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Short communication

Preparation and Characterization of Alumina-Supported Co and Ag/Co Catalysts

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The effect of silver addition as a promoter in alumina supported cobalt oxide catalysts is investigated in this study. The Co/Al_2O_3 and $Ag/Co/Al_2O_3$ catalysts were prepared by incipient wetness impregnation. The catalysts were characterized by inductively-coupled plasma spectrometry, X-ray diffraction (XRD), temperature programmed reduction with hydrogen (TPR-H_2), Raman spectroscopy and nitrogen adsorption at 77 K. XDR and Raman Spectroscopy results indicated the presence of Co_3O_4 species. The peaks observed in the TPR-H_2 patterns were attributed to the reduction of Ag_2O, Co_3O_4 crystallites and Co^{+3}, Co^{+2} species interacting with alumina. It is suggested that silver used as a promoter favors the reduction of cobalt, facilitating the formation of active Co^0 sites.

Keywords: *cobalt catalysts, Ag-Co/Al_2O_3*

1. Introduction

Alumina supported Cobalt catalysts has been studied for several reactions, such as mitigation of nitrogen oxides (NOx)[1-3], oxidation of volatile organic compounds (VOCs)[4], Fischer-Tropsch synthesis[5] and hydrodesulfurization reaction[6].

The catalytic removal of nitrogen oxides from the exhaust stream of various combustion sources has become increasingly important, because of the serious environmental damages, which they cause. The active catalysts known for this reaction are mainly the zeolite-based catalysts. However, these catalysts present some disadvantages as the deactivation in presence of water steam and sulfur compounds[7]. Therefore, there is an interest in the study of other catalytic systems, which can be active, selective and resistant to the deactivation process.

Alumina-supported catalysts, such as Co/Al_2O_3 [1-3] and Ag/Al_2O_3 [8] have shown promising perspectives to the NO_x reduction reactions. It has been reported that metal-supported interactions may appreciably affect the surface properties and hence, catalytic activity. These interactions depend upon factors such as the concentration of metal species, nature of the support and calcinations temperature[2].

Hamada *et al.*[9] verified that for NO decomposition reaction, the catalytic activity of Co_3O_4 with the addition of small amounts of silver is superior to that the obtained with simple metallic oxide. The introduction of silver as a promoter generates a Ag-Co_3O_4 system that reduce the reaction inhibition caused by the irreversible deposition of oxygen. However, the cobalt dispersion on a high surface support, such as alumina, can increase the number of active Co^0 sites, improving the catalytic activity of these catalysts.

In order to study the potential of the catalysts Co/Al_2O_3 and $Ag/Co/Al_2O_4$ it is necessary to elucidate the structural and textural characteristic caused by different preparation. In this paper we study the effect of different Co e Ag loading on the final properties of the catalysts, as well as the effect caused by the addition of silver in Co/Al_2O_3 catalysts. Co/Al_2O_3 and $Ag/Co/Al_2O_3$ catalysts were characterized using X-ray diffraction (XRD), Raman spectroscopy and temperature programmed reduction (TPR) to identify the species formed and to obtained evidences on the interaction between the metallic compounds.

2. Experimental

2.1. Catalyst Preparation

The Co/Al_2O_3 catalysts were prepared using the impregnation method. The support (Al_2O_3, Degussa) was first calcined at 650 °C in order stabilize the γ-Al_2O_3 form with a surface area of 198 m^2/g. The support was impregnated with

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cobalt nitrate ($(Co(NO_3)_2 \times 6 H_2O$ (Riedel-deHaën) solution with concentration adequate to produce catalysts with 5 and 9% cobalt. The excess of water was removed in a rotary evaporator, the solids were dried for 24 h at 60 °C and calcined at 600 °C, for 3 h. The addition of silver on Co/Al_2O_3 catalysts was accomplished by the same method, using $AgNO_3$ (Cenna Bras) solution. After the promoter addition, the solids were dried at 60 °C for 24 h and calcined at 600 °C, in a synthetic air atmosphere for 3 h.

