Catalysis Letters Vol. 82, No. 3–4, October 2002 (©2002)

Selective catalytic reduction of NO by ammonia at low temperatures on catalysts based on copper oxide supported on a zirconium-doped mesoporous silica

R. Moreno-Tost, J. Santamaría-González, P. Maireles-Torres, F. Rodríguez-Castellón, and A. Jiménez-López *

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

Received 19 March 2002; accepted 13 May 2002

Copper-oxide-containing zirconium-doped mesoporous silica catalysts (1–12 wt% Cu) have been tested in the selective catalytic reduction of NO by ammonia in excess of oxygen. The catalyst with 6 wt% Cu exhibits a maximum NO conversion of 94% at low temperature (250 °C), with a stoichiometric conversion of ammonia and minimal N_2O formation. The catalytic behavior can be correlated with the high degree of dispersion and easy reduction of the supported CuO.

KEY WORDS: copper-containing catalysts; NO SCR; ammonia; zirconium-doped mesoporous silica.

1. Introduction

The abatement of nitrogen oxides (NO_x) emitted during high-temperature combustion processes, mainly from mobile and stationary sources, is one of the most important subjects to be resolved in order to protect the environment due to their role in acid rain and photochemical smog. For stationary sources, the selective catalytic reduction (SCR) of NO using ammonia as the reducing agent, leading to environmentally nonpoisonous reaction products (N_2 and H_2O), has been intensively studied in the past 20 years. Thus, it has become a technologically important process for NO control in Japan, the USA and Europe. Chemical and mechanistic aspects of SCR of NO_x with ammonia on metal-oxide-based catalysts have been recently reviewed [1,2]. The current commercial catalysts are based on supported vanadium(V) oxide or molybdenum(VI) oxide, but they present environmental problems for the disposal of spent catalysts [3].

Metal-exchanged zeolites are generally more active as catalysts than the corresponding supported transition metal ions [2,4]. For instance, Cu-zeolites (mainly Cu/ZSM-5) have been extensively investigated [5], but the catalytic activities reported are far below that required for industrial applications [6,7]. Moreover, the cost of the Cu-zeolite synthesis and the difficulty in obtaining the mechanical strength required for industrial use have instigated several paths of research on high-surface-area oxides as supports. CuO based catalysts such as CuO/ZrO_2 [8], $CuO/MgO/Al_2O_3$ [9] and Cu/SiO_2 [10] have been reported to be active in the SCR of NO by ammonia. All these studies show that the SCR activity increases with the copper dispersion and that isolated copper species are highly active.

On the other hand, at the beginning of the 1990s, the discovery of a new family of molecular sieves [11], generically denominated as MCM-41, opened new and exciting possibilities in catalysis and sorption fields [12,13]. These mesoporous materials usually exhibit a great versatility in terms of both chemical nature and structural characteristics, and provide large surface areas that can provide a good dispersion of copper oxide. Moreover, their hydrothermal stability can be ameliorated by introducing heteroatoms in the siliceous structure [14]. Recently, Fe^{3+} exchanged MCM-41 has been tested in the SCR of NO using NH_3 as a reducing agent [15], which exhibited a high turnover number due to the favorable mass transfer along the uniform cylindrical pores. Other noble metals containing MCM-41 catalysts have also been studied [16–18], but the presence of isocyanate and cyanide species was detected [19]. Now, in this paper, we report the catalytic activity of copper supported on a zirconium-doped mesoporous silica for the abatement of NO with ammonia, in the presence of O_2. The choice of this support instead of a pure mesoporous silica lies in the better results obtained using the more acidic zirconium-doped mesoporous silica, as support for attaining good dispersion with chromia [20,21] and vanadia [22], and especially because the SCR activity is known to be related to the acidity of the catalyst [23,24].

