrangement and size of particles, and adsorption properties.¹⁶

Niobium pentoxide as a support material for CO hydrogenation metal catalysts was the subject of a few studies.^{5,14–15,22–27} These studies have reported that the use of Nb₂O₅ as a support results in higher CO hydrogenation activities for Rh/Nb₂O₅ in comparison to Rh supported on ZrO₂, Al₂O₃, SiO₂, or MgO²⁵ and for Ni/Nb₂O₅ in comparison to Ni/SiO₂.²⁶ Enhanced selectivity for high molecular weight hydrocarbons in CO hydrogenation over Co/Nb₂O₅^{14,22} and Ni/Nb₂O₅,²⁷ compared to more traditional supports, such as Al₂O₃^{14,22,27} and SiO₂,²² was also observed.

In addition, niobia^{4,14,15} and titania-supported^{19,20} cobalt catalysts showed a high selectivity toward long chain hydrocarbons in the F–T synthesis after reduction at high temperature. These results might be explained by the formation of new sites during high temperature reduction.

In this study, we investigate the structure and surface properties of cobalt niobia/alumina systems, when niobia is coated at different concentrations over an alumina of high surface area (Co/*x*%Nb₂O₅/Al₂O₃). The performance in a CO hydrogenation reaction, in an attempt to explain the effect of niobia on the product selectivity of Co-based catalysts, has been compared to the binary Co/Al₂O₃ and Co/*x*%Nb₂O₅ systems. CO hydrogenation tests with in situ DRIFT data are discussed along with complementary characterizations by diffuse reflec-

* Corresponding author: schmal@peq.coppe.ufrj.br.

[†] Federal University of Rio de Janeiro—NUCAT-PEQ-COPPE.

[‡] Instituto Nacional de Tecnologia.

[§] Fritz-Haber Institut.

TABLE 1: Surface Areas (BET), Total Hydrogen Consumption during TPR, and Contents of Nb₂O₅ and Cobalt

sample	BET area (m ² g ⁻¹)	Nb ₂ O ₅ content (%)	Co content (%)	TPR total H ₂ consumption (μmol g cat ⁻¹) ^b
Co/Al ₂ O ₃	186.9		4.25	0.39
Co/Nb ₂ O ₅	13.1	~95.50	4.50	1.58
Co/5%Nb ₂ O ₅ /Al ₂ O ₃	201.1	4.30	5.00 ^a	0.46
Co/20%Nb ₂ O ₅ /Al ₂ O ₃	178.3	19.9	4.80	0.69

^a Nominal. ^b The theoretical consumption of H₂ for Co₃O₄ ⇒ Co⁰ is 1.17 μmol g cat⁻¹.

tance spectroscopy (DRS), and X-ray photoelectron spectroscopy (XPS) techniques.

2. Experimental Section

2.1. Catalyst Preparation. The niobium ammonium complex material obtained from CBMM (Companhia Brasileira de Metalurgia e Mineração (CBMM, AD 1264)) was calcined at a heating rate 2 K min⁻¹ up to 873 K and kept at this temperature for 4 h to convert an amorphous phase to the crystalline form of niobium pentoxide. Alumina (Harshaw, BET area 197 m² g⁻¹) was pretreated in an aerated furnace (50 mL min⁻¹) at 823 K for 16 h.

The x%Nb₂O₅/Al₂O₃ (x = 5 and 20 weight of Nb₂O₅) was prepared by wet impregnation of alumina with a solution of an ammonium niobium complex in a rotator evaporator for 16 h, as described elsewhere.^{4,5} After drying at 353 K, under vacuum, the sample was set in a furnace and heated at 373 K for 16 h, followed by calcination under flowing air at 823 K (2 K min⁻¹) for 16 h.

The cobalt catalyst was prepared by incipient wetness impregnation with a Co(NO₃)₂·6H₂O (Riedel-de Hën, 99% purity) solution. The Co content was kept constant at approximately 5 wt %.^{1,5} After impregnation, all catalysts were dried overnight at 383 K followed by calcination at 2 K min⁻¹ up to 673 K, kept at this temperature for 3 h, and stored for characterization and catalytic tests. Table 1 shows Nb₂O₅ and cobalt contents plus the total hydrogen consumption during temperature programmed reaction (TPR) experiments. Cobalt concentrations were determined by atomic absorption and the corresponding surface areas of the catalysts were obtained using the BET method.

2.2. CO Hydrogenation. Catalytic evaluation of the catalysts with the CO hydrogenation reaction was performed on a small-scale stainless steel unit. Operational conditions and procedures were selected based on the results from previous studies.^{4,5,14,23,24,28} The gases used were the following: H₂ (commercial grade, for sample reduction), N₂ (commercial grade, for reactor purge), and 31.7% CO/64.3% H₂/4% He (feed gas for reaction). Helium was used as an internal standard to calculate the total CO conversions. These gases passed through filtering elements at room temperature to remove residual O₂ and water traces.

The fixed bed reactor was a vertical stainless steel tube with an approximately 1.5 cm i.d., a wall thickness of 2 mm, and a length of 15 cm. A stainless steel screen was placed 5 cm from the bottom of the reactor to hold the catalyst sample. The gas flow went from top to bottom. The thermocouple tip reached the center of the reactor. A mass of sample between 0.7 and 2 g was dried overnight at 383 K and then reduced after helium flow for ~5–10 min to purge air from the reactor. Hydrogen flow for catalyst reduction was 30 mL min⁻¹. The oven temperature programmer was set to heat from room temperature

to the chosen reduction temperature (573 or 773 K) at a slow rate of 2 K min⁻¹. The final temperature was maintained for 16 h. Immediately after the reduction, the reactor was purged with He at the reduction temperature for ~5–10 min and then cooled under He flow to the reaction temperature (543 K). The reaction was performed at atmospheric pressure and started after the temperature had stabilized by the CO/H₂/He mixture flow into the reactor at a rate of 10–20 mL min⁻¹ to ensure constant space velocity for all experiments. The conditions were established for isoconversion around 5–10%. The total reaction time was approximately 50 h.

Reaction products were analyzed online with two gas chromatographs in series: first through a VARIAN-STAR3400 equipped with a flame ionization detector and then through a thermal conductivity detector (TCD). A Megabore HP-1 column was installed on the VARIAN-STAR3400 (methyl-silicone; 0.53 mm diameter; 30 m length; oven operated from 258 to 523 K at 5 K min⁻¹ for each analysis; initial temperature was kept constant for 3 min). The TCD had a Porapak Q packed column, 3.18 mm (1/8 in.) in diameter and 9 m long (oven operated at constant temperature, 383 K). After the reactor, the tubing lines were kept at ~503 K to avoid product condensation. This hot stream passed through a six-way injection valve that collected ~0.1 cm³ of gas sample.

2.3. Characterizations. *Diffuse Reflectance Spectroscopy (DRS) UV-visible.* Diffuse reflectance spectra were recorded in the range of 200–900 nm using an UV-vis near infrared (NIR) spectrophotometer (Cary 5E, Varian) equipped with an integrating sphere (Harrick). The support (alumina, niobia) and Nb₂O₅/Al₂O₃ samples were used as reference for the Co/Al₂O₃, Co/Nb₂O₅, and Co/Nb₂O₅/Al₂O₃ samples, respectively.

The DRS spectra were recorded on both calcined and pretreated samples. Samples were pretreated in the chamber passing He flow at 5 K min⁻¹ up to 423 K for 30 min and cooled to room temperature for analysis. Then, it was switched to 10% H₂/Ar flow (20 mL min⁻¹) for the reduction and heated to 573 or 773 K, kept there for 30 min, and cooled to room temperature (RT) for analysis.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). A Fourier transform infrared (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 a ZnSe mirror assembly was used to study the CO + H₂ reaction at different temperatures. These experiments were carried out after in situ reduction with pure H₂ (99.99) at 30 mL min⁻¹ at 10 K min⁻¹ up to 773 K for 6 h and then purged with He for 30 min. Subsequently, the sample was cooled to the reaction temperature. A feed mixture of 1 CO:2 H₂ (32% CO, 64% H₂, 4% He) was introduced at 25 mL min⁻¹, under similar reaction conditions. All spectra were obtained after an average of 64 scans from 650 to 4000 cm⁻¹, with a resolution of 4 cm⁻¹ in the presence of the gas-phase species. Each spectrum was referenced to the spectrum of the reduced sample.

