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TPSR of CO hydrogenation on $Co/Nb_2O_5/Al_2O_3$ catalysts

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Abstract

This study involves the characterization of a series $Co/x\%\ Nb_2O_5/Al_2O_3$ catalysts.

The temperature-programmed surface reaction technique (TPSR) and in situ diffuse reflectance spectroscopy (DRS) results have shown a transient behavior of the catalysts, distinguishing very well the Co/Al_2O_3 from the $Co/Nb_2O_5{\cdot}Al_2O_3$ catalysts.

DRS and temperature-programmed reduction (TPR) results indicate the presence of Co^{2+}, besides Co^0 and Co^0–NbO_x, which affect greatly the performance of the catalysts.

These results allowed us to propose that the interface Co^{2+}–Co^0 is responsible for the mathanation reaction, while the Co^0–NbO_x is responsible for the hydrocarbon chain grow. The relative amount of each specie on the surface plays a fundamental role on the selectivity behavior of CO hydrogenation.

Keywords: CO hydrogenation; Niobia; Cobalt; Niobia/alumina

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1. Introduction

The reduction reserves and high crude oil prices make alternative routes for the production of petroleum derivatives and raw materials attractive. CO hydrogenation product spectrum includes hydrocarbons from methane to wax, depending on catalyst selection. In this context, cobalt-based catalysts have been applied worldwide for Fischer–Tropsch synthesis (FT) [1]. The polymerization nature of the FT conversion imposes constrains on selectivity manipulation, such as the product distribution by the conventional FT catalyst (selectivities for gasoline or diesel fuel) are relatively low [2]. Reducible support such as niobia [3–8] and titania [9,10] have been used in order to overcome the selectivity limitations. A high selectivity toward long chain hydrocarbons in the FT synthesis after reduction at high temperature was observed over Co/Nb_2O_5 [3–8] and Ni/Nb_2O_5 [9] catalysts. These results might be explained by the formation of new sites involving the metal and the partially reduced support during high temperature reduction.

The anchoring of niobia over large surface area supports favors the enhancement of metal dispersion, since niobia itself exhibits low surface area. One important question arises, whether the niobium oxide when dispersed over a support with high surface area affects the surface properties and consequently the activity or the product distribution of the CO hydrogenation. Ko et al. [9] compared the Nb_2O_5 and Nb_2O_5–SiO_2-supported nickel catalyst on CO hydrogenation. They expected to obtain the same SMSI extent on both systems, since there was sufficient supply of niobia. However, the catalytic activity of a Ni–Nb_2O_5 was 50% greater than on a Ni–Nb_2O_5–SiO_2 system. They could not totally rule out the possibility of some crystallites sitting on uncovered SiO_2 contributing to the chemistry. They found that such an effect was small and suggested the lower availability of Nb_2O_5 in the Nb_2O_5–SiO_2 system.

Different niobium oxide precursors and preparation methods have been used for the preparation of supported niobium oxide catalysts such as: (i) aqueous impregnation with niobium oxalate [11,12]; impregnation of niobium ethoxide using organic solvents [13,14]; chemical vapor deposition of niobium ethoxide or niobium pentachloride [15]. The niobium oxalate possesses low solubility in aqueous solutions, which can be increased by the addition of

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oxalic acid. However, the niobium oxalate and the oxalic acid precipitate from solution at high oxalic acid concentrations. The use of niobium ethoxide or niobium pentachloride requires a controlled environment and special procedures to avoid the decomposition of the precursor in the presence of water and to control the density of surface hydroxyls groups. The preparation of supported niobium oxide catalysts using an ammonium complex of niobium as a precursor is not so usual [16]. This precursor salt is easily solubilized in water at room temperature.

The preparation method and niobium precursors do not affect the molecular structures of surface niobia species, but they determine their dispersion [17]. The nature of the precursor had a strong effect on the distribution of the niobium oxide species over the alumina and consequently, on the reduction of niobium oxide species [18]. We prepared Nb_2O_5/Al_2O_3 materials by using two different precursors salts: niobium ammonium complex and niobium oxalate salt [18]. The results showed that the niobium precursor influence the species growing leading to phases with different reducibility. The XPS revealed the presence of multilayers of niobium oxide on the Nb_2O_5/Al_2O_3 samples prepared by using niobium ammonium complex while the ones obtained from niobium oxalate led to Nb_2O_5 particles islands. Therefore, the nature of the precursor affected significantly the reduction of niobium oxide species. The Nb_2O_5/Al_2O_3 (niobium oxalate salt) samples exhibited a high reducibility due to the lower interaction between the niobium oxide species of the islands and the support.