2.2. Catalyst Characterization

Chemical analysis

The metal contend in the catalysts were determined by Inductively Coupled Plasma Optical Emisson Spectrometry, using a Perkin Elmer equipment.

Adsorption of N_2 at 77 K

The textural characterization of catalysts was determined by Adsorption of N_2 at 77 K using a Quantachrome Nova 2.0 instrument. Surface area was obtained by application of the BET equation and pore size distributions were obtained using BJH method.

X-Ray diffraction

The X-ray powder diffraction patterns of the samples were obtained using an automatic Rigaku diffractometer model D Max 2050 PC with monochromatized Cu Kα radiation (λ = 1.5406 Å). The spectra were scanned at a rate of 2°/min in the range 2θ = 3° – 80°.

Raman Spectroscopy

The Raman spectroscopy measures were carried out in a Jobin-Yvon T64000 spectrometer with a laser power of 73 µW. The Raman spectra of the catalysts were collected between 150 and 800 cm^{-1}, projecting a continuous wave laser of argon ion (Ar^+) green (5.145 Å) through the samples exposed to air at room temperature.

Temperature programmed reduction with hydrogen

TPR profiles of catalysts were recorded using a Micromeritics Pulse Chemisorb model 2705.

The sample was heated from 25 to 1000 °C using a heating ramp of 10 °C/min, the gas reducer employed was a mixture of $5\%H_2/N_2$ with a flow of 30 ml. The consumption of H_2 was measured in a thermal conductivity detector.

3. Results and Discussion

Table 1 shows the results of chemical analysis and textural characterization of the catalysts.

Results of surface area measurements by adsorption of nitrogen at 77 K shown that the BET surface of the alumina (198 m^2/g) decreases 17% for the 5% Co catalyst and 27% for the 9% Co catalysts. It is interesting to observe that the cobalt content practically does not alter the average pore radius, but increasing cobalt from 5 to 9% causes a small decrease in the pore volume of the catalyst. This occurs because the impregnation of the support with metal clogs the pores with smaller diameter of the alumina. As a consequence, it occurs a decrease in the surface area and in the pore volume and an increase in the average pore radius. The silver addition to the Co/Al_2O_3 catalysts practically did not alter the values of surface area, the pore volume and average pores radius, probably due to the low contends impregnated.

TPR-H_2 patterns obtained for the Co/Al_2O_3 and $Ag/Co/Al_2O_3$ catalysts are presented in Fig. 1.

TPR-H_2 pattern of unsupported cobalt oxide (Fig. 3g) exhibits a single peak at 460 °C, where the reduction of $Co^{+3} \rightarrow Co^{+2} \rightarrow Co^0$ occurs. This result is in agreement with those obtained by Arnoldy and Moulijn[10], which also presents a pattern with a single peak for the Co_3O_4 reduction. According to these authors, the reduction peaks observed in the TPR-H_2 pattern (Figs. 3a-3f)) can be attributed as follows:

- Phase I (120 °C): small peak in the samples which contain silver, attributed to the Ag_2O reduction;
- Phase II (380 °C): weak interaction of Co_3O_4 with the support; it is observed in the Co (5) catalyst and is very hard to be distinguished in the Co (9) catalyst TPR-H_2 curve;

Table 1. Composition and surface area, pore volume and pore radius of the catalysts.

Sample	Contends metal (%)		Surface area (m^2/g)	Pore volume (cm^3/g)	Pore radius(Å)
	Co	*Ag*			
Co (5)*	5.1	-	163.8	0.35	43.4
Ag (0.5)/Co (5)	5.0	0.3	158.0	0.36	45.7
Ag (1)/Co (5)	4.9	1.1	158.3	0.36	45.4
Co (9)	8.9	-	144.8	0.32	44.4
Ag (0.5)/Co (9)	8.7	0.5	140.5	0.31	44.2
Ag (1)/Co (9)	8.6	1.1	141.8	0.32	44.7

* Nominal metal contends.