X-ray Photoelectron Spectroscopy (XPS). The X-ray photoelectron spectra were obtained using Mg Kα (hν = 1253.6 eV) monochromatized radiation with a Perkin-Elmer 1257 spectrometer. The spectra were analyzed in terms of relative peak area intensity and chemical shifts of the Co_{2p}, Nb_{2p}, and Al_{2p}. The charging effects were corrected using the C_{1s} peak, which was fixed on all the samples at a binding energy (BE) at 284.6 eV. The surface composition was determined by measuring the peak area intensities of the Nb_{3p} and Co_{3p}. The catalysts were

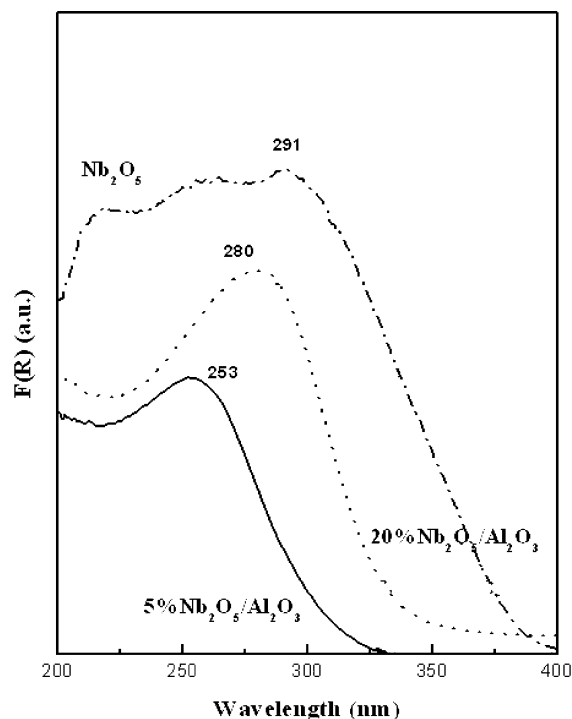


Figure 1. DRS of the $x\%Nb_2O_5/Al_2O_3$.

priori calcined and pretreated in the pretreatment chamber before analysis in the ultrahigh vacuum (UHV) chamber at 10^{-10} mbar.

Temperature-Programmed Reaction (TPR). The temperature-programmed reaction was performed in the same microreactor system; however, samples were collected in a multiloop valve (VCI-Valco) at different temperatures during heating, and at the end, all samples were analyzed online in a TCD chromatograph (Varian-STAR 3400). The catalyst (0.5 g) was previously reduced with pure hydrogen at 573 or 773 K during 16 h and then cooled to room temperature. Then, the catalyst was switched to the reaction mixture $H_2/CO = 2$ flowing at 30 mL min^{-1} and the temperature was raised at a heating rate of 20 K min^{-1} up to 773 K. Products were analyzed using a Porapak Q column under specific conditions: He flow (20 mL min^{-1}) at 323 K for 20 min and then heating, raising the temperature at 20 K min^{-1} up to 443 K.

3. Results

3.1. DRS Results. Figure 1 displays the DRS spectra of bulk Nb_2O_5 and of the $x\%Nb_2O_5/Al_2O_3$ samples. The alumina support was used as reference. The $5\%Nb_2O_5/Al_2O_3$ shows the d–d transition bands at 253 nm that with increasing niobia concentration are shifted to higher wavelengths and in the direction of the bulk sample (291 nm).

On the other hand, DRS spectra of the reduced Co-supported Co/Al_2O_3 , $Co/5\%Nb_2O_5/Al_2O_3$, and Co/Nb_2O_5 catalysts are displayed in Figures 2, 3, and 4, respectively, showing different line shapes.

First of all, the Co/Al_2O_3 spectrum of the calcined sample (Figure 2) presented two strong absorption bands at 402 and 700 nm and a shoulder at 458 nm. These bands (402 and 700 nm) are attributed to Co^{3+} species in octahedral coordination,²⁹ whereas the shoulder (458 nm) is assigned to the octahedral Co^{2+} species.³⁰ After reduction at 573 K, it displays the same profile but is completely modified after reduction at 773 K (solid line), where cobalt species were partially reduced; however, the band around 300 nm remains. According to the literature,^{31,32}

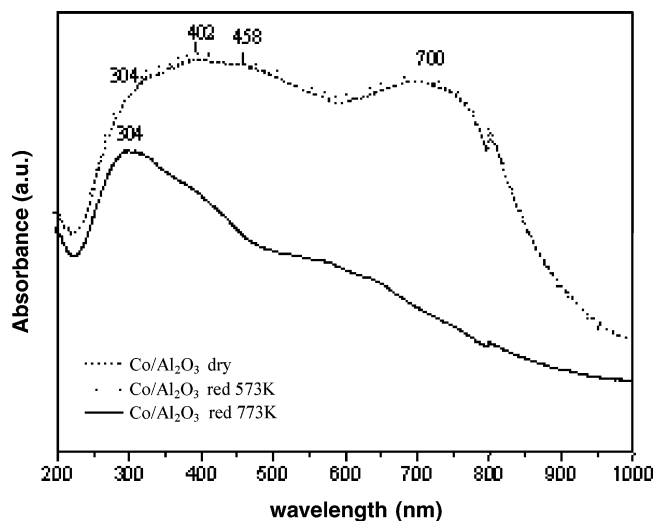


Figure 2. DRS spectra of the Co/Al_2O_3 catalyst after calcination and reduction at 573 and 773 K.

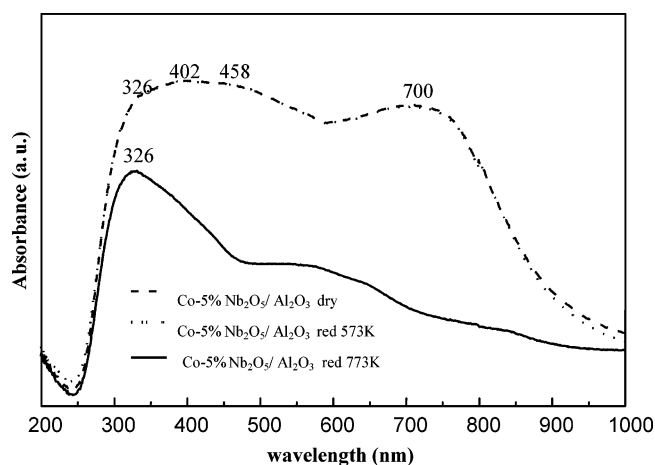


Figure 3. DRS spectra of the $Co/5\%Nb_2O_5/Al_2O_3$ catalyst after calcination and reduction at 573 and 773 K.

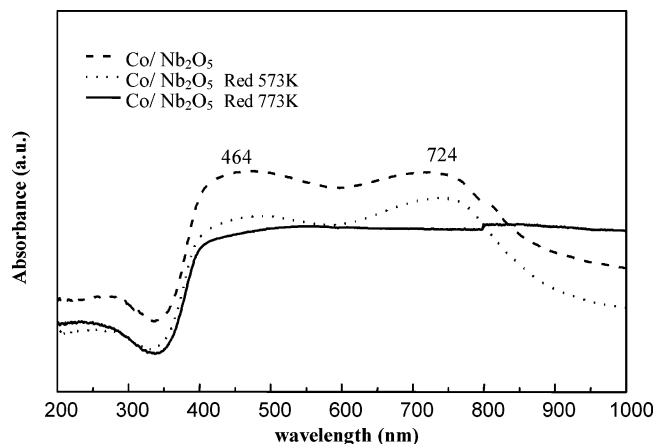


Figure 4. DRS spectra of the Co/Nb_2O_5 catalyst after calcination and reduction at 573 and 773 K.

this band could be assigned to tetrahedral Co^{2+} species. The spectral features of the $Co/5\%Nb_2O_5/Al_2O_3$ catalyst were similar to those of the Co/Al_2O_3 catalyst.