---

* To whom correspondence should be addressed.
E-mail: ajimenezl@uma.es

1011-372X/02/1000-0205/0 © 2002 Plenum Publishing Corporation

2. Experimental

2.1. Preparation of catalysts

Zirconium-doped mesoporous silica, with an Si/Zr molar ratio of 5, was prepared by following the method described in previous papers [20,25]. The material was calcined in air at 550 °C (1 °C min^{-1} heating rate) for 6 h and was denoted as SiZr5. This support is very stable under hydrothermal conditions, because the treatment of crushed pellets (0.85–1.25 mm) at 550 °C in a tubular reactor, flowing N_2 saturated with water (flow rate of 5.5 l h^{-1}) for 5 h, does not affect either its textural or its structural characteristics. Catalysts with copper loadings of 1, 3, 6 and 12 wt% were prepared by the incipient wetness method. Thus, 2 g of SiZr5 materials were treated with an ethanolic solution of copper nitrate. After impregnation, the samples were dried at 60 °C and calcined in air at 550 °C for 4 h (1 °C min^{-1} heating rate). These catalysts were labelled as SiZr5-XCu, where X indicates the amount of Cu added expressed as wt%. A new reference material (a wolfram-doped titanium oxide hereafter called Eurocat) with the composition (wt%) TiO_2 (78%), WO_3 (9%). SiO_2 (6.5%). V_2O_5 (3.15%), Al_2O_3 (1.5%), CaO (1%) and SO_4^{2-} (0.85%) was tested in the selective catalytic reduction of NO.

2.2. Characterization methods

The Cu content was determined by atomic absorption (AA) spectroscopy. All catalysts were characterized by X-ray powder diffraction using a Siemens D501 diffractometer (Cu K_α source) provided with a graphite monochromator. Textural parameters were obtained from N_2 adsorption–desorption isotherms (BET method) as determined using a glass conventional volumetric apparatus at −196 °C, after outgassing the catalysts at 200 °C and 10^{-4} Torr overnight. Temperature-programmed desorption of ammonia (NH_3-TPD) was used to determine the total acidity of the catalysts. Before the adsorption of ammonia at 100 °C the samples were heated at 400 °C in a He flow (35 ml min^{-1}) for 1 h. The NH_3-TPD was performed between 100 and 550 °C, with a heating rate of 10 °C min^{-1}. The desorbed ammonia was analyzed by an on-line gas chromatograph (Shimadzu GC-14) provided with a thermal conductivity detector (TCD). Pyridine adsorption coupled to IR spectroscopy was employed to determine the nature and concentration of the acid sites of the catalysts. Adsorption–desorption of pyridine was followed according to the method described elsewhere [26].

The X-ray photoelectron spectra were recorded with a Physical Electronics 5700 instrument provided with a multichannel hemispherical electroanalyzer, and Al and Mg K_α X-ray as excitation sources ($h\nu = 1486.6$ and 1253.6 eV, respectively). 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. Spectra of C 1s and Cu 2p regions were recorded using a pass energy of 29.35 eV for 10 min. This short acquisition time was used to avoid, as much as possible, reduction of Cu^{2+} species to Cu^{+} by the action of the X-ray excitation source as previously reported by several authors [27–29]. Then, spectra of O 1s, Si 2p and Zr 3d regions were also obtained. A further study of the Cu 2p and Cu_{KLL} regions after more than 30 min of irradiation revealed a significant reduction of Cu^{2+} species. A PHI ACCESS ESCA-V6.0F software package was used for acquisition and data analysis.

Temperature-programmed reduction (H_2-TPR) of thermally-treated impregnated samples was performed between room temperature and 800 °C using a flow of Ar/H_2 (40 $\mathrm{cm}^3\,\mathrm{min}^{-1}$, 10 vol% of H_2) and a heating rate of 10 °C min^{-1}. Water produced in the reduction was eliminated by passing the gas flow through a cold finger (−80 °C). The consumption of hydrogen was controlled by an on-line gas chromatograph provided with a TCD.

Temperature-programmed desorption of NO (NO-TPD) was performed by adsorbing NO onto the catalysts at room temperature (150 $\mathrm{cm}^3\,\mathrm{min}^{-1}$ 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 550 °C under He flow for 1 h. During desorption, helium was flushed and the eluted gas phase was carefully monitored and quantified using an on-line quadrupole mass speetrometer, Balzer GSB 300 02.

