Selective catalytic reduction of NO by propane on copper containing alumina pillared α-zirconium phosphates


Departamento de Química Inorgánica, Cristalográfia y Mineralogía, Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos, 29071 Málaga, Spain

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Abstract

Copper containing alumina pillared α-zirconium phosphates with different copper loadings, where copper was incorporated by ion exchange and by impregnation, have been synthesized and characterized by using techniques such as XPS, UV–VIS spectroscopy, H2-TPR and NO-TPD. The catalytic activity of the synthesized materials in the selective catalytic reduction of NO using propane as a reducing agent in the presence of oxygen at 623–823 K has been evaluated. In the exchanged sample, copper is mainly present as isolated Cu2+ species, whereas the impregnated materials show copper to be present as small CuO clusters (not detectable by XRD) and a fraction as spinel-like structures within the alumina pillars. NO-TPD displayed a stronger interaction of NO molecules with the copper exchanged materials, because N2O and O2 are detected at temperatures higher than 773 K. Under the selected experimental conditions, the most active catalyst in the SCR of NO is the copper exchanged catalyst, attaining conversions of NO close to 30% at 823 K. Moreover, the competitiveness factor is high and the TOF number is 1.57×10^{−4} molecules NO per second atCu for the copper exchanged catalyst, this being comparable to that obtained with a Cu-ZSM-5 used as a reference. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Pillared layered solids; Zirconium phosphate; NO SCR; Propane; Copper containing catalysts

1. Introduction

Nitrogen oxides (NOx) produced during high temperature combustion processes, both from stationary and automotive sources, are nowadays one of the most dangerous sources of environmental pollution due to their role in acid rain and photochemical smog formation. For this reason, the reduction of the NOx pollution is receiving growing attention in the field of environmental catalysis. 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, has been commercialized in Japan and Europe for power plants. Recently, Busca et al. reviewed the state of the art of SCR of NO with ammonia [1]. However, hydrocarbons are preferred as reducing agents instead of ammonia for practical reasons, especially in automotive sources.

Cu-ZSM-5 is a very active catalyst for SCR of NO by hydrocarbons in the presence of oxygen [2]. However, this catalyst fails in durability because it
suffers from high deactivation in engine tests, possibly due to the presence of water and SO$_2$ in the gas effluents [3,4]. Moreover, other studies have revealed that, at high temperatures, dealumination of the zeolite can occur with a concomitant migration of active metals to sites not accessible to the reactants [5]. For this reason, more thermally stable supports such as alumina and modified aluminas have been proposed as carriers to study the SCR of NO, in which high dispersion of the active metal and good performance has been attained [6–8].

Another strategy to increase the dispersion of the active metal is the use of carriers based on alumina diluted within another inorganic matrix, such as pillared materials. These pillared layered solids can be considered as two-dimensional zeolite-like structures, which are prepared from layered substances (clays, metal(IV) phosphates, etc.) by cation exchange with inorganic polyhydroxocations. Upon heating, these oligomeric cations give rise to oxide nanoparticles, which prop the layers permanently apart, and they create zeolite-like interlayer and interpillar spaces, thus giving solids with high surface areas and acidity [9]. Pillared materials prepared from layered α-zirconium phosphate have been extensively studied and they have been shown to be active in acid catalyzed reactions [10], in oxidative dehydrogenation of light alkanes [11], or as a support of phases active in reactions such as hydrogenation of aromatic hydrocarbons [12] and hydrodesulfurization of thiophene [13].

The aim of the present work is to study the properties of an alumina pillared zirconium phosphate as a support for copper species and its effect on the dispersion, reducibility and activity of the active metal in the SCR of NO. Copper species were incorporated both by impregnation and by cation exchange in order to assess the influence of the incorporation method on the performance in the previously mentioned catalytic reaction. For this purpose, the catalysts were previously characterized using techniques such as XRD, XPS, temperature-programmed reduction (TPR) with hydrogen, temperature-programmed desorption (TPD) of NO, and UV–VIS spectroscopy, and finally tested in the SCR of NO at different temperatures.