DRS spectra of $5\% Co/Nb_2O_5$ exhibited bands at 464 and 724 nm, which according to Noronha et al.³³ could be attributed to octahedral Co^{3+} and Co^{2+} species.

Figure 5 presents the absorbance spectra of all samples after reduction at 773 K. The addition of niobia shifted the band at

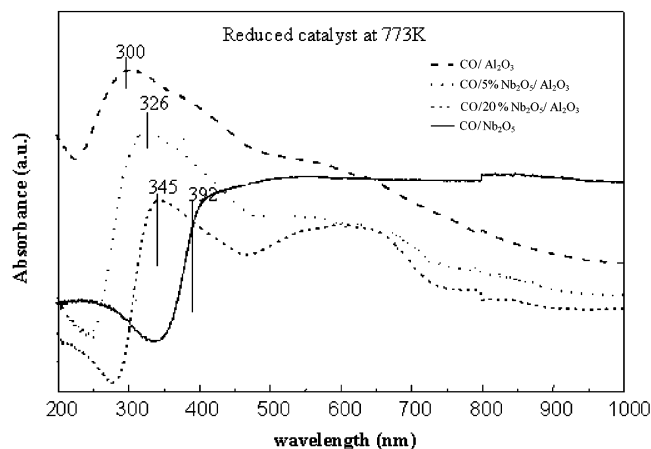


Figure 5. DRS spectra of all prepared catalysts after reduction at 773 K.

300 nm toward higher wavelength, compared to the $\text{Co}/\text{Al}_2\text{O}_3$ catalyst, while the intense band at 400 nm decreased with an increasing amount of niobia. However, it is worth noticing that the band at 300 nm was not observed for the $\text{Co}/\text{Nb}_2\text{O}_5$ catalyst, indicating surface cobalt species in intimate contact with the alumina support.

3.2. DRIFTS Results. Typical spectra of the samples 5% $\text{Co}/5\%\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ and 5% $\text{Co}/20\%\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ are displayed in Figure 6A and B, respectively. After in situ reduction with H_2 , the $\text{CO}/\text{H}_2/\text{He}$ flow mixture was introduced at a ratio of $\text{H}_2/\text{CO} = 2$ during 6 h. The reference spectrum was the reduced catalyst prior to gas admission. Spectra were obtained at different temperatures. Figure 6A $\text{Co}/5\%\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$: (a) alumina at

473 K, (b) catalyst at 523 K, (c) catalyst at 543 K, (d) 523 K closed chamber/30 min, (e) 543 K closed chamber for 5 min. Figure 6B $\text{Co}/20\%\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$: (f) 473 K, (g) 523 K, (h) 543 K, (i) 523 K closed chamber/30 min, (j) 543 K closed chamber/30 min in flow system and after that in a closed chamber for 30 min of exposition and evacuation.

Figure 6A presents the spectrum of Al_2O_3 (spectrum a) under similar reaction conditions and were used with the reference spectrum. At 473 K, it displays characteristic bands of CO in the gas phase (2176 cm^{-1})^{7,35,43} and formate species at 2902 cm^{-1} ($\nu\text{C-H}$), 1592 cm^{-1} ($\nu_{\text{ass}}\text{ C-O}$), 1393 cm^{-1} ($\delta_s\text{ C-H}$), and 1371 cm^{-1} ($\nu_s\text{ C-O}$).^{44,45}

The $\text{Co}/5\%\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalyst shows CO bands at different temperatures, 523 and 543 K (spectra b and c), indicating linear adsorption on top of metallic Co particles (2063 cm^{-1}). On the other hand, the band at 2060 cm^{-1} is attributed to the CO adsorption on $\text{Co}^{\delta+}$ species.³⁵ Zhang et al.⁷ suggest the presence of ionic $\text{Co}^{\delta+}$ species with less electron donation capacity. With increasing temperature (523–543 K), this band is shifted toward 2039 cm^{-1} , suggesting an increase of reduced Co species.

Formate bands were observed at 2902 cm^{-1} ($\nu\text{C-H}$), 1592 cm^{-1} ($\nu_{\text{ass}}\text{ C-O}$), 1393 cm^{-1} ($\delta_s\text{ C-H}$), and 1371 cm^{-1} ($\nu_s\text{ C-O}$)^{34,44,45} that increased with the temperature increase. Above 543 K, the band at 2354 cm^{-1} , relative to CO_2 formation was observed, which may be related to the “shift” reaction or/and the decomposition of formate species. The shoulder at 1650 cm^{-1} is assigned to the formation of $-\text{C}=\text{C}-$, suggesting the formation of olefins.

On the other hand, bands around $3000\text{--}2800\text{ cm}^{-1}$ evidence the presence of CH_x species during the reaction, suggesting also the formation of hydrocarbons, in particular the band at 3010

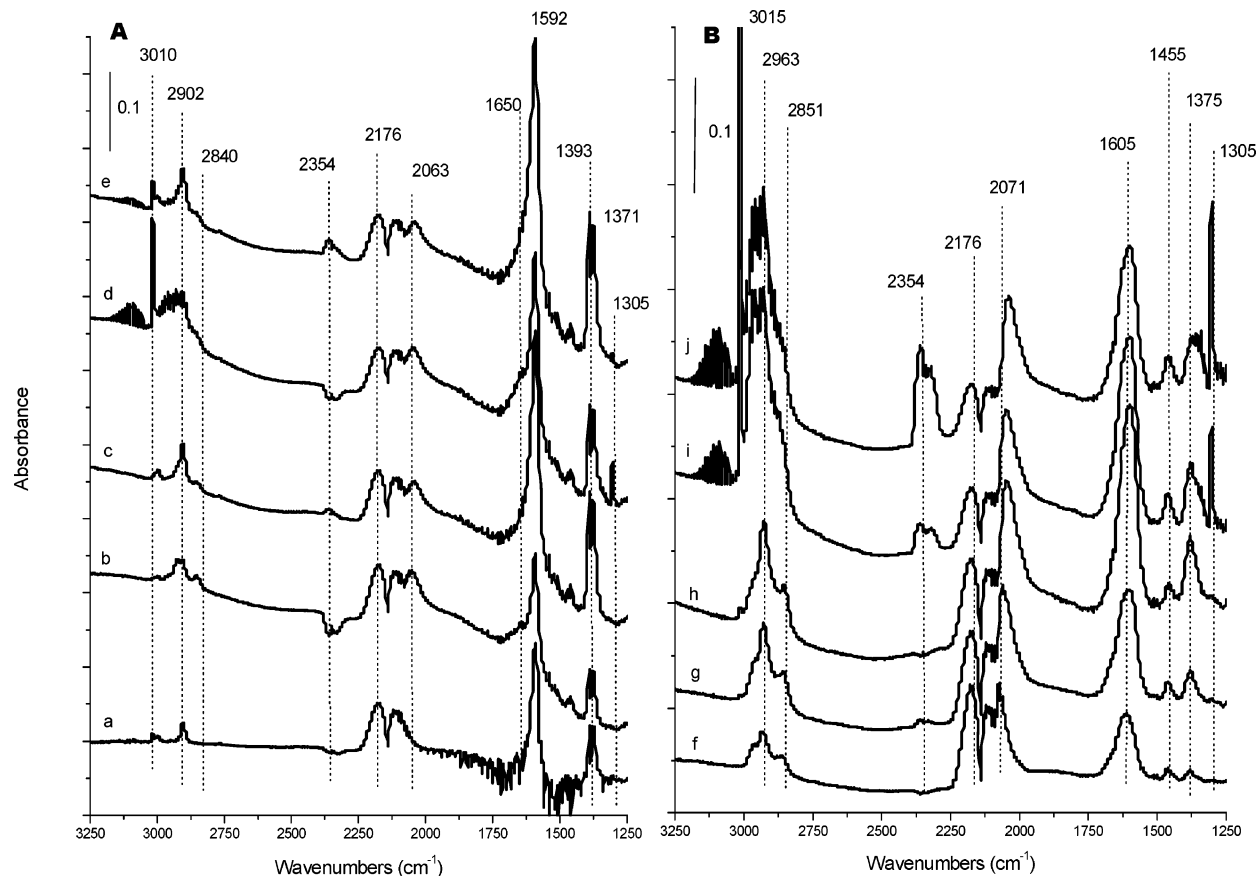


Figure 6. DRIFT spectra of the $\text{CO}/\text{H}_2/\text{He}$ mixture on catalysts. (A) $\text{Co}/5\%\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$: (a) alumina at 473 K, (b) catalyst at 523 K, (c) catalyst at 543 K, (d) 523 K closed chamber/30 min, (e) 543 K closed chamber for 5 min. (B) $\text{Co}/20\%\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$: (f) 473 K, (g) 523 K, (h) 543 K, (i) 523 K closed chamber/30 min, (j) 543 K closed chamber/30 min.