2.3. Catalysis

Catalysts were tested in the SCR of NO by using a Pyrex glass tube microreactor (0.27 inch o.d.) working at atmospheric pressure in a steady-state flow mode and with a catalytic charge of 150 mg of pelletized solids, sieved to 0.3–0.4 mm, in all cases without dilution. Samples were pretreated at 350 °C *in situ* for 2 h under a He flow (30 $\mathrm{cm}^3\,\mathrm{min}^{-1}$). Ammonia was chosen as the reducing agent. The gas reaction mixture was composed of 1000 ppm NO, 1000 ppm ammonia 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 42 $\mathrm{cm}^3\,\mathrm{min}^{-1}$ was used in the feed. The space velocity (F/W) was 3300 h^{-1}; in these conditions, both external and internal diffusional limitations were absent. The interval of reaction temperatures explored was 100–600 °C. The analysis of reactants and products (NO, N_2O, N_2 and ammonia) was monitored by using the on-line quadrupole mass spectrometer described above.

Table 1
Main characteristics of the copper oxide containing mesoporous SiZr5 catalysts

Catalyst	Cu (%)	d_{100} (Å)	S_{BET} ($m^2\,g^{-1}$)	V_p ($cm^3\,g^{-1}$)	d_p (Å)	Total acidity ($\mu mol\,NH_3\,g^{-1}$)
SiZr5	–	44.2	632	0.62	30.9	389
SiZr5-1Cu	0.7	33.7	624	0.58	31.7	428
SiZr5-3Cu	2.8	34.0	627	0.62	31.4	497
SiZr5-6Cu	5.9	33.5	532	0.52	30.4	708
SiZr5-12Cu	11.9	n.d.	337	0.28	38.1	566

3. Results and discussion

3.1. Characterization of catalysts

The X-ray powder diffraction patterns of the catalysts only exhibit the diffraction lines corresponding to the presence of CuO crystallites ($\bar{1}11$, 111 and 202 planes) [30] for copper loading higher than 6 wt%. Moreover, the structural stability of the support can be assumed by the presence in all cases of a relatively broad diffraction peak (d_{100} line, presupposing a hexagonal arrangement) centered at 44 Å, which is progressively broadened as the copper loading increases (figure 1).

However, the incorporation of copper *via* impregnation produces a steady decrease of the specific surface area of catalysts (table 1), which is more pronounced especially for the sample with the highest copper content, SiZr5-12Cu. This suggests that CuO crystallites produced by calcination are blocking some pores, preventing the access of N_2 molecules.

The reduction of copper species was studied by H_2-TPR. In general, the reducibility of copper(II) is a function of both the nature of the support and the dispersion degree of the active phase [31]. The normalized H_2-TPR curves (figure 2), obtained by dividing the H_2 consumption signal by the amount of copper present in the catalyst, show, in all cases, the existence of a reduction peak at low temperature, centered between 190 and 240 °C, whose intensity increases with the copper content. This peak could be assigned to the reduction of Cu^{2+} ions to Cu^0 [31,32]. For samples with high copper loadings (6 and 12 wt%), the maximum reduction peak appears at temperatures lower than that of bulk CuO (223 °C), which indicates, according to other authors [31], good dispersion of this phase. In contrast, the hydrogen consumption of the catalyst with the lowest copper content (SiZr5-1Cu) is carried out through a wide range of temperatures, revealing the existence of copper(II) species in different environments including less reducible copper(II) strongly interacting with the support [28].

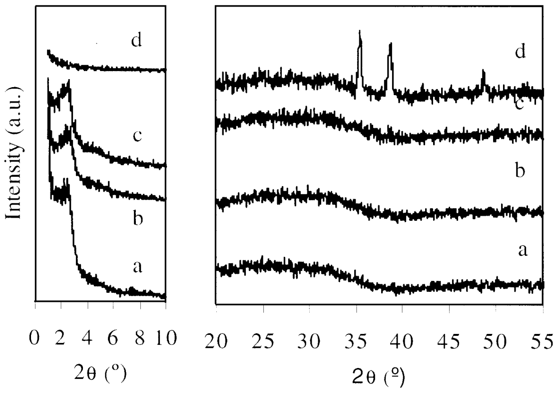

Figure 1. Powder XRD patterns of (a) SiZr5-1Cu, (b) SiZr5-3Cu, (c) SiZr5-6Cu and (d) SiZr5-12Cu catalysts.