2. Experimental

2.1. Preparation of catalysts

Two porous alumina pillared α-zirconium phosphates have been obtained by calcining a precursor phase in air at 673 K (AlZrP-673) and 873 K (AlZrP-873) for 6 h. The synthesis of the precursor phase has been described elsewhere [14]. The incorporation of copper was carried out by using two different methods: impregnation and ion exchange. Copper impregnated catalysts were prepared through the incipient wetness impregnation of the AlZrP supports with an aqueous solution of copper acetate. The copper weight loadings were 3 and 6 wt.% The solvent was evaporated at 333 K in air, and the dry samples were treated at 673 or 873 K in air in order to obtain the catalysts labeled as Cu-x-y (where x is the copper weight loading and y is the calcination temperature). A copper exchanged catalyst was prepared by putting the AlZrP-673 support in contact with an aqueous solution of copper acetate for 1 day at room temperature. After this, the solid phase was recovered by centrifugation, washed with water, air dried and finally calcined at 673 K. The amount of copper added to obtain the fully exchanged catalyst was equivalent to 10 times the theoretical cation exchange capacity of the original α-zirconium phosphate (6.6 meq g$^{-1}$).

Thereby a copper loading of 3.8 wt.% was achieved. This catalyst has been labeled as Cu-ex. A Cu-ZSM-5, prepared by ion-exchange with copper acetate at room temperature of a synthesized ZSM-5 (with a Si/Al ratio of 13.5, copper content of 2.8 wt.% corresponding to a exchange level of 79%), was used as a reference.

2.2. Characterization methods

XRD patterns were obtained with a Siemens D501 diffractometer provided with a graphite monochromator and using Cu Kα radiation. Adsorption–desorption of nitrogen on the copper containing samples (77 K, outgassing at 473 K and 10$^{-4}$ Torr overnight) was measured on a conventional volumetric apparatus. Temperature-programmed desorption of ammonia (NH$_3$-TPD) was used to determine the total acidity of the catalysts. Before the adsorption of ammonia at 373 K, the samples were heated at 673 K in a He flow (35 cm$^3$ min$^{-1}$) for 1 h. The NH$_3$-TPD was
performed between 373 K and the corresponding calcination temperature of catalysts, with a heating rate of 10 K min\(^{-1}\). Evolved ammonia was analyzed by on-line gas chromatograph (Shimadzu GC-14A), provided with a TC detector. For the adsorption of pyridine, self-supported wafers, with a weight-to-surface ratio of about 8 × 10\(^{-2}\) kg m\(^{-2}\) were placed in a vacuum cell assembled with Teflon stopcocks and CaF\(_2\) windows. The samples were evacuated (623 K, 10\(^{-4}\) Torr, overnight) and exposed to pyridine vapors at room temperature for 5 min. Then, infrared spectra were recorded after outgassing the catalysts at different temperatures. Diffuse Reflectance UV–VIS spectra of the catalysts were obtained using a spectrophotometer Shimadzu 8100 and BaSO\(_4\) as reference.

XPS analysis was carried out with a Physical Electronics 5700 instrument with Mg K\(\alpha\) X-ray excitation source (\(hv=1253.6\) eV) and a hemispherical electron analyzer. Accurate ±0.1 eV binding energies were determined with respect to the position of the adventitious C 1s peak at 284.8 eV. The residual pressure in the analysis chamber was maintained below 10\(^{-9}\) Torr during data acquisition. Hydrogen TPR of samples was performed between 323 and 823 K, using a flow of Ar/H\(_2\) of 40 cm\(^3\) min\(^{-1}\) (10% of H\(_2\)) and heating at 10 K min\(^{-1}\). The water produced in the reaction was eliminated by passing the gas flow through a cold finger (193 K). The consumption of the reducing agent was controlled by an on-line gas chromatograph equipped with a TC detector.