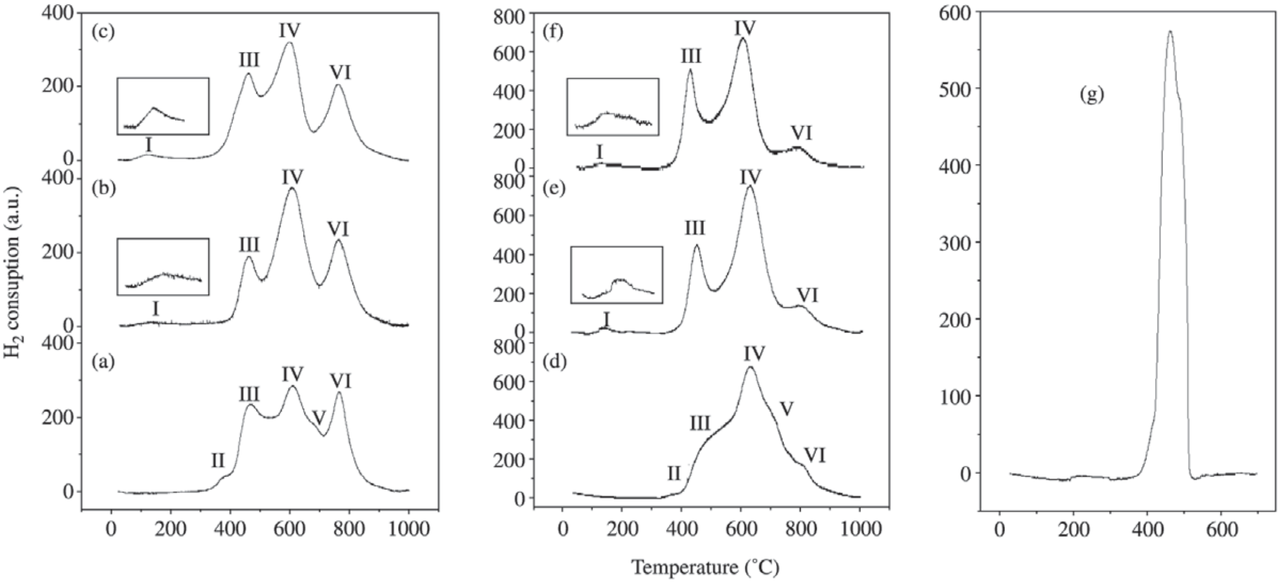

Figure 1. TPR-H2 patterns of catalysts: a) 5Co; b) 0,5Ag/5Co; c) 1Ag/5Co; d) 9Co; e) 0,5Ag/9Co; f) 1Ag/9Co; g) Co_3O_4.

- Phase III (430 - 460 °C): interaction of Co_3O_4 crystallites with alumina;
- Phase IV (600 - 630 °C): Co^{+3} ions in crystallites, probably with stoichiometry Co_3AlO_6 (Co_3O_4-AlO_2);
- Phase V (700 °C): Co^{+2} ions in well-dispersed surface species, just observed in the samples that do not contain silver;
- Phase VI (770 - 800 °C): Co^{+2} ions interacting with the support, forming a CoO-Al_2O_3 phase.

Arnoldy and Moulijn[6] suggested that these last two existing phases IV and V are formed by diffusion of cobalt ions with the aluminum ions of the support, resulting in non-stoichiometric spinel structures, which is not the $CoAl_2O_4$, since it is reduced at temperatures higher than 1000 °C. These authors also mention that the number of Al^{+3} ions that surround the Co ions determines the reduction temperature, while the valence and the cobalt coordination are less important.

It can be observed in Fig. 1 that the silver addition to the catalysts induces a decrease of the phases III and VI in favor of the phase IV. An evidence for this hypothesis it is the fact that calcination of the catalyst impregnated with silver nitrate causes the formation of Ag_2O and Ag^0. Therefore, the reduction of the silver oxide during calcination causes the oxidation of cobalt Co^{+2} to Co^{+3}, which is confirmed by the increase of the area of under the peak IV and the decrease of the areas under the peaks III and disappear of peak V.

