

Heavier alcohols synthesis on cobalt phyllosilicate catalysts

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Abstract

The ammonia method was used to prepare cobalt phyllosilicates catalysts. Simultaneous thermogravimetry analysis and its derivative–differential scanning calorimetry (TGA-DTG–DSC) comparison studies on $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, SiO_2 aerosil 200 precursor, after being treated with the ammonia method, and on the final synthesized catalyst, indicated that the first step during the synthesis process is the cobalt aqua-complex formation that interacts with the silica aerosil 200 forming Co–phyllosilicate.

Temperature-programmed reduction studies (TPR) show at least two phases for such catalysts. One, is a lower-temperature phase (603 K), corresponding to free cobalt aqua-complex, and the other a cobalt phyllosilicate phase at higher temperature (1123 K). Such phases can be separated by washing and filtration and were identified by Fourier transform infrared (FTIR) spectroscopy. The capability of the sample (high solubility) being separated into two phases excluded the possibility of having a cobalt hydroxide as the low-temperature phase.

The catalyst is active for carbon monoxide hydrogenation and very selective to methanol and ethanol formation in the proportion 2:1, similar to that found for the two metal phases in the catalyst by TPR.

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1. Introduction

Cobalt catalysts, both supported and unsupported, have been widely applied industrially in carbon monoxide hydrogenation to produce fuels and chemicals via Fischer Tropsch synthesis [1,2]. The activity and selectivity of such catalysts is strongly influenced by the preparation method and the nature of precursor salts involved [1–6], together with the thermal pretreatment and the way in which the reactor is started up [1,7]. Among the catalyst preparation methods, the ammonia method has been proposed [8] to prepare silica-supported cobalt and nickel catalysts with no pores, high metal dispersion and small particle sizes, which are desirable structural properties to avoid reactant diffusion limitations and catalyst deactivation [9–11]. Contrary to other preparation methods such as impregnation or precipitation, in which the metal is simply deposited on the support, the

ammonia method provides strong interactions between the metal and support. Previous characterization studies carried out by X-ray electron spectroscopy (XPS), scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) of such solids [12–14] suggested that cobalt phyllosilicate is a composite sheet in which a layer of octahedrally coordinated cations is sandwiched between two identical layers of linked SiO_4 tetrahedra of composition Si_2O_5 . Additional hydroxyl ions, together with the oxygens from the tetrahedron, complete the octahedral coordination of the sandwiched cations. The reduction process of such solids under hydrogen flow at temperatures higher than 973 K destroy the phyllosilicate structure leading to fine cobalt particles dispersed on the silica support.

This work evaluates, by thermogravimetry analysis and its derivative (TGA-DTGA), differential scanning calorimetry (DSC), temperature-programmed reduction (TPR) and Fourier transform infrared spectroscopy (FTIR), the chemistry involved in the cobalt phyllosilicate synthesis and catalytic performance of cobalt phyllosilicate in the

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higher alcohol synthesis reaction after pretreatment under hydrogen flow.

2. Materials and methods

The silica-supported cobalt catalysts were prepared according to the method described by Barbier et al. [8] except for the inert atmosphere that was not necessary because it was demonstrated that the metal complex, formed during the synthesis step, is not easily reducible. The catalysts preparation of 10% cobalt was as follows: 5.5 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (high purity, J.T. Baker) was added to 96 mL of distilled water at room temperature and stirred by a magnetic rod. Cobalt hydroxide was precipitated by addition of some drops of ammonia solution (25% NH_3 , Riedel de-Haën). A large excess of ammonia solution (96 mL) was added to dissolve the precipitate. After 1 h of stirring, 10 g of silica aerosil 200 (200 m^2/g , specific surface area, Degussa) was added to the solution. The system was dried in an oven at 353 K for 48 h after stirring for 2 more hours. Except when otherwise indicated, the samples were reduced under a hydrogen flow (10 mL/min) by slowly increasing the temperature at a heating rate of 1 K/min. The final temperature was 723 K and the total reduction time was 55 h.

Thermal decomposition studies of the fresh catalysts (dried by evaporation at 353 K) and its precursors were done using simultaneous thermogravimetric analysis, its derivative and differential scanning calorimetry on a SDT Q600 TA instrument in air flowing at 100 mL/min and with a $10^\circ\text{C}/\text{min}$ heating rate.