Concerning the total superficial acidity of the studied catalysts, as determined by NH_3-TPD, the values (table 1) are always higher than that of the support, pointing to Cu^{2+} ions being responsible for this enhancement of the total acidity, due to its high tendency to form amino complexes. This has been confirmed by pyridine adsorption coupled with IR spectroscopy, where an almost exclusive sharp band at 1445 cm^{-1} typical of pyridine coordinated to Lewis acid centres such as Cu^{2+}, was observed in the IR spectra. The highest acidity was attained with the SiZr5-6Cu catalyst (708 $\mu mol\,NH_3\,g^{-1}$), in spite of the higher copper content of the SiZr5-12Cu catalyst. This points to a low dispersion of the CuO species in this latter catalyst owing to the formation of larger crystallites with a low external area and which can also block the access of NH_3 molecules to the porous network.

On the other hand, the temperature-programmed desorption curves of adsorbed NO (NO-TPD) on the studied catalysts (figure 3) only show NO as the main desorption product, although traces of N_2O (1–2 ppm) were also observed. However, other catalytic systems such as copper supported on mordenite show the desorption of NO and O_2 at high temperatures, as a consequence of the decomposition of adsorbed NO_3^- and NO_2^- species [33]. Moreover, for copper-ion-exchanged ZSM-5, N_2O desorption at low temperature is detected [34]. In our case, the NO desorption curves exhibit a peak centered at 150 °C together with a shoulder at higher temperature (figure 3). In general, when the copper content increases, the intensity of the desorption peak also increases or a wider desorption temperature range is observed. However, the NO-TPD

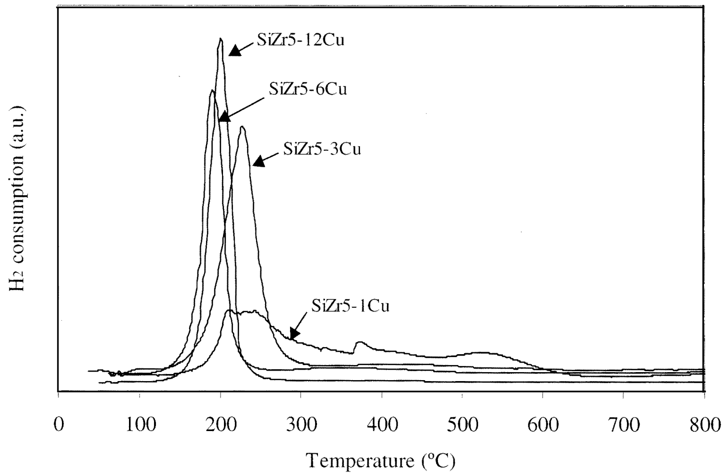

Figure 2. H_2-TPR curves of copper-oxide-supported zirconium-doped mesoporous silica catalysts.

curves for the catalysts with the highest copper content (6 and 12 wt%) are very similar and exhibit maximum NO uptake capacity. This result reveals that in the catalyst with 6 wt% Cu the maximum dispersion seems to be attained.

This family of catalysts, before and after the catalytic test, was studied by XPS. Moreover, the SiZr5-3Cu and SiZr5-12Cu samples were also studied after impregnation with copper nitrate solution, but before calcination. Such samples were labeled as SiZr5-3Cuimp and SiZr5-12Cuimp, respectively. The core level Cu 2p signal of the SiZr5-3Cuimp sample exhibited an asymmetric Cu $2p_{3/2}$ signal that can be deconvoluted into two peaks at 933.1 eV (23%) and 935.5 eV (77%). According to Grünert *et al.* [28], the former and weaker peak could be assigned to the presence of Cu^+ or more correctly to the presence of $Cu^{2+}O^-$ species, *i.e.*, Cu^{2+} ions neutralizing the exchange sites of HO-Zr groups which exist on the surface of the support [35]. The peak at the higher binding energy is assigned to Cu^{2+} associated to nitrate species [36]. This splitting band in the catalyst with a low copper content, and therefore with the active phase highly dispersed, cannot be attributed to a reduction effect of the X-ray flux in the ultra-high vacuum of the analysis chamber of the XPS equipment because the irradiation time was only 10 min. When the dispersion is not so high, as in the case of the SiZr5-12Cuimp sample, no splitting band was observed. Thus, the core level Cu 2p signal of the SiZr5-12Cuimp sample showed a Cu $2p_{3/2}$ peak centered at 935.5 eV, and an intense and asymmetric shake-up satellite composed of two bands at 941.7 and 945.1 eV, characteristics of $Cu(NO_3)_2$.