On the other hand, the reduction peaks of the cobalt species in Ag/Co/Al_2O_3 catalysts present a lower reduction temperature than the Co/Al_2O_3 catalysts, indicating that silver promotes the reduction of the cobalt species in the presence of molecular hydrogen. According to Luo *et al.*[4], silver oxide is reduced at lower temperature, then H_2 is dissociated over the reduced silver and hydrogen spillover reduce the surface of cobalt oxides.

As the silver favors the formation of the Co_3O_4-AlO_2 phase, which are easier to be reduced than the CoO-Al_2O_3 phase, this promoter addition facilitates the formation of active Co^0 sites.

XRD patterns of the Co/Al_2O_3 and Ag/Co/Al_2O_3 catalysts are shown in Fig. 2 and the main lines of Co_3O_4 and γ-Al_2O_3, from JCPDS[11] files are also presented for comparison. In this figure it can be observed the peaks of high intensity at $2\theta = 36.8°$, 65.5°, 31.6°, 59.5° and 19.2°. The diffraction peaks at $2\theta = 67.1°$ and 45.8° of the γ-Al_2O_3 for the catalysts containing 5% of cobalt are quite intense, however they decrease with the increase of the metal loading, evidencing the peaks of cobalt specie at 65.5° and 45.2°.

It is important to stress that both Co_3O_4 and $CoAl_2O_4$ have a cubic spinel structure with almost identical diffraction peaks. Therefore it is not possible to distinguish which species was formed using the only diffraction measurements. However, stoichiometric aluminates were not observed in the TPR-H_2 curves. This suggests that the observed peaks in XRD patterns can be attributed to Co_3O_4.

In the XRD patterns the presence of peaks of Ag_2O and Ag^0 were not observed ($2\theta = 38.6°$, 50.4°, 66.7°)[11]. According to Luo *et al.*[4] only in Ag/Al_2O_3 catalysts with Ag loading larger than 15%, the crystalline Ag_2O and Ag^0 diffraction peaks become apparent.

In Fig. 2, the $AgCoO_2$ diffraction peaks (2θ = 37.6°, 65.3°, 41.4° and 29.2°)[11] were not observed due to the low Ag loading. This species could be formed by the Ag-Co interaction[12].

Raman spectra of the Co/Al_2O_3 and $Ag/Co/Al_2O_3$ catalysts are shown in Fig. 3. These spectra show five bands at 670, 600, 505, 460 and 182 cm^{-1}. These bands, according to Ohtsuka *et al.*[13], are characteristic of Co_3O_4 spinel structure. In the Raman spectra of the catalysts were not observed bands at 753 e 412 cm^{-1} that characterize the presence of the $CoAl_2O_4$ [14].

Thus, associating the DRX results with Raman Spectroscopy analyses, we can confirm the presence of Co_3O_4.

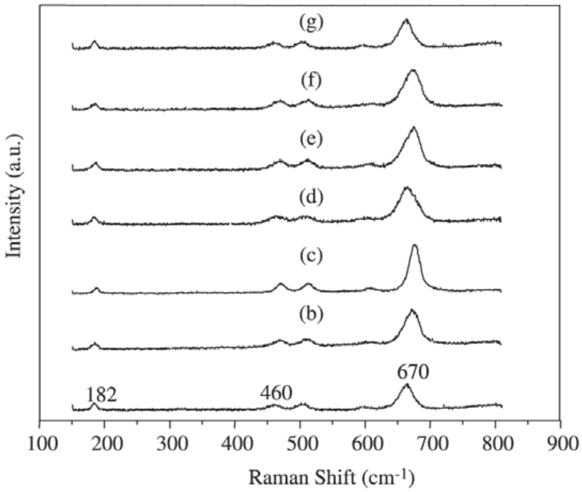

Figure 3. Raman Spectra of catalysts: a) 5Co; b) 0.5Ag/5Co; c) 1Ag/5Co; d) 9Co; e) 0.5Ag/9Co; f) 1Ag/9Co; g) Co_3O_4.

