Cobalt-based alumina pillared zirconium phosphate catalysts for the selective catalytic reduction of NO by propane

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Abstract

A series of cobalt containing alumina pillared zirconium phosphate materials have been prepared by ion exchange or by impregnation, and fully characterised. The catalytic behaviour of these materials in the selective catalytic reduction of NO by propane, in excess of oxygen, at temperatures ranging between 350 and 550 °C, has been also evaluated. A maximum NO conversion close to 14% is obtained on Co-impregnated catalysts heated at 600 °C. The NO reduction seems to be related to the presence of Co³⁺, thus the calcination temperature of samples influences the resulting activity much more than the cobalt content. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: NO SCR; Pillared layered solids; Zirconium phosphate; Propane; Cobalt containing catalyst

1. Introduction

Nitrogen oxides (NOₓ) produced during high temperature combustion processes, taking place in mobile and stationary engines, are becoming an environmental problem which is faced more stringent regulations, because nitrogen oxides play an important role in acid rain, photochemical smog and depletion of ozone layer. For this reason, the reduction of the NOₓ pollution is receiving growing attention in the field of environmental catalysis (Pereira and Amiridis, 1995). Selective catalytic reduction (SCR) is actually the most efficient technology for the abatement of NO from combustion sources. In fact, SCR, using ammonia as a reducing agent, is the most used commercial process for NOₓ emission control (Busca et al., 1998). However, hydrocarbons are preferred in stead of ammonia for practical reasons, especially in automotive sources.

Cu-ZSM-5 is by far the most studied catalyst for SCR of NO by hydrocarbons in the presence of oxygen (Zhang et al., 1993). However, this catalyst fails in durability because it suffers from high deactivation in engine tests, possibly due to the presence of water and SO₂ in the gas effluents (Armor, 1994). For this reason, cobalt containing catalysts have been proposed as an alternative system, due to their high hydrothermal and catalytic activity in the NO reduction by methane (Li et al., 1994).

On the other hand, the ease tuning of chemical, textural and acid properties of the porous materials belonging to the family of pillared layered structures make them very attractive as supports of catalytically active phases. They are prepared from layered substrates (clays, metal(IV) phosphates, etc.) by cation exchange with inorganic polyhydroxocations and subsequent
thermal treatment to originate the corresponding metal oxide nanoparticles. These species prop the layers permanently apart creating zeolite-like interlayer spaces, which confer to these solids a high surface area and acidity (Mitchell, 1990; Olivera-Pastor et al., 1996; Perathoner and Vaccari, 1997; De Stefani et al., 2000). Concerning the inorganically pillared layered α-zirconium phosphates, they have shown to be active in several catalytic reactions (Corma, 1997; Mérídez-Robles et al., 1997; Alcántara-Rodríguez et al., 1998). Moreover, they exhibit a moderate activity in the SCR of NO using propane as reducing agent, in excess of oxygen, after incorporation of copper species by impregnation or by cation exchange (Hernández-Huesca et al., 2001).

We present in this paper the synthesis and characterisation of a series of cobalt containing alumina pillared zirconium phosphate materials, with the aim of correlating their catalytic behaviour with the nature of the metal species and the interaction between the active sites and the NO molecules.

2. Experimental

2.1. Preparation of catalysts

The synthesis and full characterisation of the porous alumina pillared α-zirconium phosphate used as support, after thermal treatment at 400 °C (AlZrP-400) or 600 °C (AlZrP-600), have been described elsewhere (Mérídez-Robles et al., 1996). Cobalt species supported on AlZrP with two cobalt weight loadings (3 and 6 wt.%) were prepared by impregnation, using the incipient wetness method with a cobalt(II) acetate aqueous solution. The catalysts were obtained after calcination in air either at 400 or 600 °C, thus resulting in the catalysts labelled as Co-x-y (x denotes the weight percentage of cobalt and y the calcination temperature). A cobalt exchanged catalyst (Co-ex-400) has also been prepared by putting in contact the AlZrP-400 support with an aqueous solution of cobalt(II) acetate, containing an amount of Co^{3+} corresponding to 10 times the theoretical cation exchange capacity of the original phosphate (6.6 meq g^{-1}), for 1 day at room temperature. In this way, a cobalt weight loading of 3.5 wt.% was attained.