The infrared spectra of the fresh material and the phyllosilicates washed in distilled water were obtained on KBr in a Perkin-Elmer 1725 X FTIR. Temperature-programmed reduction profiles were performed using a Micromeritics TPR/TPD 2900 from room temperature to 1475 K at $10\text{ K}/\text{min}$ heating rate under 10% hydrogen in Argon. Samples of 150 mg were pretreated in air before the TPR measurements.

The catalytic performance of the cobalt phyllosilicates for the synthesis of heavier alcohols was tested in a continuous, fixed-bed tubular reactor described previously [13]. A controlled heater ensured a uniform bed temperature monitored by a thermocouple placed in the reactor center. Carbon monoxide, carbon dioxide and light hydrocarbons were analyzed by online gas chromatography (Hewlett Packard 6890 Plus) equipped with a thermal conductivity detector and a Porapak Q column ($10' \times 1/8''$, 80/100 mesh) and by online low resolution mass spectrometry (quadrupole) using a Balzer Instruments Omnistar GSD 300, operating at 1140 eV ionization energy, in the residual gas analysis (RGA) mode. In this way, it is possible to monitor every 14 s the composition (% concentration) of the gases as a function of time. The monitoring was done by measuring the molecular peak intensity of each compound in the reactor exit mixture (i.e. for CO , H_2O , CO_2 , CH_4 , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, from the m/e value at

28, 18, 44, 16, 32 and 46 amu, respectively). Condensed C_5+ and oxygenated hydrocarbons (mainly alcohols) were collected during the run time in an ice-water trap and analyzed by gas chromatography using a flame-ionization detector and an HP-1 (100 m \times 0.25 μm \times 0.5 μm) capillary column. One cc of the catalyst was reduced “in situ” with a 10 mL/min hydrogen flow at a heating rate of 1 K/min from room temperature to 723 K for 55 h. The reactions were performed at 513 K, 34 bar pressure and $48,000\text{ H}^{-1}$ gas hour space velocity (G.H.S.V.) using a 1.0 feed molar ratio (H_2/CO). After runs the gas feed was closed and the reaction temperature was sharply decreased to room temperature.

3. Results and discussion

3.1. Thermal characterization

3.1.1. TGA-DTG–DSC study in air flow

Thermo gravimetric patterns of the cobalt phyllosilicate catalyst and its precursors, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and silica aerosil 200 as received, and after treatment with the ammonia method, are shown in Fig. 1. The patterns were measured in flowing air at $10^\circ\text{C}/\text{min}$.

It was observed that the silica aerosil 200 and the silica aerosil treated with the ammonia method display similar decomposition patterns, except for a small increase in weight loss at low temperatures (300–325 K) observed for the silica treated with the ammonia method that could be due to hydrated water from the preparation method.

The $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ decomposition pattern shows five steps before degradation to CoO in the last step. It has been stated [15] that dehydration of metal nitrate hydrates, except for cadmium nitrate hydrate, cannot be achieved by heating, because dehydration proceeds together with partial decomposition of nitrate groups. Thus, the production of anhydrous

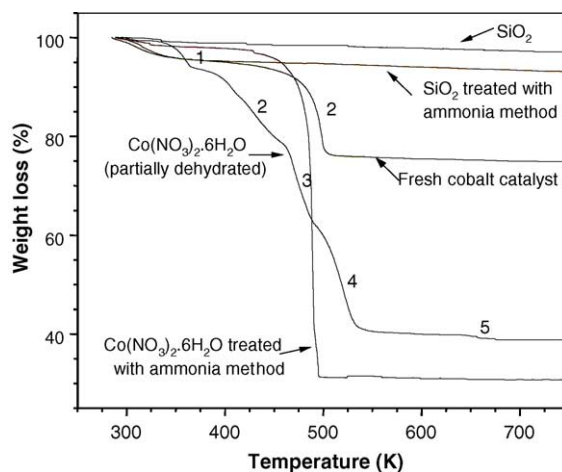
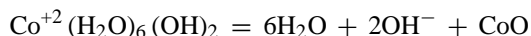


Fig. 1. Thermogravimetric analysis (air at $10^\circ\text{C}/\text{min}$), comparison of silica aerosil 200, silica aerosil treated with the ammonia method cobalt catalyst, cobalt nitrate hexahydrate and cobalt nitrate hexahydrate treated with the ammonia method.

salt by simple dehydration requires complete reconstruction of the crystallographic lattice accompanied by partial decomposition of nitrate ions.