Temperature-programmed desorption of NO (NO-TPD) was performed between 313 and 823 K, using a heating rate of 10 K min\(^{-1}\). Before the adsorption of NO at room temperature, the samples were heated at 673 or 873 K in a He flow for 1 h. The adsorption of NO was carried out by passing a flow of 150 cm\(^3\) min\(^{-1}\) (0.05 vol-% NO) for 30 min. During the desorption, helium was flushed and the eluted gas phase was carefully monitored and quantified using an on-line quadrupole mass spectrometer Balzer GSB 300 02.

The catalytic activities were measured using a micro-reactor in a steady-state flow mode. The reactor was a quartz tube with 0.27 in. o.d. Samples of about 150 mg, with particle size of 0.3–0.4 mm, were packed into the reactor and plugged with glass wool. Catalysts were treated at 623 K for 30 min under a helium flow. The reaction mixture typically consisted of 1000 ppm NO, 1000 ppm propane and 2.5% O\(_2\) (balanced with helium). The flows were independently controlled by four channel mass flowmeters (Brooks) and the flow rate of the feed was 150 cm\(^3\) min\(^{-1}\). Under these experimental conditions, the space velocity (F/W) was 60,000 cm\(^3\) h\(^{-1}\) g\(^{-1}\). The interval of temperatures studied ranged between 623 and 823 K. An on-line quadrupole mass spectrometer Balzer GSB 300 02 was incorporated to monitor the gas effluent at each temperature and thus to know the composition of NO and propane. The activity was obtained on the basis of disappearance of NO fed. The competitiveness factor of the reaction is calculated as the ratio of mole of propane reacted with NO with respect to the total mole of propane consumed in the reaction.

3. Results and discussion

3.1. Characterization of catalysts

The alumina pillared \(\alpha\)-zirconium phosphate, used as support after calcination at 673 K, has the empirical formula \(\text{Zr(Al}_{3.39}\text{O}_{1.12}\text{(OH)}_{1.60}\text{F}_{4.90}\text{H}_{0.57}\text{(PO}_{4})_{2}\). From its XRD pattern, a basal spacing of 18.4 Å is obtained, which corresponds to a free interlayer height of 12.3 Å. Moreover, this AlZrP-673 support is a porous solid with a BET specific surface area of 135 m\(^2\) g\(^{-1}\) and the solid becomes mainly mesoporous but with a contribution of micropores. It seems to be generally accepted that edge–edge and face–edge platelet interactions give rise to mesopores, whereas the microporosity stems from the presence of alumina nanoparticles, acting as pillars, between the zirconium phosphate layers.

The calcination at 873 K reduces the BET surface area to 85 m\(^2\) g\(^{-1}\) and the solid becomes mainly mesoporous. These porous fluorinated alumina pillared \(\alpha\)-zirconium phosphates are acidic solids with a total acidity, as determined by ammonia temperature-programmed desorption (NH\(_3\)-TPD), of 1.1 mmol NH\(_3\) per gram and 0.64 mmol NH\(_3\) per gram for the AlZrP-673 and AlZrP-873 samples, respectively. Pyridine adsorption coupled to infrared spectroscopy reveals that both solids exhibit almost exclusively Lewis acid centers. Furthermore, after thermal treatment, these solids still retain ion-exchange properties. Thus, Cu\(^{2+}\) ions have been incorporated by
Table 1
Main characteristics of the copper containing alumina pillared zirconium phosphates