2.2. Characterisation methods

Chemical analysis of cobalt, aluminium and zirconium were carried out by atomic absorption spectroscopy. The water content was determined by thermal analysis with a Rigaku Thermoflex instrument (calcined Al_{2}O_{3} was used as reference and the heating rate was 10 °C min^{-1}).

The adsorption–desorption isotherms of nitrogen at -196 °C (after outgassing at 200 °C and 10^{-4} Torr overnight) on the cobalt containing catalysts were obtained in a conventional glass volumetric apparatus. Thermal programmed desorption of ammonia (NH_{3}-TPD) was used to determinate the total acidity of the samples. Before the adsorption of ammonia at 100 °C, the samples were heated at 400 °C in a He flow. The NH_{3}-TPD was performed between 100 °C and the corresponding calcination temperature of catalysts, with a heating rate of 10 °C min^{-1}, and analysed by on line gas chromatograph (Shimadzu GC-14A) provided with TC detector. Diffuse reflectance ultraviolet–visible–near infrared spectra were obtained using a spectrophotometer Shimadzu 8100 and BaSO_{4} as reference. Magnetic measurements were carried out at room temperature with a Cahn microbalance (Model C.2000) provided with an electromagnet Oxford. XRD powder patterns were obtained with a Siemens D501 diffractometer provided with a graphite monochromator and using CuKα radiation.

X-ray photoelectron spectra were obtained using a physical electronics PHI 5700 spectrometer with a non-monochromatic MgKα radiation (300 W, 15 kV, hv = 1253.6 eV) as excitation source. Spectra were recorded at 45° take-off-angle by a concentric hemispherical analyser operating in the constant pass energy mode at 25.9 eV, using a 720 μm diameter analysis area. Under these conditions the Au 4f_{7/2} line was recorded with 1.16 eV FWHM at a binding energy of 84.0 eV. The spectrometer energy scale was calibrated using Cu 2p_{3/2}, Ag 3d_{5/2} and Au 4f_{7/2} photoelectron lines at 932.7, 368.3 and 84.0 eV, respectively. Charge referencing was done against adventitious carbon (C 1s at 284.8 eV). Powdered solids were mounted on a sample holder without adhesive tape and kept overnight at high vacuum in the preparation chamber before they were transferred to the analysis chamber of the spectrometer for analysis. Each region was scanned several sweeps until a good signal to noise ratio was observed. The pressure in the analysis chamber was maintained lower than 10^{-9} Torr. PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gauss–Lorentz curves in order to determine more accurately the binding energy of the different element core levels. The accuracy of BE’s values was within ±0.1 eV.

Temperature-programmed reduction with hydrogen (H_{2}-TPR) of catalyst was studied between 100 and 650 °C, using an Ar/H_{2} flow of 40 cm^{3} min^{-1} (10 vol.% of H_{2}) and a heating rate of 10 °C min^{-1}. The water produced in the reduction reaction was trapped by passing the gas flow through a cold finger at ~80 °C. Hydrogen consumption was monitored by an on-line gas chromatograph provided with a TC detector.
Temperature-programmed desorption of NO (NOTS) experiments were performed by previous adsorption of NO on the catalysts at room temperature (150 cm$^3$ min$^{-1}$ flow rate and 0.05 vol.% NO balanced with He) for 1 h, and desorption between 40 and 550 °C, using a heating rate of 10 °C min$^{-1}$. Before the adsorption of NO, the catalysts were heated at 400/600 °C under a He flow for 1 h. During the desorption, helium was flushed, and the composition of the evolved gases was measured by using an on-line quadrupole mass spectrometer Balzer GSB 300 02.

2.3. Catalysis

The performance of the catalysts in the SCR of NO was studied by using a Pyrex glass tube microreactor (0.27 in.o.d.) in a steady-state flow mode. About 150 mg of pelletised solids, sieved to 0.3–0.4 mm, were packed into the reactor and plugged with glass wool. Before the catalytic runs, the catalysts were pretreated in situ for 30 min under a helium flow, at the same temperature to which they were calcined after the impregnation or ion exchange processes. Propane was chosen as reducing agent. The reaction mixture typically consisted of 1000 ppm NO, 1000 ppm propane and 2.5 vol.% O$_2$ (balanced with helium). The flows were independently controlled by channel mass flowmeters (Brooks) and a total flow rate of 150 cm$^3$ min$^{-1}$ was used in the feed. Under these experimental conditions, the space velocity was 60000 cm$^3$ h$^{-1}$. The interval of temperature explored was 350–550 °C. NO and propane concentrations were monitored using an on-line quadrupole mass spectrometer described above. The competitiveness factor of the reaction, defined as the ratio of mole of propane reacted with NO with respect to the total mole of propane consumed in the reaction, was calculated as follows:

$$\frac{([\text{NO}]_{\text{initial}} - [\text{NO} + \text{NO}_2]_{\text{final}})/2}{[\text{propane}]_{\text{initial}} - [\text{propane}]_{\text{final}}} \times 100$$

This equation can be explained taking into account that NO or NO$_2$, formed according to 2NO + O$_2$ $\rightarrow$ 2NO$_2$, reacts with propane as follows:

$$2\text{NO} + \text{C}_3\text{H}_8 + 4\text{O}_2 \rightarrow \text{N}_2 + 3\text{CO}_2 + 4\text{H}_2\text{O} \quad (1)$$

$$2\text{NO}_2 + \text{C}_3\text{H}_8 + 3\text{O}_2 \rightarrow \text{N}_2 + 3\text{CO}_2 + 4\text{H}_2\text{O} \quad (2)$$

Both reactions have the same molar ratio 2NO/C$_3$H$_8$ or 2NO$_2$/C$_3$H$_8$. In consequence, the difference ([NO]$_{\text{initial}} - [\text{NO} + \text{NO}_2]_{\text{final}})/2$ is the number of propane mole reacted with NO or NO$_2$.

On the other hand, propane can be oxidized according to the equation:

$$\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O} \quad (3)$$

Thus, the total number of propane mole disappeared in the reactions (1)–(3) is the difference: [propane]$_{\text{initial}} -$ [propane]$_{\text{final}}$.

3. Results and discussion

Table 1 compiles the main characteristics of the supports and the cobalt containing catalysts. The Al-ZrP-400 support has a basal spacing of 18.4 Å and an empirical formula of Zr(Al$_{1.30}$O$_{1.12}$)(OH)$_{1.01}$Ga$_{0.90}$H$_{0.57}$-(PO$_{4}$)$_{2}$. This material possesses a BET surface area of 135 m$^2$ g$^{-1}$, which decreases to 85 m$^2$ g$^{-1}$ after calcination at 600 °C (AlZrP-600 support). Both supports are mainly mesoporous with a variable contribution of micropores, lower in the case of the AlZrP-600 support. Regarding their acid properties, the total acidity values, as determined by NH$_3$-TPD, are 1.1 mmol NH$_3$ g$^{-1}$ and 0.64 mmol NH$_3$ g$^{-1}$ for AlZrP-400 and AlZrP-600, respectively. Pyridine adsorption coupled to infrared spectroscopy has revealed the almost exclusive presence of Lewis acid sites (Mérida-Robles et al., 1996).

On the other hand, the impregnation and ion exchange processes generally produce an important decrease of the S$_{\text{BET}}$ and acidity of the resulting catalysts in comparison with the values found for the supports.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>S$_{\text{BET}}$ (m$^2$ g$^{-1}$)</th>
<th>Total acidity (mmol NH$_3$ g$^{-1}$)</th>
<th>UV–VIS–NIR DRS (nm)</th>
<th>$\mu$ (BM)</th>
<th>Co 2p$_{3/2}$ BE (eV)</th>
<th>%Co as spinel</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlZrP-400</td>
<td>135</td>
<td>1.12</td>
<td></td>
<td></td>
<td>781.6, 783.8</td>
<td>28</td>
</tr>
<tr>
<td>AlZrP-600</td>
<td>85</td>
<td>0.64</td>
<td></td>
<td></td>
<td>781.0, 782.8</td>
<td>34</td>
</tr>
<tr>
<td>Co-3-400</td>
<td>91</td>
<td>0.29</td>
<td>582, 1390</td>
<td>5.57</td>
<td>781.2, 783.2</td>
<td>45</td>
</tr>
<tr>
<td>Co-6-400</td>
<td>86</td>
<td>0.23</td>
<td>644, 1360</td>
<td>4.79</td>
<td>781.3, 783.2</td>
<td>30</td>
</tr>
<tr>
<td>Co-3-600</td>
<td>55</td>
<td>0.34</td>
<td>586, 1384</td>
<td>5.20</td>
<td>781.2, 783.2</td>
<td>45</td>
</tr>
<tr>
<td>Co-6-600</td>
<td>50</td>
<td>0.69</td>
<td>652, 1376</td>
<td>4.33</td>
<td>781.3, 783.2</td>
<td>30</td>
</tr>
<tr>
<td>Co-ex-400</td>
<td>88</td>
<td>0.30</td>
<td>582, 1390</td>
<td>4.87</td>
<td>781.6, 783.9</td>
<td>28</td>
</tr>
</tbody>
</table>