The decomposition pattern of the salt used as a catalyst precursor is very similar to those reported by other authors [15,16]. Thus, the first two steps could correspond to water loss (300–425 K), water and N_2O_5 for the next two steps (425–500 K) to form $\text{Co}(\text{OH})_2$ and then water loss to form CoO .

The decomposition pattern of the salt changes dramatically when it was treated with the ammonia method. In such a case, one decomposition step was mainly observed. The experimental weight loss was about 69% corresponding to the following reaction:



that is very close to the calculated value (70.35%) for the proposed equation.

It is well known that small cations (Co, Ni, Fe) from metal nitrate hydrates can lead to the formation of large ions like $\text{M}(\text{H}_2\text{O})_6^{k+}$ ($k > 2$) with the electric charge spread over its surface. The hydrated ions can coordinate sufficient nitrate ions to neutralize the M^{k+} charge. In our case, the salt solution treated with the ammonia method was evaporated at 353 K (to obtain a solid) before the TGA experiment. At such a temperature, partial dehydration accompanied by the decomposition of nitrate ions could occur leading to a cobalt (II) aqua-complex neutralized mainly by OH groups from solution.

The decomposition pattern (TGA) of the fresh cobalt catalyst (dried at 353 K) is similar to that found for the salt treated with the ammonia method. In the first step, the solid loses hydration water (3%) from the silica aerosil present in the sample and then loses all the water (21.2%) in the cobalt aqua-complex, suggesting that all the cobalt present in the catalyst was in the cobalt aqua-complex form.

Fig. 2 shows the derivative of weight loss versus temperature of the same compounds. The decomposition processes of

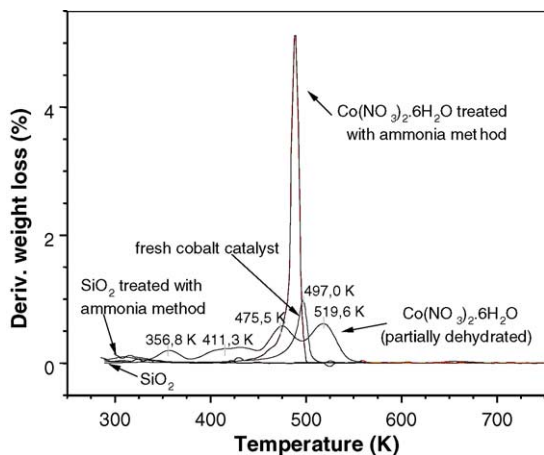


Fig. 2. DTGA of cobalt phyllosilicate catalyst synthesized with the ammonia method and its precursors as received and treated with the ammonia method.

the hydrated cobalt nitrate treated with the ammonia method and the phyllosilicate seems to be very similar, even though the ammonia-treated catalyst decomposes at high temperatures, both processes present sharp peaks in similar temperature intervals, around 500 K.

Differential scanning calorimetry of the samples under study is shown in Fig. 3. The transformations taking place on cobalt nitrate hexa-hydrated treated with the ammonia method, and on cobalt phyllosilicate, are exothermic and are very different from those found for the cobalt salt as received (endothermic). The heat flow of the cobalt salt treated with the ammonia method is 2272 J/g and that of the catalyst is about 604 J/g. For similar compounds, a heat flow of the same order is expected and proportional to the amount of sample. On the cobalt catalyst, the heat flow is about 30% of the value found for the cobalt aqua-complex and the expected value is about 10% suggesting that part of the cobalt aqua-complex present in the catalyst is bonded to the phyllosilicate, Si_2O_5 .

3.1.2. Temperature programmed reduction

Fig. 4(a) shows the temperature-programmed reduction profile of the silica aerosil treated with the ammonia method. In this case, hydrogen uptake was not observed over the entire interval of temperature tested. Fig. 4(b) shows the profile of temperature-programmed reduction of 10% Co phyllosilicate catalyst. Two main reduction peaks in 603 K (330 °C) and 1123 K (850 °C) can be observed. The first peak could be assigned to $\text{Co}(\text{OH})_2$ (formed during the dissolution process of the cobalt salt) or to part of the cobalt aqua-complex not reacted with the silica surface like $\text{Co}^{+2}(\text{H}_2\text{O})_6$ or $\text{Co}^{+3}(\text{H}_2\text{O})_6$ formed during catalyst preparation. The second peak could be assigned to cobalt aqua-complex that interacts strongly with the support to form cobalt phyllosilicates of the type $\text{CoO}(\text{OH})(\text{Si}_2\text{O}_5)_2$ or $\text{Co}(\text{OH})_2(\text{Si}_2\text{O}_5)_2$ [1].