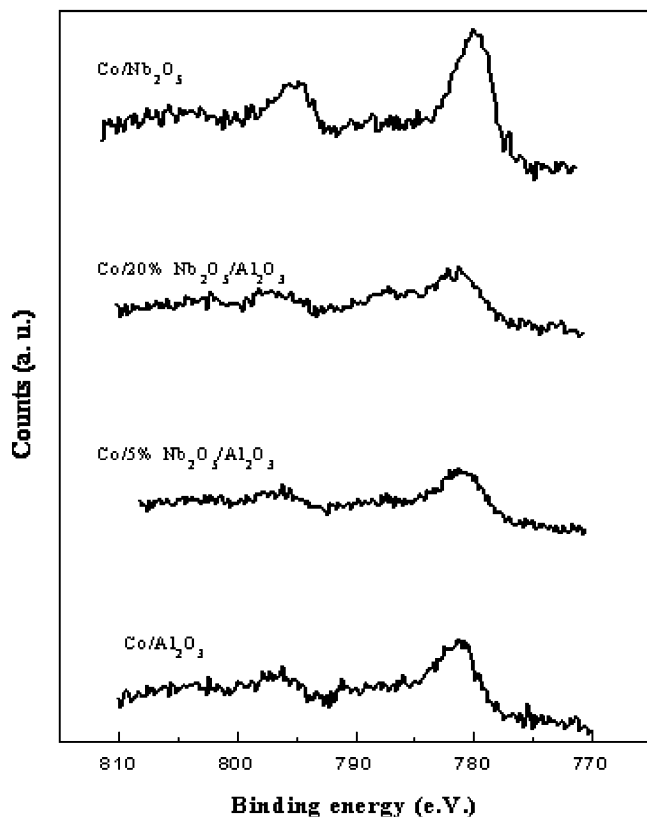


Figure 7. XPS of Co/*x*%Nb₂O₅/Al₂O₃ precursors.

cm⁻¹, which corresponds to axial deformation, and that at 1305 cm⁻¹, corresponding to the angular deformation of the C–H bond of the gas methane. According to Rygh et al.,³⁵ these bands are due to the formation of intermediate CH_{*x*} species.

The Co/5%Nb₂O₅/Al₂O₃ catalyst displays the symmetric stretching of –CH₂ at 2840 cm⁻¹, that evidences this intermediate species. Spectra d and e confirm these bands taken in a closed chamber after evacuation.

The Co/20%Nb₂O₅/Al₂O₃ (Figure 6B) displays similar behavior for CO adsorption on Co^{δ+} species (~2070 cm⁻¹), that changes with increasing temperatures. However, significant modifications were observed between 3000 and 2800 cm⁻¹ and 1650–1250 cm⁻¹. One can see that the formation of CH_{*x*} intermediates at 523 K, related to the bands at 2951 cm⁻¹ (ν_s CH₂), 2928 cm⁻¹ (ν_{ass} CH₂), and 2963 cm⁻¹ (ν_{ass} CH₃), and the band at 3015 cm⁻¹ related to the CH₄ gas; while at 1455 cm⁻¹ (δ_{ass} CH₂+CH₃) and 1375 cm⁻¹ (δ_s CH₃) and at 1305 cm⁻¹ (δ C–H), there are bands related to methane. The band at 1605 cm⁻¹ (ν C=O) is due to the adsorption of bidentate carbonate species, which are responsible for CO₂ formation. The identification of formate species (~1590 cm⁻¹) is not so evident, because this band can superpose the band 1605 cm⁻¹. Moreover, the band at 2902 cm⁻¹ was not observed as before and is attributed to the axial deformation of the C–H bonding of formate. The presence of carbonates and absence or small formation of formate indicate the influence of the niobia content in the catalyst.

3.3. X-ray Photoelectron Spectroscopy. XPS spectra of the calcined precursors Co/*x*%Nb₂O₅/Al₂O₃, Co/Nb₂O₅, and Co/Al₂O₃ are shown in Figure 7. Table 2 presents the binding energy of all studied systems, while Table 3 contains the spin–orbital coupling values as well as the relative intensities between the satellite peaks and the principal peak of the precursors. Co/Nb₂O₅ displays a binding energy of 780.0 eV for Co2p_{3/2} (Table

TABLE 2: Binding Energy of Cobalt-Supported Catalysts

catalysts	Co2p _{3/2}		O1s	Nb3d _{5/2}	Nb3d _{3/2}	Al2p
	Co2p _{1/2}	(eV)	(eV)	(eV)	(eV)	(eV)
Co/Al ₂ O ₃	796.2	781.4	531.6			74.4
Co/5%Nb ₂ O ₅ /Al ₂ O ₃	796.2	781.2	531.4	207.2	210	74.4
Co/20%Nb ₂ O ₅ /Al ₂ O ₃	798.2	781.8	531.4	207.6	210.2	74.6
Co/Nb ₂ O ₅	795.4	780.0	530.2	207.0	209.6	
Co ₃ O ₄	795.4	780.4	530.0			
niobate	797.2	781.2	534.0	206.8	209.6	
aluminate	797.2	781.6	531.2			74.0

2), without a satellite peak and a spin–orbital coupling of 15.4 (Table 3). The calcined precursor of Co/Al₂O₃ displays a binding energy of 781.4 eV for Co2p_{3/2} and a spin–orbital coupling of 14.80 with a small satellite relative intensity peak to the Co2p_{3/2} of 0.334. For the Co/*x*%Nb₂O₅/Al₂O₃ precursors, the addition of niobia does not change this ratio noticeably.

3.4. CO Hydrogenation. Table 4 presents the product distribution of the CO hydrogenation at 543 K for all catalysts reduced at different temperatures for 24 h on stream. These results were obtained at isoconversion. The Co/Al₂O₃ catalysts reduced at 573 and 773 K presented similar selectivities: high selectivity to methane (45–53.2%), light hydrocarbons (34–31.5%), and a low fraction of higher chain carbon hydrocarbons C₅⁺ (17–10.6%). The Co/Nb₂O₅ catalyst reduced at 573 K was also similar to Co/Al₂O₃ (CH₄ = 56.2% and C₅⁺ = 14.8%). However, a considerable change was observed when the same catalyst was reduced at 773 K. The CH₄ selectivity was 5 times lower, with a significant increase of C₅⁺, mainly indicating the formation of linear hydrocarbons in the gasoline and diesel fraction. On coating niobia over alumina catalysts (Co/*x*%Nb₂O₅/Al₂O₃) reduced at 573 K, the results were not significantly different as compared with those of the Co/Al₂O₃ catalyst. However, with higher niobia loading and, in particular, after reduction at 773 K (see Co/20%Nb₂O₅/Al₂O₃), those systems behaved like the monometallic Co/Nb₂O₅ catalyst; although less active, methane was low and C₅⁺ selectivity was higher as well.