Table 1: BET surface area, total acidity, main bands in the diffuse reflectance electronic spectra, magnetic moments, Co 2p$_{3/2}$ binding energies and percentage of Co as Co$_3$O$_4$ spinel corresponding to the supports and catalysts.

These modifications might stem from the rearrangement of layered packets during the impregnation process. However, it cannot be discarded that cobalt ions or CoO species hinder the access of the probe molecules (N₂ or NH₃) to the interstices located between the lamellar packets or to the micropores located in the interlayer space of the zirconium phosphate.

Regarding to the hydrogen temperature-programmed reduction profiles (Fig. 1), it is noticeable, in all cases, the presence of a reduction peak at low temperature (250–300 °C). This peak shows the highest intensity for the catalyst with the maximum cobalt content and higher calcination temperature (Co-6-600). According to some authors (Da Cruz et al., 1998; Querini et al., 1999), this peak could be assigned to the presence of Co³⁺ species formed during the thermal treatment of Co²⁺ containing catalysts in air, where the oxidation of a fraction of Co²⁺ species to Co³⁺ takes place. This oxidative process is favoured for higher cobalt percentages and calcination temperatures. Nevertheless, the formation of a segregated cobalt spinel, Co₃O₄, was not detected in the X-ray diffraction patterns.

At temperatures higher than 450 °C, cobalt impregnated catalysts exhibit in their H₂-TPR curves another hydrogen consumption band. On this broad band, one or two maxima between 620 and 680 °C can be distinguished. This second hydrogen consumption step may correspond to the reduction of Co²⁺ to Co⁰. The band width and the presence of different maxima could be due to the existence of Co²⁺ ions in different environments. It can be either as dispersed CoO units or possibly forming cobalt spinel, CoAl₂O₄, in the internal surface of the alumina pillars by diffusion of Co³⁺ ions during the calcination. The H₂ consumption curve for the cobalt exchanged catalyst is more complex, because the appearance of several maxima at high temperatures might indicate the existence of Co³⁺ ions which are neutralising surface charges but in different environments.

Concerning the XPS analysis, it must firstly be stated that the assignation of the different signals in the Co2p core level region is a difficult task due to the proximity of the binding energy values corresponding to Co²⁺ and Co³⁺ species, and also to the dependence of the binding energy of each oxidation state on the chemical environment of the metallic ion. The spectrum of the Co-exchanged sample, Co-ex-400, presents an asymmetric peak at 782.0 eV with a satellite at 787.3 eV (Fig. 2). The Co 2p₃/₂ asymmetric signal was decomposed in two peaks at 781.6 and 783.9 eV. The latter, with a lower intensity, is very close to that reported by Da Cruz et al. (1998) for Co-ZSM-5 samples (784.0 eV), and accordingly it can be ascribed to Co²⁺ ions neutralising surface charge sites on the AlZrP support. The former at 781.6 eV, with a higher intensity, could be attributed to Co²⁺ species in oxidic environments together with the presence of Co³⁺ ions formed during the thermal treatment.

![Fig. 1. H₂-TPR curves of (a) Co-ex-400, (b) Co-6-600, (c) Co-6-400, (d) Co-3-600 and (e) Co-3-400 catalysts.](image1)

![Fig. 2. Co2p core level X-ray photoelectron spectra for (a) Co-3-600 and (b) Co-ex-400 catalysts.](image2)
in air, as previously noted in the H₂-TPR discussion, although the existence of some surface CoO units can not be completely ruled out. In fact, several authors have assigned a similar binding energy (781.7 eV) to Co³⁺ species formed during the calcination process in air of a Co-ZSM-5 zeolite (Lunsford et al., 1978; Fierro et al., 1996).