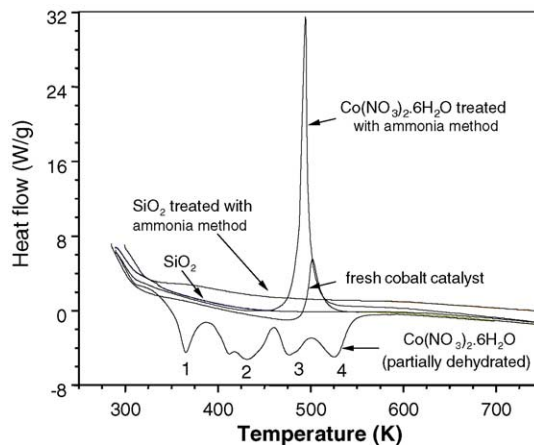


Fig. 3. Differential scanning calorimetry (air at 10 °C/min.) of cobalt phyllosilicate and its precursors as received and after treatment with the ammonia method.

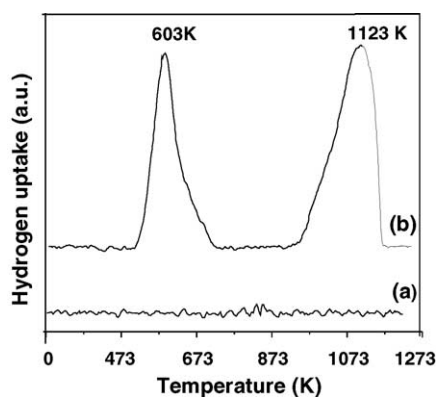


Fig. 4. Temperature-programmed reduction profiles: (a) silica aerosil 200 treated with the ammonia method; (b) 10% cobalt phyllosilicate dried at 353 K.

3.2. FTIR study

Fig. 5 shows the FTIR spectra of: (a) the fresh cobalt phyllosilicate catalyst (dried by evaporation at 353 K) (b) the solid obtained by washing in distilled water (one hour stirring), filtered and dried at 353 K, of the cobalt catalyst and (c) the solid obtained from the liquid filtrated after evaporation for several days at 353 K. The spectra (a) and (b) show the bands characteristic of silica aerosil 200. The shoulders of about 3444 and 3282 cm^{-1} presents in the spectrum (a) can be attributable to O–H stretching vibration modes of hydrogen bonded to OH of polymeric association and hydrogen bonded to OH intermolecular or chelate compounds. The symmetric stretching Si–O vibration of silica can be observed at around

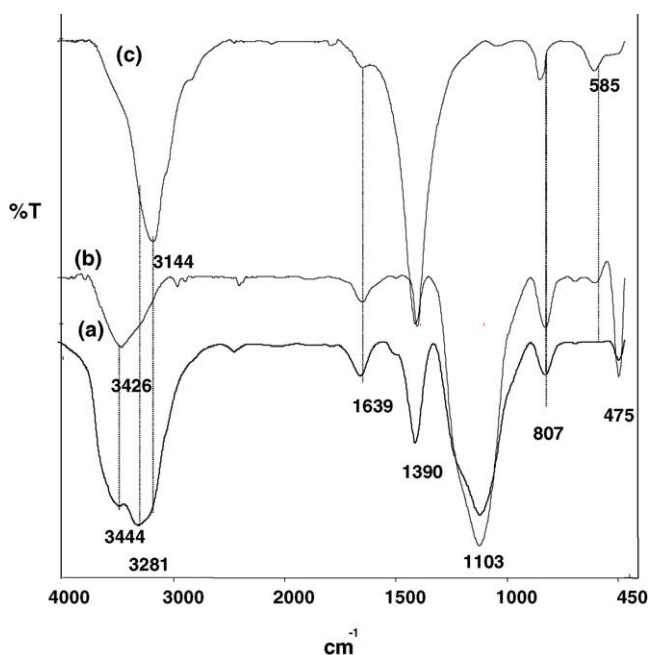


Fig. 5. FTIR of: (a) 10% cobalt phyllosilicate; (b) 10% cobalt phyllosilicate after washing in distilled water (1 h stirring), filtration and drying at 353 K for 48 h; (c) solid obtained by evaporation of 10% cobalt phyllosilicate filtrated.