<table>
<thead>
<tr>
<th>Sample</th>
<th>Copper loading (wt.%)</th>
<th>$S_{BET}$ (m² g⁻¹)</th>
<th>Total acidity a (mmol NH₃ per gram)</th>
<th>$Cu\ 2p_{3/2}$ BE b (eV)</th>
<th>Absorption bands c (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlZrP-673</td>
<td>–</td>
<td>135</td>
<td>1.12</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>AlZrP-873</td>
<td>–</td>
<td>85</td>
<td>0.64</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Cu-ex</td>
<td>3.8</td>
<td>85</td>
<td>0.48</td>
<td>933.1</td>
<td>12690</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10520</td>
</tr>
<tr>
<td>Cu-3-673</td>
<td>3</td>
<td>99</td>
<td>0.78</td>
<td>932.8 (78%)</td>
<td>12500</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>935.1 (22%)</td>
<td>10604</td>
</tr>
<tr>
<td>Cu-6-673</td>
<td>6</td>
<td>89</td>
<td>0.47</td>
<td>932.5 (73%)</td>
<td>12500</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>934.9 (27%)</td>
<td>10604</td>
</tr>
<tr>
<td>Cu-3-873</td>
<td>3</td>
<td>60</td>
<td>0.84</td>
<td>932.6 (75%)</td>
<td>12285</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>934.8 (25%)</td>
<td>10604</td>
</tr>
<tr>
<td>Cu-6-873</td>
<td>6</td>
<td>50</td>
<td>0.80</td>
<td>932.6 (70%)</td>
<td>12285</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>934.8 (30%)</td>
<td>10900</td>
</tr>
</tbody>
</table>

a As determined from NH₃-TPD between 373 K and the corresponding calcination temperature of catalysts.
b From XPS analysis.
c Absorption bands of maximum intensity in the DRS spectra.

ion exchange, and its catalytic behavior will be compared with the analogous copper containing catalysts where different loading of Cu²⁺ have been introduced by the incipient wetness impregnation method.

In Table 1, it can be observed that the incorporation of copper into the AlZrP support causes a decrease in the $S_{BET}$, with a reduction of 37% for the Cu-ex catalyst and ranging between 27 and 41% for the copper impregnated catalysts. These changes suggest that Cu²⁺ species could hinder the access of the nitrogen molecules to the smaller pores, hence reducing the specific surface area. Moreover, it can not be discarded that, during the exchange process, copper cations occupy positions on cut layers, thus favoring an inhomogeneous reordering of the layer packets.

On the other hand, the incorporation of copper into the AlZrP support has a different influence on the acid properties of the resulting catalysts. There is a significant reduction in the total acidity values for catalysts activated at 673 K with respect to the AlZrP-673 support (Table 1), which corroborates that copper cations could hinder the access of ammonia molecules to the acid sites located in micropores. In contrast, the reverse situation is found for the catalysts calcined at 873 K. This latter result indicates that copper cations could be now responsible for this acidity enhancement. In fact, the latter catalysts became dark blue after exposition to pyridine vapors, which reveals that pyridine molecules can also interact with the copper species. Infrared spectroscopy indicates that acid sites are mainly of the Lewis type, as can be deduced, for instance, from the intense peak appearing at 1450 cm⁻¹ in the spectrum of the Cu-3-873 catalyst. However, the darkness of the other samples after pyridine adsorption impedes the study of the nature of the acid sites by IR spectroscopy.

XRD patterns of impregnated catalysts do not exhibit neither the peaks at 2.52 and 2.32 Å, typical of CuO crystallites, nor the peak at 2.44 Å corresponding to CuAl₂O₄ [6], clearly indicating a good dispersion of the active phase.

X-ray photoelectron spectroscopy has allowed us to show that a fraction of Cu²⁺ cations in the copper impregnated catalysts are forming part of spinel-like structures. The XPS spectrum of Cu-6-873 in the Cu $2p_{3/2}$ region (Fig. 1) exhibits a large and asymmetric peak with a maximum at 933 eV, accompanied by the characteristic Cu²⁺ shake-up satellite peak at 943.1 eV. This asymmetric peak can be fitted to two principal peak components at 932.6–933.1 and at 934.7–935.4 eV, which could be assigned to CuO [15] and Cu²⁺ in spinel-like structure occupying octahedral sites [16,17], respectively. This latter coordination contrasts with that in bulk spinel where copper has a predominantly tetrahedral environment [18]. Table 1 depicts the percentage of each component. As can be seen, the diffusion of Cu²⁺ toward alumina to form spinel-like structure increases with
both the copper loading and the calcination temperature. However, XPS spectrum of Cu-ex sample only shows a symmetrical peak centered at 933.1 eV, typical of octahedral Cu$^{2+}$ sites, which could be assigned to isolated Cu$^{2+}$ species.