In the case of the cobalt impregnated samples, the spectra are apparently similar, although the peaks obtained after the deconvolution of the bands are shifted to lower binding energies in comparison with those observed for the Co-exchanged sample. The peak at 782.8–783.8 eV was assigned to Co²⁺ ions, which are forming a surface aluminate (CoAl₂O₄). This spinel was originated upon calcination of the samples at 400 or 600 °C, in agreement with other authors (Tan et al., 1991). The percentage of Co²⁺ forming part of the CoAl₂O₄ spinel, calculated from XPS data analysis, considerably increases in the case of the samples with 3 wt.% of cobalt when heating from 400 to 600 °C (Table 1). However, in the case of the samples with higher cobalt content, the diffusion of Co²⁺ ions into the reticular holes of alumina is lower. This could be due to the simultaneous tendency of this ion to oxidise forming Co³⁺ and thereby a surface cobalt spinel, Co₃O₄, as deduced from the H₂-TPR data of the catalysts with higher cobalt content. On the other hand, the main peak at lower binding energy now appears between 781.0 and 781.6 eV, and it can be assigned, as in the case of the Co-exchanged catalyst, to the presence of CoO and Co³⁺ species, indistinctly.

The two catalysts with 6 wt.% of Co are dark green and the sample Co-6-600 shows in its electronic spectrum (Fig. 3 and Table 1) two bands at 652 and 1376 nm that are coincident with those observed in the spectrum of Co₃O₄ (Lo Jacono et al., 1973; Fierro et al., 1996). The electronic spectrum of the Co-6-400 catalyst is also similar (bands at 644 and 1360 nm). Furthermore, their magnetic moments, 4.79 and 4.33 BM respectively, are lower than that found for the catalyst precursor before calcination (5.20 BM), thus confirming the formation of Co³⁺ ions. Therefore, it can be inferred the formation of a surface cobalt spinel, Co₃O₄. However, the values found for both 6 wt.% Co catalysts are higher than that reported in the literature for a cobalt spinel (Porta et al., 1992). This is probably due to the presence of an important fraction of Co²⁺ species either as CoO or CoAl₂O₄.

The effective magnetic moments for cobalt in the Co-3-400 and Co-3-600 catalysts are 5.6 and 5.2 BM, respectively. These values are higher than that expected for tetrahedral Co²⁺ species (3.8 BM), thus precluding this coordination environment. Therefore, the absorption bands at 582–586 and 1390–1384 nm can be assigned to the 4T₁g → 4T₁g (P) and 4T₁g → 4T₂g transitions, respectively, typically of octahedral Co²⁺ ions.

With regard to the Co-ex-400 catalyst, the effective magnetic moment of 4.87 BM, its greenish grey colour and its electronics spectrum with bands at 582 and 1390 nm also point to the presence of octahedral Co²⁺ ions.

Temperature-programmed desorption curves of NO on Co-6-600 and Co-ex-400 catalysts are shown in Fig. 4. Species different from NOₓ were not detected, except traces of N₂O at high temperatures; moreover, the curves exhibit a single peak corresponding to NO. These results are similar to those reported by Li and Armor (1993a) and Stakheev et al. (1996). Moreover, this peak for the Co-ex-400 catalyst is ten times more intense than that observed for the Co-6-600 catalyst. This higher intensity can be explained taking into account the great amount of surface Co₃O₄ formed in the Co-6-600 catalyst and the lower tendency of Co³⁺ to form nitrosyl complexes. However, the interaction of NO molecules with the surface sites of the Co-6-600 catalyst seems to be stronger since the NO desorption occurs at a higher temperature than that observed in the case of the exchanged catalyst, Co-ex-400. The evolution of oxygen, observed in the NO-TPD curve of the Co-6-600 catalyst,
concomitantly with NO, is possibly due to the decomposition of nitrate or nitrite ions present on the catalyst surface (Torre-Abreu et al., 1997).

### 3.1. Catalytic results

The cobalt containing catalysts have been tested in the SCR of NO using propane as reducing agent in the presence of oxygen.