1100 cm^{-1} . At lower frequencies, the bands at around 807 and 475 cm^{-1} correspond to asymmetric Si–O stretching and Si–O bending modes of silica in that order. At medium frequencies, the band at around 1640 corresponds to the H–O–H bend of crystallization water and the band at 1390 cm^{-1} corresponds to the NO_3^+ vibration of the nitrate ion [17]. The spectrum (b) is very similar to the spectrum (a) of the catalyst, except for the high-frequency region where only one broad shoulder was observed at 3427 cm^{-1} , suggesting the presence of one phase constituted mainly of silica. Spectrum (c) is very different. Indeed, at medium frequencies the shoulder at 1100 cm^{-1} characteristic of the silica aerosil was not observed, while in the high-frequency region, one shoulder was observed at 3144 cm^{-1} , also attributable to O–H stretching vibrational modes of hydrogen-bonded OH due to polymeric associations or intermolecular compounds, suggesting that such a band can be associated with a metal phase like the cobalt aqua-complex not reacted with the silica during the catalyst preparation. The solubility in water of such a compound is higher than $\text{Co}(\text{OH})_2$ and corresponds to the first peak observed in TPR (Fig. 4). Then, the second phase at high temperature observed by TPR could correspond to the spectrum (b) that is similar to the silica aerosil spectrum. Such phase should contain the cobalt aqua-complex bonded to the silica Si_2O_5 [8].

3.3. Catalytic tests

The catalytic activity as a function of time on the carbon monoxide and hydrogen stream, for the cobalt phyllosilicate catalyst at 34 atm, is shown in Fig. 6 for an experiment carried out at hydrogen to carbon monoxide inlet ratio of 1.0, 513 K and 44,000 H^{-1} . The test was followed by low-resolution mass spectrometry (quadrupole) every 14 s. It was observed (Fig. 6) that the cobalt phyllosilicate catalyst exhibits a great increase in activity to about 35% during the first 1000 s, followed by a gradual increase to 40%, and then remains constant thereafter. At the same time, the carbon dioxide selectivity (Fig. 7) shows a gradual increase up to a maximum of about 25% in the first 5000 s of reaction, and then decrease to values close to zero for remainder of the reaction time. The selectivity to hydrocarbons (Fig. 8) was approximately constant and close to 40% during the reac-

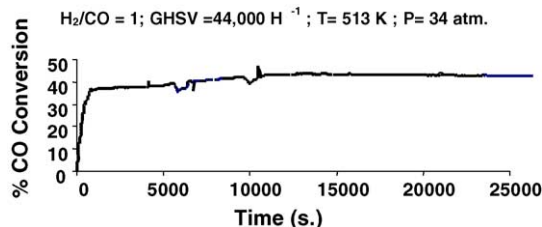


Fig. 6. Carbon monoxide hydrogenation vs. time on 10% cobalt phyllosilicate at the following conditions: G.S.H.V. = 48,000 H^{-1} ; $P = 34$ atm; $T = 513$ K; $\text{H}_2/\text{CO} = 1$. The reaction was monitored by low-resolution mass spectrometry (quadrupole) using the residual analysis gas method (RGA).

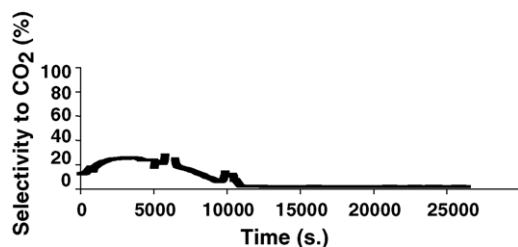


Fig. 7. CO₂ Selectivity vs. time in the carbon monoxide hydrogenation on 10% cobalt phyllosilicate at the following conditions: G.S.H.V. = 48.000 H⁻¹; P = 34 atm; T = 513 K; H₂/CO = 1.