The Auger modified parameter, α', is generally a very useful tool to study the chemical state of elements. This parameter has been determined using

$$\alpha' = 1486.6 + \mathrm{KE}(\mathrm{Cu_{LMN}}) - \mathrm{KE}(\mathrm{Cu\,2p_{3/2}})$$

where $\mathrm{KE}(\mathrm{Cu_{LMN}})$ is the kinetic energy of the Auger electron of $\mathrm{Cu_{LMN}}$ and $\mathrm{KE}(\mathrm{Cu\,2p_{3/2}})$ the kinetic energy of the photoelectron Cu $2p_{3/2}$. The values found, 1849.9 eV for the SiZr5-12Cuimp sample and 1847.3 eV for the SiZr5-3Cuimp sample, can be assigned to Cu^{2+} and Cu^+, respectively [36]. The presence of Cu^+ in the SiZr5-3Cuimp sample confirmed that it was reduced by the X-ray flux, because more than 1 h is the irradiation

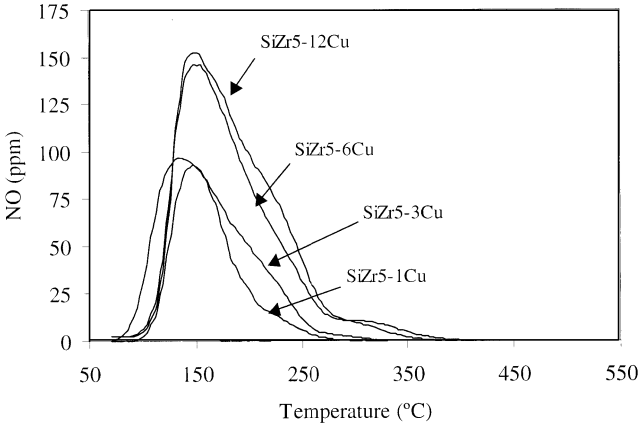

Figure 3. TPD curves of NO adsorbed on supported copper oxide on SiZr5 catalysts.

Table 2
Binding energies and Cu/Zr atomic ratios of the studied copper-oxide-based catalysts, as determined by XPS

Sample	Cu $2p_{3/2}$ (eV)	Cu $2p_{3/2}$ shake-up satellite (eV)	Surface Cu/Zr atomic ratio
SiZr5-1Cu	933.0 (76%) 936.3 (24%)	946.6	0.074
SiZr5-1Cu spent	933.4 (73%) 936.0 (27%)	943.8	0.069
SiZr5-3Cuimp	933.1 (23%) 935.5 (77%)	943.4	0.382
SiZr5-3Cu	933.4 (70%) 935.6 (30%)	943.7	0.166
SiZr5-3Cu spent	933.1 (64%) 935.1 (36%)	943.4	0.163
SiZr5-6Cu	934.0 (73%) 936.3 (27%)	943.7	0.259
SiZr5-6Cu spent	934.6	943.4	0.275
SiZr5-12Cuimp	935.5	943.7	4.991
SiZr5-12Cu	934.5	943.7	0.180
SiZr5-12Cu spent	934.0	943.2	0.278

time necessary to obtain a clear Auger spectrum. Thus, Auger lines cannot be used in this case to study the chemical state of copper species.

After calcination at 550 °C, two peaks for Cu $2p_{3/2}$ are still observed at 933.4 and 935.6 eV in the SiZr5-3Cu catalyst. The former appears now with an enhanced intensity (70%) due to the diffusion of the other Cu^{2+} species to the inner channel or to the formation of particles of CuO, thus the Cu–O–Zr species became the most relevant ones on the external surface. The second signal at 935.6 eV (30%) is assigned to CuO species strongly interacting with the surface of the support. Similar results are observed with the SiZr5-6Cu catalyst. The Cu 2p spectra of fresh and spent SiZr5-12Cu catalyst show a Cu $2p_{3/2}$ peak centered at 934.5 and 934.0 eV, respectively, typical of Cu^{2+} in CuO. The Cu/Zr atomic ratio of this sample suffers a dramatic decrease with respect to the impregnated material, varying from 4.99 to 0.18. This behavior was general for all the catalysts (table 2) and means that during calcination, a substantial migration of Cu^{2+} deposited on the external surface to the inner channel structure of the support or the formation of large aggregates of CuO take place. This phenomenon was also observed in other Cu/zeolites systems [28,29]. After catalytic testing, the Cu/Zr atomic ratios for all the catalysts are generally maintained, as expected. In short, while on the catalyst with the highest copper loading a single species of Cu^{2+} is detected by XPS analysis, in the catalyst with the lowest loading two kinds of Cu^{2+} ions are observed, the $Cu^{2+}–O^{-}$ species being the most abundant.

