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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 $Co(NO_3)_2 \cdot 6H_2O$, 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.

Keywords: Cobalt phyllosilicate; Ammonia method; Higher alcohols

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 Co $(NO_3)_2{\cdot}6H_2O$ (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 °C/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 K/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, C_2H_5OH, 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 × 0.25 μm × 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 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, $Co(NO_3)_2{\cdot}6H_2O$ 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 °C/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 $Co(NO_3)_2{\cdot}6H_2O$ 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

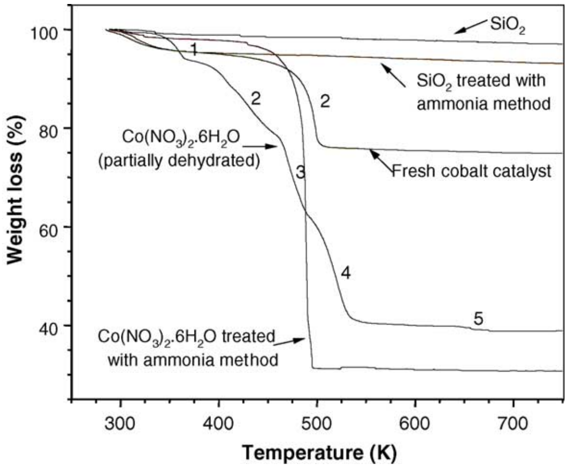

Fig. 1. Thermogravimetric analysis (air at 10 °C/min), comparison of silica aerosil 200, silica aerosil treated with the ammonia method cobalt catalyst, cobalt nitrate hexahydrate and cobalt nitrate hexahydrate treated with the ammonia method.