Table 5 collects the reaction rates for different reduction temperatures, including, for comparison, our previous results.¹⁴ On the basis of these results, we observed that the activity decreases as follows: Co/Al₂O₃ > Co/Nb₂O₅ > Co/20%Nb₂O₅/Al₂O₃.

The TPSR profiles for methane formation are shown in Figure 8, displaying the molar fraction of methane as a function of the reaction temperature. The Co/Al₂O₃ reduced at 573 K shows an increase of methane with increasing temperature, while when reduced at 773 K the formation of methane reaches a maximum around 630 K, which could be attributed either to coke formation or sintering.

On the other hand, the Co/Nb₂O₅ catalyst exhibited two peaks after reduction at 573 K, with a maximum around 575 and 750 K, while the catalyst reduced at 773 K, although less active, shifted the first peak to a lower temperature. In both cases, the maximum of the second peak was shifted to higher temperatures compared to the Co/Al₂O₃ catalyst.

4. Discussion

Figure 1 shows the DRS spectra of the Nb₂O₅ and Nb₂O₅/Al₂O₃ samples. All Nb₂O₅/Al₂O₃ samples exhibited a metal–ligand charge transfer band. This band was shifted to higher wavelength as the niobium content increased. Tanaka et al.³⁷ have already discussed the transition bands of supported niobium oxides and claimed that they are dependent on the degree of polymerization of surface ions, suggesting an increasing degree of polymerization of niobium species. According to the authors,

TABLE 3: Atomic Ratios, Spin–Orbital Coupling, Rationed Satellite Peaks, and Main Peak of Calcined Precursors

sample	fraction of surface Co ^a (XPS)	fraction of bulk Co ^a	$I_{\text{Nb}}/I_{\text{Al}}$ XPS	$I_{\text{Nb}}/I_{\text{Al}}$ bulk	ΔE^b	R^c
Co/Al ₂ O ₃	0.0110	0.0180			14.80	0.3340
Co/5%Nb ₂ O ₅ /Al ₂ O ₃	0.0180	0.0180	0.0865	0.0213	15.00	0.3706
Co/20%Nb ₂ O ₅ /Al ₂ O ₃	0.0240	0.0200	0.1578	0.1023	16.40	0.5820
Co/Nb ₂ O ₅	0.0300	0.0340			15.40	0.2305
Co ₃ O ₄					15.00	0.1723
niobate					16.00	0.5103
aluminate					15.60	0.4699

^a $I_{\text{Co}}/(I_{\text{Co}} + I_{\text{Al}} + I_{\text{Nb}})$, where I_i is the intensity signal of Co, Al, and Nb. ^b ΔE = distance between lines Co2p_{3/2} and Co2p_{1/2} (spin–orbital). ^c R = ratio between satellite peak and line of Co2p_{3/2}.

TABLE 4: Selectivity to Methane (CH₄), Hydrocarbons (C₂–C₄), Gasoline (C₅–C₁₂), Diesel (C₁₃–C₁₈), and Fractions above (C₁₉)^a

catalysts	T_{red} (K)	light						
		CH ₄	HC	gas ^b	diesel	C ₁₉ ⁺	alcohol	C ₅ ⁺ ^c
Co/Al ₂ O ₃	573	45.0	34.0	13.6	2.6	1.2	3.4	17.0
	773	53.2	31.5	9.2	1.9	0.2	3.9	10.6
Co/5%Nb ₂ O ₅ / Al ₂ O ₃	573	53.4	32.7	9.0	0.9	0.1	3.9	10.0
	773	50.4	33.8	10.5	0.9	0.05	4.3	11.5
Co/20%Nb ₂ O ₅ / Al ₂ O ₃	573	50.1	30.1	9.3	5.2	0.4	4.8	14.9
	773	41.8	30.5	14.0	8.2	2.2	3.2	24.4
Co/Nb ₂ O ₅	573	56.2	24.9	10.8	3.8	0.2	5.1	14.8
	773	10.3	29.0	33.8	18.8	2.3	5.8	55.0

^a Conversions: 5–10%. ^b gas = gasoline. ^c C₅⁺ = $\sum(\text{C}_5 \dots \text{C}_{13}) + (\text{C}_{13} \dots \text{C}_{18})$ and C₁₉⁺.

TABLE 5: Influence of the Reduction Temperature and Nb₂O₅ Content on the Reaction Rate of CO^a

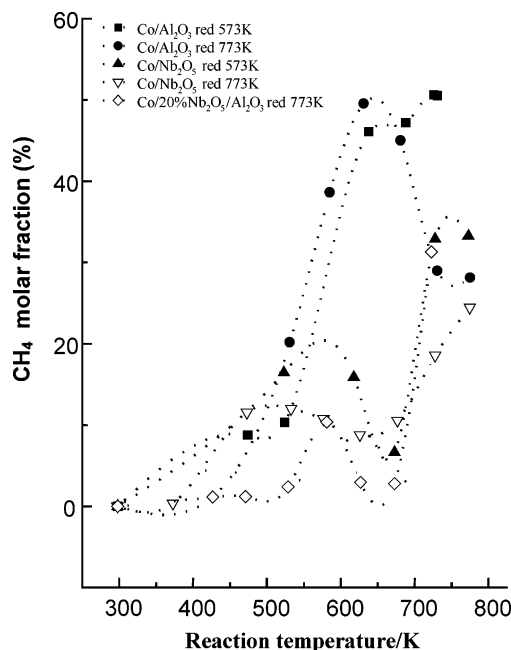
catalysts	T_{red} (K)	conversion (%)	rate CO ^b ($\mu\text{mol s}^{-1} \text{g cat}^{-1}$)	ratio $R_{\text{CNbAl}}/R_{\text{CAI}}$
Co/Al ₂ O ₃	573	12.2	2.13	1.0
	773	10.9	2.30	1.07
Co/5%Nb ₂ O ₅ / Al ₂ O ₃	573	13.7	1.50	0.70
	773	14.3	1.56	0.73
Co/20%Nb ₂ O ₅ / Al ₂ O ₃	573	10.9	1.20	0.56
	773	10.9	1.10	0.51
Co/Nb ₂ O ₅	573	13.0	1.42	0.66
	773	3.8	0.05	0.023

^a Ratio H₂/CO = 2; $P = 1$ atm; $T_{\text{reaction}} = 543$ K. ^b Reaction rate after stabilization for 24 h ($\mu\text{mol s}^{-1} \text{g cat}^{-1}$).

the samples containing low niobium oxide loading have monomeric and oligomeric NbO₄ tetrahedra species, whereas the high loading catalysts contain Nb₂O₅ particles. Therefore, it is possible to infer a polymeric formation of intermediate niobium species with increasing niobium content, that are the precursors of the bulk niobium oxide (Nb₂O₅), exhibiting a d–d band at 291 nm. Indeed, the d–d bands of the intermediate species are 253, 280, and 291 nm for 5, 20, and 100% of niobium contents, respectively (see Figure 1).

Concerning the Co-supported catalysts, we have analyzed the TPR results of these catalysts, which have shown different reduction peaks for Co/Al₂O₃, changing with increasing Nb₂O₅ content, as reported previously.⁴³ The total H₂ consumptions are presented in Table 1, and it can be seen that the reduction is not complete. The total H₂ consumption for the complete reduction of Co₃O₄ to metallic Co⁰ is 1.17 $\mu\text{mol g cat}^{-1}$. The excess of H₂ for the Co/Nb₂O₅ catalyst is due to the reduction of Nb₂O₅ at the surface.

There are three different cobalt species identified in the Co/Al₂O₃ catalyst: Co₃O₄ particles, Co²⁺ species, and a spinel structure of CoAl₂O₄,^{37,38} which occurs at higher temperature

**Figure 8.** TPSR plot of methane formation with reaction temperature of the catalysts reduced at 573 and 773 K.

and is related to the reduction of surface Co²⁺ species with strong interaction with the alumina support. The reduction of Co₃O₄ to Co⁰ corresponds to only 33%.