Fig. 2 shows the H$_2$-TPR curves obtained for the different copper containing catalysts. The influence of the copper loading, the incorporation method and the thermal treatment on the corresponding profiles can be observed. Quantitative analysis was not possible due to the gradually rising baseline in each TPR profile. Thus, impregnated catalysts with the lowest loading (3 wt.%) only exhibit a very broad peak with an ill-defined maximum; however, at a higher Cu$^{2+}$ loading (6 wt.%), two peaks can be distinguished close to 473 and 553 K. Taking into account that the H$_2$-TPR curve of bulk CuO displays a single peak of reduction at low temperature (496 K), corresponding to the reduction of Cu$^{2+}$ to Cu$^{0}$, the existence of two peaks in impregnated samples might result from the presence of Cu$^{2+}$ in two different environments, differing in their interaction with the support. These data confirm that a fraction of the Cu$^{2+}$ cations has diffused during the thermal process into the alumina pillars forming mixed Cu–Al oxide (vide supra). According to the literature, these Cu$^{2+}$ species in spinel-like structure are more difficult to reduce [6], hence the high temperature peak in the reduction curve might be tentatively associated with the reduction of these species. Moreover, the intensity of the high temperature peak increases with the thermal treatment of the catalysts, being more intense for the Cu-6-873 catalyst than for Cu-6-673 catalyst. The lower temperature peak may be assigned to CuO species highly dispersed on the external surface of the alumina pillars [7]. This temperature is lower than that corresponding to bulk CuO, which indicates a good dispersion [19].

On the other hand, the reduction profile of the Cu-ex catalyst exhibits two peaks of H$_2$ consumption, centered at 479 and 598 K. The hydrogen consumption peak situated at lower temperature could correspond to the reduction of Cu$^{2+}$ to Cu$^{+}$ in isolated Cu$^{2+}$ species [19,20], although the reduction of Cu$^{2+}$ to Cu$^{0}$ due to some CuO units cannot be ruled out. The second reduction peak at higher temperature corresponds to the reduction of Cu$^{+}$ to Cu$^{0}$. The high temperature (564 K) of the second reduction peak for the exchanged sample can be accounted for a strong interaction between the exchanged copper cations and the support and, at the same time, the stabilization of
the Cu⁺ species. This result is very interesting since the high activity of Cu-ZSM-5 for NO decomposition has been correlated with the stability of Cu(I) valence state [21,22].

UV–VIS spectra of copper impregnated catalysts show a very broad absorption band which can be decomposed into a band centered at 12,500 cm⁻¹ and a shoulder near to 10,600 cm⁻¹, which are typical of octahedral Cu²⁺ in a distorted tetragonal environment. Table 1 compiles the absorption bands of the different copper containing catalysts. The absorption bands for the Cu-ex sample, before calcining at 673 K, appear at high energies according to the position of water in the spectrochemical series. Therefore, these data reveal that Cu²⁺ in impregnated samples always exhibits distorted octahedral coordination either in the CuO units or in spinel-like structure, as has been previously described in the literature [16,17].

The NO TPD profiles of Cu-ex and Cu-3-873 catalysts are depicted in Figs. 3 and 4, respectively. Only NO, N₂O and O₂ were detected during the NO desorption of the studied catalysts. However, there are noteworthy differences between both catalysts. Thus, for Cu-3-873, NO molecules are almost exclusively desorbed at low temperature (peak centered at 393 K), and only traces of N₂O are detected during the thermal process. At temperatures higher than 700 K, evolution of O₂ takes place. This gas might come from the spontaneous reduction of CuO units which gives also Cu⁺ [23,24]. In contrast, the Cu-ex catalyst exhibits a small NO desorption peak at low temperature (433 K) and another two peaks of N₂O and O₂ centered at 823 K, possibly due to the decomposition of nitrate or nitrite ions adsorbed onto Cu²⁺ species [20]. However, a contribution to the oxygen peak could also come from the decomposition of the N₂O formed from the adsorbed NO molecules [25], from the decomposition of the little amount of CuO present in the catalyst and from the spontaneous reduction of Cu²⁺ to Cu⁺ [24]. The NO-TPD of the Cu-ex sample is quite different to that of Cu-mordenite [26] where a single peak of NO desorption was observed and that of Cu-ZSM-5 [25] with N₂O only evolved at low temperatures. All these data point to the existence of a strong interaction between copper ions and NO molecules in the Cu-ex sample.