4. Conclusions

The association of XRD and Raman Spectroscopy techniques revealed formation of Co_3O_4 species in the γ-alumina supported Co and Ag/Co prepared by impreg-

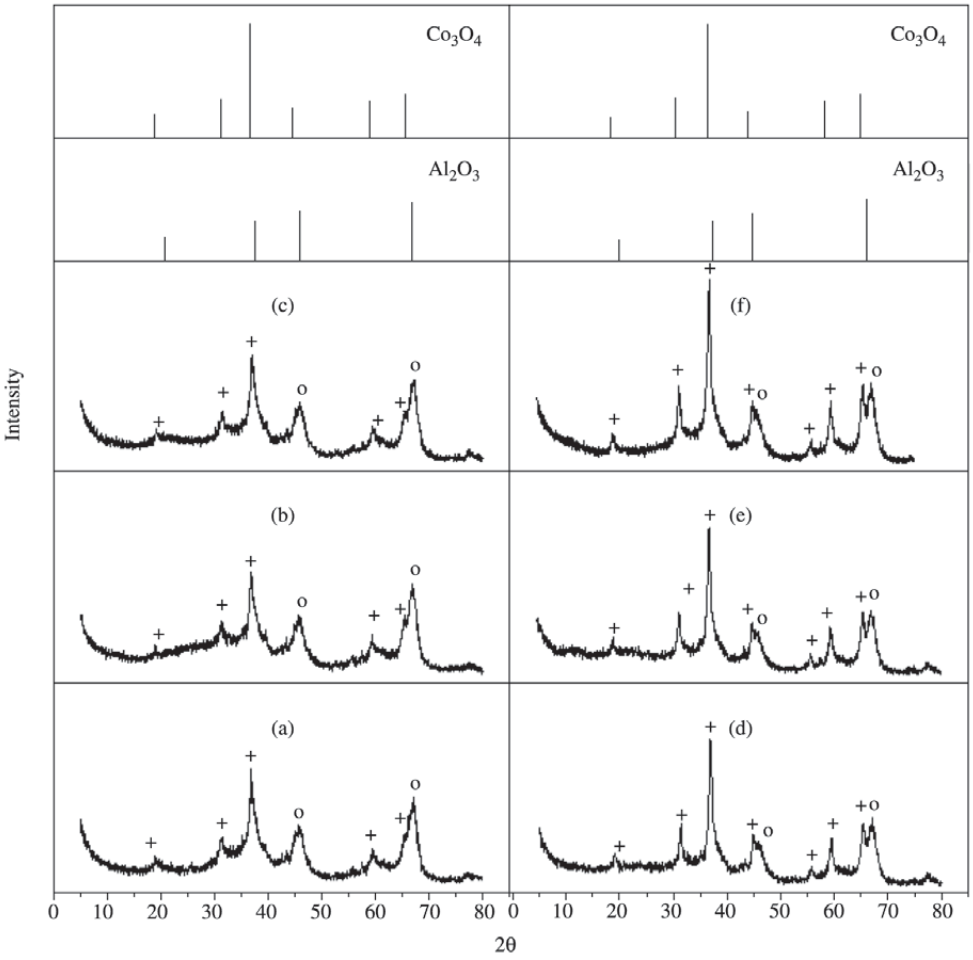

Figure 2. Diffractograms of the catalysts: a) 5Co; b) 0.5Ag/5Co; c) 1Ag/5Co; d) 9Co; e) 0.5Ag/9Co; f) 1Ag/9Co. (+) Co_3O_4, (o) Al_2O_3.

nation. In the of TPR-H_2 analyses both the existence of Co_3O_4 phases and Co^{+2} and Co^{+3} ions interacting with Al_2O_3 were evidenced, indicating the possible formation of non-stoichiometric aluminates.

The presence of silver in the catalyst was observed only in the chemical analyses and in the TPR-H_2 measurements. Both DRX and Raman Spectroscopy are not sensitive to the small amount of silver added to the catalyst. From the TPR-H_2 results it is suggested that the use of silver as promoter favors the reduction of cobalt, facilitating the formation of active Co^0 sites.

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