The Co/Nb₂O₅ presents different degrees of reduction at different temperatures: reduction of Co₃O₄ to Co⁰, partial reduction of Co²⁺ species, and partial reduction of the support at elevated temperatures, which correspond to an H₂ consumption of 135%, indicating reduction of Nb⁵⁺ in contact with Co particles at the surface. On the other hand, the Co/20%Nb₂O₅/Al₂O₃ sample shows only one reduction peak, corresponding to a reduction of 59% of the Co₃O₄ to Co⁰, leaving Co²⁺ species at the surface in contact with niobia. In this case, it seems that at least 40% of the Co²⁺ remain as surface species.

These results are in agreement with the DRS and XPS findings, relative to the presence of Co²⁺ species at the surface, regarding niobate compounds such as Co₂Nb₅O₁₄ and of CoNb₂O₆, which can be reduced at elevated temperatures to metallic cobalt. For higher temperatures, the reduction of NbO₂ particles was also observed.¹⁵

In fact, DRS results of the Co-supported calcined samples exhibited bands, which can be attributed to Co³⁺ in octahedral coordination and octahedral Co²⁺ species, in agreement with Ashley and Mitchell.³² DRS spectra of the catalysts containing 5 and 20 wt % Nb₂O₅ show broader bands, but the spectral features were similar to those of the Co/Al₂O₃ catalyst. DRS spectra of 5%Co/Nb₂O₅ exhibited bands at 464 and 724 nm, which are attributed to octahedral Co³⁺ and Co²⁺ species.

Figure 3 shows the DRS absorbance spectra of the Co/5%Nb₂O₅/Al₂O₃ catalysts after reduction in situ at 573 and 773

K. It appears that at 573 K the cobalt species did not change, exhibiting the same profiles and suggesting that little metallic cobalt is present at the surface, the cobalt ions Co³⁺ and Co²⁺ being the prevailing species. However, after reduction at 773 K, the DRS profile was different, indicating that beside the reduction of cobalt oxide the cobalt species were partially reduced, as seen by the band at 300 nm (Figure 5), which is assigned to tetrahedral Co²⁺ species^{21,31} and still remains after the reduction treatment. These results suggest that the amount of cobalt species which are in contact with the support affect the intensity bands and therefore the coordination of Co species. Thus, the in situ DRS results reinforce qualitatively the presence of metallic cobalt and cobalt species (Co⁰⁺), which are dependent on the degree of reduction and the degree of the contact between cobalt and the support or the intermediate niobium species over the support.

For complementing the identification of Co⁰⁺ species, XPS line shapes of Co2p were taken for Co₃O₄, aluminate, and niobate compounds and could not be distinguished alone through the binding energy of Co2p.³³ Secondary aspects, such as the relative intensity of satellite peaks (*R*) and spin–orbital coupling (ΔE between lines Co2p_{3/2} and Co2p_{1/2}) have to be taken in account (Table 3). The binding energy of Co2p_{3/2} of Co₃O₄ is 780.4 eV without a satellite peak, while niobate, aluminate, and CoO present a satellite peak. The spin–orbit coupling of Co₃O₄ is around 15.0, but it is larger for Co²⁺ (CoO = 16.0, niobate = 16.0, and an intermediate value for aluminate = 15.6).³³

Both Co/Al₂O₃ and Co/Nb₂O₅ present spin–orbit splitting values close to those of Co₃O₄. However, the precursor containing 20% Nb₂O₅ gives rise to higher values.

A comparison between the Co/Al₂O₃ catalyst and the compound references suggests that most particles consist of Co₃O₄, because ΔE and *R* are consistent with the value of this compound. According to the literature,³³ for the calcined 5% Co/Nb₂O₅ precursor, the binding energy for Co2p_{3/2} is 780.3 eV and spin–orbit splitting is 15.4, which are close to our findings and suggest that Co₃O₄ particles are prevailing at the surface.

The Co/Nb₂O₅/Al₂O₃ systems show an increase of 0.7 eV in the spin–orbit splitting coupling value and suggest an increase of Co²⁺ species. The calcined precursor Co/20%Nb₂O₅/Al₂O₃ shows significant increase of the satellite peak and spin–orbital values.

4.1. Reactivity and Selectivity. The dispersions were obtained by H₂ chemisorption measurements (not shown). The dispersions on the Co/Al₂O₃ catalyst reduced at 573 and 773 K are very low, 12 and 6.7%, respectively, and based on the irreversible adsorption at 448 K, suggesting the presence of big cobalt particles; however, for higher reduction temperatures, the particles become even larger due to sintering. The dispersions of the Co/Nb₂O₅ are lower than those for Co/Al₂O₃ and, in particular, for a temperature of reduction of 773 K, where the dispersion is even much lower, 9.3% at 573 K and 4.8% at 773 K, respectively. This is not surprising, has already been observed for reducible supports, such as TiO₂ and Nb₂O₅, and has been attributed to the SMSI effect, due to the migration of reduced Nb₂O_x patches over the cobalt particles.^{14,27,38,39} Measurements of metallic cobalt dispersion onto an Nb₂O₅ surface are imprecise due to the reduction of Nb⁵⁺ in contact with metallic Co⁰ at the surface, which makes the determination of the activity based on the metallic dispersion difficult. Therefore, one can calculate the relative activity of the different catalysts, using, as a reference, the rate of CO production (*R*) ($\mu\text{mol s}^{-1} \text{g cat}^{-1}$) of the Co/Al₂O₃ catalyst reduced at 573 K, as shown in Table 5 for different reduction temperatures. The activity of Co/Al₂O₃

is practically equal for both reduction temperatures at 573 and 773 K; however, it was 30% lower for the Co/5%Nb₂O₅/Al₂O₃ catalyst but approximately equal for both reduction temperatures at 573 and 773 K. With increasing Nb₂O₅ content and with a pure Nb₂O₅ support, the activity of Co/20%Nb₂O₅/Al₂O₃ and Co/Nb₂O₅ catalysts decreased around 40% compared to the Co/Al₂O₃ catalyst but was approximately equal for both reduction temperatures, with the exception of the Co/Nb₂O₅ catalyst reduced at 773 K. These results suggest that the addition of Nb₂O₅ anchored on alumina reduced the metallic sites, which, indeed, indicate the formation of larger particles and therefore lower dispersions, independent of the temperature of reduction. However, the activity of the Co/Nb₂O₅ catalyst reduced at 773 K was very low, which is in accordance with the low dispersion of cobalt compared to the other ones, indicating besides larger particles the presence of an SMSI effect due to the formation of NbO_x patches and their migration of the cobalt particles. In conclusion, the activity depends on the niobia content anchored on alumina; however, for a pure Co/Nb₂O₅ catalyst reduced at 773 K, the SMSI effect prevails. The activity depends mainly on the metallic Co⁰ particle sizes at the surface.

Table 4 presents the selectivity of the different products, and remarkable differences were observed depending on the reduction temperature, which indeed reflects the changes of the surface active sites.

The TPSR profiles of methane formation, as shown in Figure 8, display the molar fraction of methane as a function of the temperature. While the monometallic catalysts present one peak, the Co/*x*%Nb₂O₅/Al₂O₃ catalyst exhibits at least two peaks after reduction at 573 and 773 K, where the first peak is shifted to a lower temperature and the second peak shifted to higher temperatures after reduction at 773 K. These curves evidence a transient behavior of the reaction, which depends on the reduction temperature. Similar observations were observed for other systems and could be explained through different reaction mechanisms due to the formation of different surface sites.

Lee and Bartholomew⁴⁰ observed two peaks of methane formation for the Co/Al₂O₃ catalyst using the TPSR technique. They attributed the formation of the low temperature methane peak to methane formed on big metallic Co⁰ crystallites, and the second peak they considered to indicate a methane formation through CH_xO species that had been formed on the support, due to spillover, followed by decomposition of these species on metallic particles, due to back spillover.