3.2. Catalytic results

Propane was chosen as a reducing agent in the selective catalytic reduction of NO, since methane is a more stable and refractory molecule than propane. Moreover, propane is preferred to propene because olefins produce carbonaceous deposits more easily, provoking the deactivation of catalysts [27], especially at low reaction temperatures, and an excess of propane is recommended in order to obtain an overall reducing environment. It is well known that for a given feed (oxygen, hydrocarbon and NO), the NO conversion depends on several experimental parameters. Thus, for instance, the temperature at the maximum activity is a function of the type of hydrocarbon, the active cation and the support [28]. On the other hand, the presence of oxygen is essential to NO reduction. Therefore, there are two reaction pathways competing for
Fig. 5. NO conversion as a function of the reaction temperature of Cu-ex (s); Cu-3-673 (○); Cu-6-673 (●); Cu-3-873 (□) and Cu-6-873 (■) catalysts. Experimental conditions: NO (1000 ppm), C3H8 (1000 ppm) and O2 (2.5%). Total flow rate 150 cm3 min−1.

the propane oxidation which might be considered as

\[ \text{C}_3\text{H}_8 + 2\text{NO} + 4\text{O}_2 \rightarrow \text{N}_2 + 3\text{CO}_2 + 4\text{H}_2\text{O} \]  

(1)

\[ \text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O} \]  

(2)

Under our experimental conditions, the products of the reaction were N2, NO2 and CO2. Neither nitrous oxide nor CO formation were observed in the studied temperature range (623–823 K). The variation of the NO conversion as a function of the reaction temperature (Fig. 5) shows that conversion always increases with temperature. Thus, at the highest studied temperature, 823 K, the NO conversion ranges between 16 for Cu-3-873 and 30% for Cu-ex sample. A similar increase is observed for the conversion of propane (Fig. 6). The influence of temperature used for the thermal treatment of the catalyst on the NO conversion is not clear because there are two opposite factors influencing it. Calcination at higher temperature produces more migration of Cu2+ into alumina sites to form spinel like structures (see Table 1), so decreasing the number of cationic active centers. In contrast, this thermal process could also provoke texture modification in the support, appearing a mesoporous solid, where diffusion of the reactants can be favored at higher temperatures. In Fig. 7, it is observed a decay in the competitiveness factor with temperature, especially for catalysts previously treated at 873 K. At 723 K, all catalysts are very selective, with values ranging between 40 and 90%. However, the competitiveness factors decrease at higher temperatures; this

behavior can be expected taking into account that the propane combustion is enhanced at higher reaction temperatures.