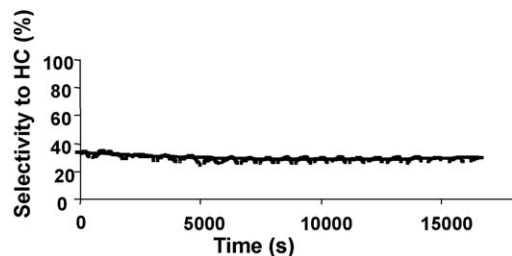


Fig. 8. Hydrocarbon selectivity vs. time for carbon monoxide hydrogenation on 10% cobalt phyllosilicate at the following conditions: G.S.H.V. = 48.000 H⁻¹; P = 34 atm; T = 513 K; H₂/CO = 1.

tion time. The selectivity to alcohols (Fig. 9) (only methanol and ethanol were tested) starts from around 60% and reaches 80% after 10,000 s of reaction suggesting that, after this time the reaction reached steady state conditions. The liquid products were collected at the end of the reaction and analyzed by gas chromatography. The composition of the liquid was mainly alcohols (methanol, ethanol, and small amounts of 1-propanol, 1-butanol and 2-butanol) and heavier hydrocarbons (C₆₊). Fig. 10 shows the alcohol distribution. It can be observed that the carbon monoxide hydrogenation reaction mainly resulted in oxygenated product formation and that mainly methanol and ethanol, in the proportion 2:1, were formed. The formation of such compounds could be related to the presence on the catalyst of two different cobalt aqua-complex phases with a similar relationship 2:1. The reaction mechanism is not clear but the catalyst behavior is consistent with the mechanism proposed by Klier et al. [18].

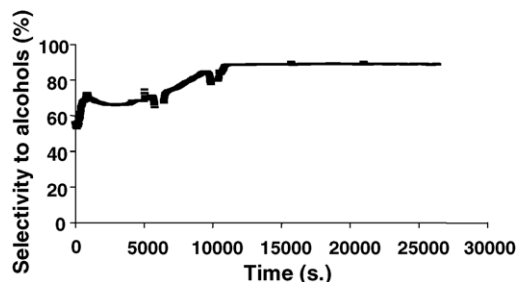


Fig. 9. Alcohol selectivity vs. time for carbon monoxide hydrogenation on 10% cobalt phyllosilicate at the following conditions: G.S.H.V. = 48.000 H⁻¹; P = 34 atm; T = 513 K; H₂/CO = 1.

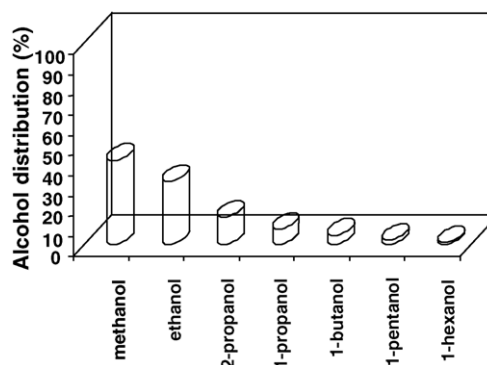


Fig. 10. Alcohol distribution obtained from the carbon monoxide hydrogenation on 10% cobalt phyllosilicate at the following conditions: G.S.H.V. = 48.000 H⁻¹; P = 34 atm; T = 513 K; H₂/CO = 1.

4. Conclusions

The ammonia method was used to prepare cobalt Phyllosilicate catalysts. Simultaneous TGA-DTGA-DSC comparison studies on Co(NO₃)₂·6H₂O, SiO₂ aerosil 200 precursors as received, and after treatment with the ammonia method, and on the final synthesized catalyst, indicated that during the synthesis process the first step is the formation of a cobalt aqua-complex that interacts with the silica aerosil 200 forming Co-phyllosilicate.

TPR analysis suggested the presence of two metallic phases responsible for hydrogen uptake. The low-temperature phase could be a free cobalt aqua-complex or not reacting with the silica surface. The second phase could be a metal silicate or phyllosilicate, where strong metal-silica interactions occur.

Such phases can be separated by washing and filtration and were identified by FTIR. The capability of the sample (high solubility) to be separated in two phases excluded the possibility of a cobalt hydroxide as the low-temperature phase.

The catalyst is active for carbon monoxide hydrogenation and very selective to methanol and ethanol formation in a 2:1 proportion similar to the proportion found for the two metal phases in the catalyst by TPR.

Acknowledgements

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