However, such oxygenate species would also depend on the nature of the surface of the support. In the case of alumina, probably, such a spillover effect could be explained by the caption of oxygen from the hydroxyl groups. On the basis of the dispersion, there are big Co particles apparently covering the external surface of alumina, which probably hamper the spillover of such species through the support. The surface area of the niobia support is much smaller than the one of alumina, and therefore, there are big cobalt particles covering the external surface of the support too. However, the question is what kind of species are there. The DRS and XPS results presented above evidence the presence of Co³⁺ and Co²⁺ species on the surface of the niobia support, in accordance with the literature.^{17,23} Metallic Co⁰ coexists with Co²⁺ species after reduction, and the majority of Co⁰ originate from Co₃O₄, which can be transformed partially into Co²⁺ and subsequently into Co⁰ in addition to a thin layer of Co²⁺ species, which still remains after calcination.¹⁷ These Co²⁺ species are strongly interacting with the support, are distributed as a thin layer at the surface, and, hence, are very difficult to reduce to metallic cobalt, but

only at elevated temperature, as reported previously.^{17,23} It was observed by DRS in situ that a majority of Co^{2+} species exist after reduction at 573 K, but for 773 K, these surface species are then reduced to metallic cobalt (Figures 4 and 5).

DRIFTS experiments on a typical $\text{Co}/x\% \text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalyst showed CO adsorption on metallic Co^0 at 2119 cm^{-1} . According to Toomes and King,⁴² this band corresponds to CO adsorption on top of metallic cobalt (2130 cm^{-1}). Moreover, Jiang et al.⁴¹ observed one band at 2080 cm^{-1} , which was taken as an indication of CO adsorbed on $\text{Co}^{\delta+}$ ($0 < \delta < 2$). In addition, Rygh et al.³⁵ attributed the band at 2060 cm^{-1} to overlapping bands from $\text{Co}(\text{CO})_n$ and $\text{Co}^{\delta+}-\text{CO}$ on a single crystal.

A new band appeared at 2170 cm^{-1} even at room temperature and was unperturbed at high temperatures. It has not been reported before for Co-supported systems. Freund et al.³⁶ attributed this band to the stretching vibration frequency of CO adsorbed on a hydroxylated $\text{CoO}(111)/\text{OH}$ surface.

On the other hand, CH_xO formate species are also displayed at 2902 cm^{-1} in the DRIFTS experiments of the sample reduced at 773 K, corresponding to the CH stretching of adsorbed formate ions. Marked differences were observed during DRIFTS experiments fluxing CO and H_2 , displaying the formation of new bands at 1650, 1592, 1393, and 1371 cm^{-1} . The band at 1647 cm^{-1} appeared at 473 K and disappeared at 543 K, which indicates the presence of an olefin $-\text{C}=\text{C}-$ at the surface. On the other hand, the bands at 1592, 1393, and 1371 cm^{-1} increased with increasing temperature, which is an indication of the formation of $-\text{CH}_n-$ fragments or geminate CH_3 groups. Other bands did not change with increasing reaction temperatures. All this suggests the formation of linear chain growth at the surface of the catalysts studied. In addition, CO hydrogenation on these catalysts reveals the prevailing presence of linear hydrocarbons (paraffins).

Rygh et al.³⁵ confirmed Lee's proposals, indicating that CO is dissociated on large metallic crystallites followed by hydrogenation of the α -carbon and a spillover of CO and H to the support with the formation of CH_xO complexes, which, in the following, diffuse back to the metal and decompose. They also claim that the H spillover promotes the reduction of Co species.

Therefore, our results suggest likewise that the CH_xO species are the precursors for the formation of hydrocarbons, and characterizations revealed the presence of Co^0 particles (big particles because of the low dispersion) which are surrounded by Co^{2+} species. CH_x^- is thought to be formed as methyl radicals on Co^0 particles, as displayed by DRIFTS. The methyl radicals might migrate toward Co^{2+} with the caption of oxygen atoms from CoO allowing for the formation of intermediate CH_xO complexes, followed by decomposition to methane on metallic Co^0 particles. With an increasing temperature of reduction, Co^{2+} species can be reduced to Co^0 , and therefore, the back spillover may occur on these new interfaces ($\text{Co}^0-\text{Co}^{2+}$), which increase during the reaction, allowing decomposition to methane on the metallic sites. Indeed, DRS results showed bands at 402 and 700 nm, which are attributed to Co^{3+} in octahedral coordination, and a shoulder around 458 nm, which corresponds to the octahedral Co^{2+} species, in addition to the band around 300 nm that remains after the reduction and is attributed to tetrahedral Co^{2+} species.

DRIFTS results displayed also growing amounts of CH_3 groups. It is noteworthy that the niobium intermediates facilitate the formation of such interfaces, probably due to the formation of NbO_x complexes. It explains why chain growth is facilitated in the presence of these complexes, disfavoring methane formation and favoring selectivity toward higher hydrocarbon

formation. The lower the methane production is, the higher the presence of long chain hydrocarbons.

Finally, the TPR results on the $\text{Co}/\text{Nb}_2\text{O}_5$ reported previously⁴³ showed that after an initial reaction at lower temperatures the catalysts suffers deactivation and then experiences an activation process, which can be explained by the SMSI effect and not by coke formation. The XPS intensity ratio ($I_{\text{Nb}}/I_{\text{Al}}$) in Table 3 indicates a high concentration of Nb at the surface, and TPR results evidence the reduction of Nb_2O_5 at the surface. Indeed, NbO_x species present at the interface migrate over Co^0 with the formation of patches, blocking metallic surface sites. However, with the formation of water during the reaction, as reported by Kunimori et al.³⁸ and Haller and Resasco,³⁹ the surface is cleaned up and the NbO_x species are partially removed from the metallic Co^0 surface. It seems that during this process formation and destruction of new interfaces involving Co^0-NbO_x sites occur. DRIFTS and selectivity results suggest that these sites might be responsible for the reaction chain growth and therefore for the drastic change in the selectivity of CH_4 and C_5^+ hydrocarbons, mainly on the $\text{Co}/\text{Nb}_2\text{O}_5$ catalyst.

The catalyst containing 20 wt % Nb_2O_5 exhibited similar behavior, approaching monometallic when reduced at high temperature. DRS results of these catalysts showed bands shifted toward higher wavelength compared to the $\text{Co}/\text{Al}_2\text{O}_3$ catalyst. A band around 300 nm remained after the catalysts have been reduced at high temperature, which suggests the presence of cobalt oxide species at the alumina support, however, in smaller amounts compared to the $\text{Co}/\text{Nb}_2\text{O}_5$ catalyst itself.

These results allow us to suggest the formation of interfacial sites, such as $\text{Co}^0-\text{Co}^{2+}$ sites and $\text{Co}^0-\text{Nb}_2\text{O}_x$ sites, leading to reaction pathways of two-site reactions: First, CO dissociates on Co^0 sites by forming α -carbon and, subsequently, methyl groups which spillover to the interfacial ($\text{Co}^0-\text{Co}^{2+}$) sites, leading to intermediary methoxy species formation. Second, in the presence of niobia, formation of methyl radicals at interfacial Co^0-NbO_x sites is suggested, which allows for chain growth, favoring the formation of higher than C_5^+ chains.

5. Conclusions

DRS and XPS results showed that NbO_x species are formed upon coating Nb_2O_5 over an alumina support, which grows like a polymer structure at the surface with increasing niobia loading until the formation of a monolayer is completed. Above 20% niobia loading, larger Nb_2O_5 particles were formed.

DRS results of Co niobia/alumina systems showed the presence of Co^{3+} and Co^{2+} species in different coordination environments. After reduction at 573 K, they are the prevailing species. When reduced at 773 K, the Co^{2+} or Co^{3+} species are partially reduced to Co^0 , an effect which decreases with Nb loading.