Table 2 compiles the catalytic properties of these catalysts at 823 K. From these data, it can be deduced that the most active sample is Cu-ex, which exhibits both the maximum conversion and reduction rate. These data demonstrate that isolated Cu2+ ions, incorporated by cationic exchange, are more active than those Cu2+ species present as CuO species. In fact, the turnover frequency (TOF), expressed as the number of nitric oxide molecules reduced per
Table 2
Catalytic properties of copper containing alumina pillared zirconium phosphate catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion of NO (%)</th>
<th>Activity $\times 10^2$ ($\text{mol s}^{-1} \text{g cat}$)</th>
<th>TOF $\times 10^4$ (molecules NO per second $\text{at Cu}$)</th>
<th>Competitiveness factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlZrP-673</td>
<td>7.3</td>
<td>1.80</td>
<td>--</td>
<td>26.1</td>
</tr>
<tr>
<td>AlZrP-873</td>
<td>7.1</td>
<td>1.75</td>
<td>--</td>
<td>23.6</td>
</tr>
<tr>
<td>Cu-ex</td>
<td>30</td>
<td>7.40</td>
<td>1.57</td>
<td>33.3</td>
</tr>
<tr>
<td>Cu-3-673</td>
<td>25</td>
<td>6.17</td>
<td>1.31</td>
<td>44.4</td>
</tr>
<tr>
<td>Cu-6-673</td>
<td>20</td>
<td>4.94</td>
<td>0.52</td>
<td>33.3</td>
</tr>
<tr>
<td>Cu-3-873</td>
<td>16</td>
<td>3.95</td>
<td>0.84</td>
<td>21.0</td>
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<tr>
<td>Cu-6-873</td>
<td>24</td>
<td>5.92</td>
<td>0.63</td>
<td>20.7</td>
</tr>
</tbody>
</table>

$^a$ Conditions: feed: 1000 ppm NO, 1000 ppm C$_3$H$_8$, 2.5% O$_2$, balance with helium, flow rate=150 cm$^3$ min$^{-1}$, 0.150 g catalyst, reaction temperature=823 K.

copper cation and second, is maximum for Cu-ex sample (1.57 $\times 10^{-4}$). This value is only comparable to that corresponding to the Cu-3-673 catalyst, but higher copper loading or calcination temperatures lead to smaller TOFs. This finding is in contrast to that observed for the Cu-ZSM-5 catalyst whose catalytic activity increases with the copper loading, suggesting the existence of copper pairs to explain this activity enhancement [29].

The higher activity for Cu-ex sample was expected if we take into account the results of NO-TPD for this sample. Indeed, a strong interaction was evidenced between NO and this catalyst as can be inferred from the formation of N$_2$O and O$_2$ at 823 K, after several minutes of desorption times. In contrast, impregnated copper catalysts only present a NO desorption peak at low temperature. Moreover, an important fraction of copper forms spinel-like structures in these catalysts, thus making copper species less active. On the other hand, according to the H$_2$-TPR results, the Cu-ex sample exhibits Cu$^+$ which is more difficult to reduce and hence more stable. The presence of cuprous ions stabilized by the support is necessary to form dinitrosyl complex species [30,31]; on the other hand, some catalysts show catalytic activity related to a high dispersion of isolated Cu$^+$ ions [32]. In any case, our Cu impregnated catalysts are more active than other materials described in literature such as Cu supported on alumina [32] or Cu supported on alumina pillared clays [33]. This means that a better dispersion of the alumina, and hence of CuO species was attained using the intercalated alumina pillars between the interlayer space of zirconium phosphate.

However, under the same experimental conditions, a synthesized Cu-ZSM-5 catalyst is more active, with conversion values close to 100%, but its turnover frequency is of the same order (6.52 $\times 10^{-4}$) as that obtained with the Cu-ex catalyst (1.57 $\times 10^{-4}$). This lower activity for the Cu-ex catalyst with respect to that of Cu-ZSM-5 could be explained by taking into account the scarce Brönsted acidity present in the former. It has been previously established that the presence of Brönsted acidity is necessary for propane activation in this catalytic reaction [33]. Nevertheless, ulterior studies focused in determining the resistance of this new family of catalysts to the presence of SO$_2$ should be done in order to evaluate its potential technological applications, since this support is very stable under steaming conditions.