Fig. 5a shows that a maximum NO conversion close to 14% is obtained at 500 °C on the Co-3-600. Similar value is found with Co-6-600 catalyst. However, although both samples present a similar NO conversion, the competitiveness factors of the reaction are quite different, being 35.3% and 7.1%, respectively, at this temperature (Fig. 5b). This difference lies in the higher acidity of the Co-6-600 catalyst, as determined by NH$_3$-TPD, which promotes the total oxidation of propane, giving rise to a propane conversion close to 85% at 500 °C (Fig. 5c). Both catalysts are more active than a CoO supported on alumina (Yan et al., 1998), where a NO conversion, using methane as reducing agent, of only 10% at 500 °C is observed, although this catalyst is slightly more active at higher temperatures. These data suggest that a good dispersion of the active phase (CoO) on the surface of the alumina pillared zirconium phosphates was attained. However, better activity could be obtained by calcination of the catalysts at higher temperatures such as 700–800 °C, as reported by other authors (Mamula et al., 2000), confirming the importance of the formation of superficial spinel of cobalt.

The cobalt-exchanged catalyst presents the lowest activity with a NO conversion value of 7% at 450–500 °C. These results are similar to those reported by other authors which point out that impregnated samples are more active, even working at a lower temperature, than the exchanged samples (Lee et al., 1997).

From the catalytic performance of these catalysts at 500 °C (Table 2), it can be inferred that the NO conversion is rather a function of the activation temperature of the catalysts than of their cobalt content. Indeed,
The Co-3-400 catalyst exhibits the lowest NO conversion whereas its thermal activation at 600 °C gives rise to the most active catalyst, together with the Co-6-600 catalyst. According to the H2-TPR and XPS results, the Co-6-600 catalyst presents higher Co3+ content. In consequence, it might be postulated a relationship between the catalytic activity and the Co3+ content. In fact, the formation of the surface cobalt spinel, Co3O4, from dispersed CoO implies an oxygen activation and transference from the gas phase to the catalyst, where the adsorbed NO is oxidised to NO2. Subsequently, the NO2 is reduced to nitrogen by the hydrocarbon.

Similarly, the high activity of over-exchanged Co-ZSM-5 has also been justified assuming that the cobalt ions in excess of the cation exchange capacity of the support are highly dispersed as CoO units which are very active in the oxidation of NO to NO2 (Stakheev et al., 1996). This assumption has also been supported by other authors (Shelef et al., 1994), who have found that the high catalytic activity of some cobalt containing catalysts in the SCR of NO with hydrocarbons can be well correlated with their capacity to form NO2.

Therefore, the formation of nitrogen dioxide seems to be a key step in the SCR of NO in the presence of hydrocarbons as anticipated by Burch and Scire (1994), although the formation of the NO2 in the gas phase is argued. However, the role of the Co3+ ions in zeolitic catalysts in this catalytic reaction is still under controversy, because in some cases the formation of Co3O4 species occurs which could block the pores of the zeolite, thus decreasing the catalytic activity (Bellusi et al., 1997). In other cases the hydrocarbon molecules can reduce NO2 forming NO again (Ohtsuka et al., 1997) with a concomitant decrease of the NO conversion and selectivity.

Yan et al. (1998) have demonstrated that the SCR reaction is not only controlled by the NO2 formation but also by the activation of the hydrocarbon molecules on the Bronsted acid centres present on the catalyst. Thus, they have found that a physical mixture of CoO supported on alumina and an acidic zeolite considerably enhances the catalytic activity. This result can be explained by a synergistic effect between the supported CoO that favours the oxidation of NO to NO2 and the activity of the Bronsted acid sites of the zeolite able to activate the hydrocarbon molecules. Thus, the limited catalytic activity observed on the cobalt containing AlZrP catalysts studied in this work could therefore be ascribed to the existence of a majority of acid centres of Lewis type. In consequence, the TOF values obtained for our catalysts (Table 2) are slightly lower than those reported for zeolites such as Co-ZSM-5 (Li and Armor, 1993a) and Co-FER-6 (Li and Armor, 1993b), which present TOF values of 4.8 × 10−4 and 9 × 10−4 molecNO s−1 atCo1 respectively, although the contact times used in these experiments were slightly different. It can be concluded that, in order to ameliorate the catalytic performance of these catalysts in the SCR of NO with propane, the creation of Bronsted acid centres is necessary, even by using a physical mixture of this catalyst with an acidic material.

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References