Characterizations including DRS, XPS, DRIFTS, and selectivity results on $\text{Co}/x\% \text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalysts have shown that surface modification takes place via the formation of metallic Co^0 , surface $\text{Co}^{\delta+}$ ions, and interfacial $\text{Co}^{\delta+}-\text{NbO}_x$ sites. It seems that during the reaction process formation and destruction of new interfaces occur, and results suggest that these sites might be responsible for the reaction chain growth and therefore for the drastic change in the selectivity of CH_4 and C_5^+ hydrocarbons, mainly on the $\text{Co}/\text{Nb}_2\text{O}_5$ catalyst.

DRIFTS results of $\text{Co}/\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalyst showed olefins disappearing with an increasing temperature of reaction and simultaneously increasing formation of methyl radical groups and methoxy, which are the precursors of longer hydrocarbon chains.

The obtained results are in good agreement with our TPR results, which have been previously published. The activity relative to methane formation for Co/Nb₂O₅/Al₂O₃ was dependent on the reduction temperature. Catalytic results showed high C₁ and low C₅⁺ formation for lower Nb contents but, on the other hand, extremely low C₁ and high C₅⁺ with higher NbO_x loading, suggesting that in the first case Co⁰–Co²⁺ are the active sites, while in the second case interfacial Co–NbO_x and Co⁰–Co²⁺ are the active sites.

References and Notes

- (1) Mendes, F.; Noronha, F. B.; Soares, R. R.; Perez, C. A. C.; Marchetti, G.; Schmal, M. *Stud. Surf. Sci. Catal.* **2001**, *136*, 177.
- (2) Schulz, H. *Appl. Catal.* **1999**, *186*, 3.
- (3) Bertole, J. C.; Mins, A. C.; Kiss, G. *J. Catal.* **2004**, *221*, 191.
- (4) Mendes, F. T.; Noronha, F. B.; Schmal, M. *Stud. Surf. Sci. Catal.* **2000**, *130*, 3717.
- (5) Mendes, F.; Noronha, F. B.; Soares, R. R.; Perez, C. A. C.; Marchetti, G.; Schmal, M. *Stud. Surf. Sci. Catal.* **2001**, *136*, 177.
- (6) Martínez, A.; Lopez, C.; Márquez, F.; Díaz, I. *J. Catal.* **2003**, *220*, 486.
- (7) Zhang, J.; Chen, J.; Ren, J.; Sun, Y. *Appl. Catal. A* **2003**, *243*, 121.
- (8) Hachenberg, H.; Wunder, F.; Leupoid, E. I.; Schmidt, H. J. European patent application 21330, 1981.
- (9) Kuznetsov, V. L.; Lisitsyn, A. S.; Golovin, A. V.; Aleksandrov, M. N.; Yermakov, Yu. I.; In *Homogeneous and Heterogeneous Catalysis*; Yermakov, Yu. I.; Likhobolov, V., Eds.; VNU Science Press: Utrecht, The Netherlands, 1986.
- (10) Lisitsyn, A. S.; Golovin, A. V.; Chuvilin, A. L.; Kuznetsov, V. L.; Romanenko, A. V.; Danilyuk, A. F.; Yermakov, Yu. I. *Appl. Catal.* **1989**, *55*, 235.
- (11) Fujimoto, K.; Oba, T. *Appl. Catal.* **1985**, *51*, 289.
- (12) Derule, H.; Blanchard, M.; Canesson, P. *Appl. Catal.* **1989**, *50*, L1.
- (13) Schnke, D. D. *New Trends of Methane Activation*; Elsevier: New York, 1990.
- (14) Silva, R. R. C. M.; Dalmon, J. A.; Frety, R.; Schmal, M. *J. Chem. Soc., Faraday Trans.* **1993**, *89* (21) 3975.
- (15) Noronha, F. B.; Frydman, A.; Aranda, D. A. G.; Soares, R. R.; Moraweck, B.; Castner, D. D.; Campbell, C. T.; Frety, R.; Schmal, M. *Catal. Today* **1996**, *28*, 147.
- (16) Sinfelt, J. H. *Bimetallic Catalysts Discoveries, Concepts and Applications*; Wiley: New York, 1983.
- (17) Frydman, A.; Campbell, C. T.; Castner, D.; Schmal, M. *J. Catal.* **1995**, *157*, 133.
- (18) Kapoor, M. P.; Lapidus, A. L.; Krylova, A. Y. In *Proceedings of the 10th International Congress on Catalysis*; Guzzi, L., Solymosi, F., Tetenyi, P., Eds.; Elsevier: Budapest, 1992; Part C, p 2741.
- (19) Iglesia, E.; Soled, S. L.; Fiato, A.; Via, G. H. *J. Catal.* **1993**, *143*, 345.
- (20) Iglesia, E. *Appl. Catal. A* **1997**, *121*, 59.
- (21) Tsubaki, N.; Sun, S.; Fujimoto, K. *J. Catal.* **2001**, *199*, 236.
- (22) Macedo, J. C. D.; Schmal, M.; Dalmon, J. A. In *Proceedings of the X Symposium Iberoamerican on Catalysis*; 1986; Part 2, p 666.
- (23) Frydman, A.; Soares, R. R.; Schmal, M. *Stud. Surf. Sci. Catal.* **1993**, *75*, 2796.
- (24) Soares, R. R.; Frydman, A.; Schmal, M. *Catal. Today* **1983**, *16*, 361.
- (25) Iizuka, T.; Tanaka, Y.; Tanabe, K. *J. Mol. Catal.* **1982**, *17*, 381.
- (26) Vannice, M. A.; Garten, R. L. *J. Catal.* **1979**, *56*, 236.
- (27) Ko, E. I.; Hupp, M. *J. Catal.* **1984**, *86*, 315.
- (28) Dietz, W. A. *J. Gas Chromatogr.* **1967**, (February), 68.
- (29) Sass, A. S.; Shvets, V. A.; Svelëva, G. A.; Kasanskii, U. B. *Kinet. Katal.* **1985**, *26* (5), 1149.
- (30) Chung, K. S.; Massoth, F. E. *J. Catal.* **1980**, *64*, 320.
- (31) Lever, A. B. P. *Inorganic Spectroscopy*; Elsevier: Amsterdam, 1968.
- (32) Ashley, J. H.; Mitchell, P. C. H. *J. Chem. Soc. A* **1968**, 2821.
- (33) Noronha, F. B.; Perez, C. A.; Schmal, M.; Fréty, R. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2861.
- (34) Busca, G.; Lamotte, J.; Lavalley, J. C.; Lorenzelli, V. *J. Am. Chem. Soc.* **1987**, *109*, 5197.
- (35) Rygh, L. E. S.; Nielsen, C. J. *J. Catal.* **2000**, *194*, 401.
- (36) Schonnenbeck, M.; Cappus, D.; Klinkmann, J.; Freund, H. J.; Petterson, L. G. M.; Bagus, P. S. *Surf. Sci.* **1996**, *347*, 337.
- (37) Tanaka, T.; Nojima, H.; Yoshida, H.; Nakagawa, H.; Funabiki, T.; Yoshida, S. *Catal. Today* **1996**, *16*, 297.
- (38) Kunimori, K.; Abe, H.; Yamaguchi, E.; Matsui, S.; Uchijima, T. In *Proceedings of 8th International Congress on Catalysis*, V; 1984; p 251.
- (39) Haller, G.; Resasco, D. E. *Adv. Catal.* **1989**, *36*, 173.
- (40) Lee, W. H.; Bartholomew, C. H. *J. Catal.* **1989**, *120*, 256.
- (41) Jiang, M.; Koizumi, N.; Ozaki, T.; Yamada, M. *Appl. Catal. A* **2001**, *209*, 59.
- (42) Toomes, R. L.; King, D. A. *Surf. Sci.* **1996**, *349*, 1.
- (43) Mendes, F. M. T.; Perez, C. A. C.; Noronha, F. B.; Schmal, M. *Catal. Today* **2005**, *101*, 45.
- (44) Colthup, N. *Introduction to infrared and Raman spectroscopy*, 2nd ed.; Academic Press Inc.: New York, 1975.
- (45) Little, L. H. *Infrared Spectra of Adsorbed Species*; Academic Press Inc.: London, 1966.