The most active Cu-ex catalyst has been selected to evaluate the kinetic parameters of this catalytic reaction. In Fig. 8, the effect of oxygen addition on the

![Fig. 8. Effect of the oxygen concentration on the propane and NO conversions for Cu-ex catalyst at 823 K. Experimental conditions: NO (1000 ppm) and C$_3$H$_8$ (1000 ppm). Total flow rate 150 cm$^3$ min$^{-1}$.](image)
NO reduction can be observed. Interestingly, the activity is completely lost in the absence of oxygen. When the feed only contains 0.25% oxygen, the catalyst significantly increases the NO conversion up to 20%. However, a further increase of the oxygen pressure to 3.5% hardly affected the NO conversion. Therefore, the presence of oxygen promotes the SCR of NO by propane in the studied temperature range, but the reaction is zero order in oxygen. In contrast, propane conversion is enhanced in an important way for partial pressures of oxygen higher than 1.5%. Similar results were reported by Li et al. in the case of Co-ZSM-5 [34]. The enhanced rate by addition of excess oxygen has been related with several important factors of this reaction such as the oxidation of carbonaceous deposits, the recuperation of the Cu$^{2+}$ oxidation state, the oxidation of NO to NO$_2$ and the formation of partially oxygenated hydrocarbons [35].

The reaction orders corresponding to propane and NO have also been calculated. This has been achieved by maintaining the concentration of the other components in standard conditions. Thus, the NO conversion at 823 K (Fig. 9) is strongly dependent on the partial pressure of propane, increasing with the propane concentration in the feed up to a value of 57% for a concentration of 3000 ppm of propane. From the plot of log rate of reduction versus log partial pressure of propane the resulting reaction order of propane is found as 0.72. These results mean that for achieving a high degree of reduction of NO a slight excess of propane is necessary. The evolution of NO and propane conversions as a function of the NO composition in the feed at 823 K (Fig. 10) shows a decay in the NO conversion, but the absolute amount of reduced NO also rises up to 550 ppm. Thus, the order of reaction with respect to NO is 0.38. Both values are very similar to those found using a Co-ZSM-5 [34].

On the other hand, the evolution of the NO conversion as a function of the space velocity ($F/W$ values ranging between 30,000 and 70,000 ml h$^{-1}$ g$^{-1}$) reveals that the NO conversion is hardly affected because only a slight decrease is observed. In contrast with short contact times (high space velocities) the propane combustion is largely reduced. For this reason, a $F/W$ value of 60,000 ml h$^{-1}$ g$^{-1}$ was selected for our experiments (Fig. 11).

Finally, the dependence of the copper exchange level in the catalyst on the NO conversion has been studied. Catalysts with an exchange level higher than 3.8 wt.% Cu were prepared, but now a previous treatment with ammonia was carried out in order to neutralize the weaker acid sites. In this way, copper exchange levels of 4.1 and 5.8 wt.% were attained. Fig. 12 exhibits the NO conversion for samples with different exchange levels. The conversion of NO increases with the copper content reaching a maximum value at a Cu$^{2+}$ exchange level close to 100%, but for over-exchanged samples conversion falls. A similar behavior has been reported in the literature [36] and it has been explained by taking into account that copper cations incorporated in severe conditions (for instance, after ammonia treatment) are possibly
located in sites of difficult access and/or impeding the diffusion of reactant through the pores of catalysts.

However, the H2-TPR curves of overexchanged solids reveal a different behavior with respect to the curves of both impregnated and exchanged samples. Only a single peak at 483 K is observed (Fig. 2), similar to that of bulk CuO. Taking into account that these overexchanged samples were prepared after exposition to vapors of ammonia it is possible that precipitation of Cu(OH)2 on the external surface of the support takes place, thus forming after calcination at 673 K big aggregates of CuO. In this way, the activities of these overexchanged catalysts are even lower than those of impregnates samples. Similar results, i.e. the formation of small clusters of CuO on the external surface has been observed in other over-exchanged zeolites [37].

In conclusion, the Cu-ex sample is a promising catalyst for SCR of NO, its performance in this reaction being similar to that of Cu-ZSM-5. This behavior might probably be due to its structure, which can be considered as a bidimensional zeolite. However, the almost exclusive presence of Lewis acid centers, which tend to activate the propane molecules, gives rise to a catalytic activity lower than that of Cu-ZSM-5. Taking into account the proposed mechanism for the SCR of NO, the catalyst presents two key features: acidity to favor the chemisorption and activation of the reducing molecules and redox centers (Cu2+ ions) to activate the NO molecules.

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