Afterwards, we studied the performance of Co supported on Nb_2O_5/Al_2O_3 prepared by ammonium complex on FT synthesis. The activity of the $Co/Nb_2O_5/Al_2O_3$ catalyst was compared to Co/Al_2O_3 and Co/Nb_2O_5 catalysts [8]. The catalytic results showed that after reduction at 773 K, the Co/Nb_2O_5 catalyst presented a low methanation activity and a high selectivity for long chain hydrocarbons in the CO hydrogenation. On the other hand, the performance of Co/Al_2O_3 and Co/5% Nb_2O_5/Al_2O_3 was quite similar, after reduction at 573 or 773 K. However, the increase of Nb_2O_5 content (Co/20% Nb_2O_5/Al_2O_3) changed the selectivity of the reaction, presenting the same product distribution observed for the Co/Nb_2O_5 catalyst, but the effect was less pronouced on the niobia-promoted Co/Al_2O_3 than on the Co/Nb_2O_5 catalyst.

The goal of this was to study Co/x% Nb_2O_5/Al_2O_3 catalysts by temperature-programmed reduction (TPR), diffuse reflectance spectroscopy (DRS) techniques and CO hydrogenation by temperature-programmed reaction (TPSR) as a potential catalyst to CO hydrogenation.

2. Experimental

2.1. Catalyst preparation

The niobium ammonium complex obtained from CBMM (Companhia Brasileira de Metalurgia e Mineração (CBMM, AD 1264)) was calcined at 873 K at a heating rate of 2 K/min for 4 h, which produced the crystalline TT or T form of niobium pentoxide. Alumina was pretreated in aerated furnace (50 ml/min) at 823 K for 16 h.

Table 1
Surface areas (BET) and contents of Nb_2O_5 and cobalt

Sample	BET area (m^2/g)	Nb_2O_5 content (%)	Co content (%)
Co/Al_2O_3	187	4.25	4.25
Co/Nb_2O_5	13	4.50	4.50
Co/5% Nb_2O_5/Al_2O_3	201	4.3	
Co/10% Nb_2O_5/Al_2O_3	196	9.45	
Co/20% Nb_2O_5/Al_2O_3	178	19.9	4.80
Co/30% Nb_2O_5/Al_2O_3	150	31.3	

The x% Nb_2O_5/Al_2O_3 ($x = 5$, 10, 20 and 30 wt.% of Nb_2O_5) was prepared by wet impregnation of alumina with a solution of an niobium ammonium complex in a rotator evaporator for 16 h. After drying at 353 K, under vacuum, the sample was dried at 373 K for 16 h, followed by calcination under flowing air at 823 K (2 K/min) for 16 h.

The cobalt catalyst was prepared by incipient wetness impregnation with a $Co(NO_3)_2 \cdot 6H_2O$ (Riedel-de Häen, 99% purity) solution. The Co content was approximately 5 wt.%. After impregnation, all catalysts were dried overnight at 383 K followed by calcination at 2 K/min up to 673 K and kept for 3 h. Table 1 shows cobalt concentrations determined by atomic absorption and the corresponding BET surface areas of the catalysts.

2.2. Catalyst characterization

2.2.1. Diffuse reflectance spectroscopy (DRS)

Diffuse reflectance spectra were recorded in the range of 200–900 nm using an UV–Vis–NIR spectrophotometer (Cary 5E, Varian) equipped with an integrating sphere (Harrick). The alumina, niobia and Nb_2O_5/Al_2O_3 samples were used as reference for the Co/Al_2O_3, Co/Nb_2O_5 and $Co/Nb_2O_5/Al_2O_3$ 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 up to 423 K for 30 min and cooled to room temperature for analysis. Then, the flow was switched to a reduction mixture of 10% H_2/Ar (20 ml/min) and the sample was heated up to 573 or 773 K and kept, at this temperature, for 30 min. After that, the sample was cooled to RT for spectral acquisitions.

2.2.2. Temperature-programmed reduction (TPR)

Temperature-programmed reduction (TPR) was conducted using a conventional apparatus equipped with a thermal conductivity detector. Each sample was pre-treated in an argon flow at 383 K, for 30 min, and cooled down to room temperature. The reduction was performed by heating the sample from 298 up to 1373 K at a rate of 8 K/min using a 1.75% H_2/Ar mixture flow.