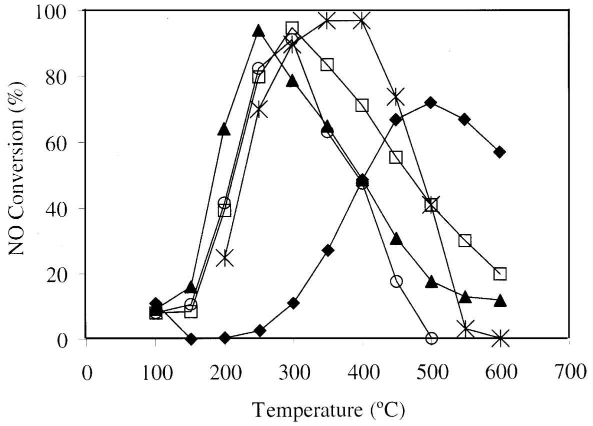

Figure 4. NO conversion as a function of the reaction temperature for SiZr5-1Cu (◆), SiZr5-3Cu (□), SiZr5-6Cu (▲), SiZr5-12Cu (○) and Eurocat (∗) catalysts. Experimental conditions: NO (1000 ppm), NH_3 (1000 ppm) and O_2 (2.5 vol%); total flow rate: 42 cm^3 min^{-1}.

3.2. *Catalytic results*

This new group of catalysts based on copper supported on zirconium-doped silica was tested in the selective catalytic reduction of NO using ammonia as a reducing agent, in the presence of an excess of oxygen, according to the reaction

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O. \qquad (1)$$

The study of the NO conversion as a function of the reaction temperature for the studied catalysts, including the reference catalyst Eurocat (figure 4), shows that the copper loading not only influences the NO conversion but also the temperature at which the conversion is maximum. The main catalytic results corresponding to this set of samples are compiled in table 3. From these data and figure 4, we deduce that the catalyst with 6 wt% Cu exhibits the maximum conversion at the

Table 3
Catalytic properties of the copper-containing mesoporous SiZr5 catalysts

Catalyst	T (°C)	NO conversion (%)	NH_3 conversion (%)	N_2 (ppm)	N_2O (ppm)	Selectivity (%)	Yield (%)	Activity (μmol NO g^{-1} s^{-1})	TOF × 10^4 (molec$_{NO}$ at$_{Cu}^{-1}$ s^{-1})
SiZr5-1Cu	300	11	29	241	0	100	11	0.04	2.26
SiZr5-3Cu	300	95	91	1000	18	98	93	0.22	4.70
SiZr5-6Cu	250	94	97	962	31	97	91	0.24	2.54
SiZr5-12Cu	300	91	90	1000	34	97	92	0.22	1.45

Note: Feed conditions: 1000 ppm NO, 1000 ppm NH_3, 2.5 vol% O_2, balance with helium; flow rate = 42 cm^3 min^{-1}; 0.150 g catalyst.

lowest temperature. The catalyst with 3 and 12 wt% of copper have similar catalytic behavior although the maxima of the conversion curves appear at a higher temperature, 300 °C. These data reveal that the maximum dispersion of the active phase was already attained with 6 wt% of Cu; in fact the turnover frequency (TOF) for this catalyst is highest at 250 °C (table 3). In general, the SiZr5-6Cu catalyst has a better performance at lower temperatures (between 200 and 400 °C), whilst the SiZr5-3Cu catalyst is better at higher temperatures (250–450 °C) with the highest TOF at 300 °C. These differences can be explained by taking into account the easy reduction of the catalyst with 6 wt% of Cu in comparison with the sample with 3 wt% of Cu (figure 2). The SiZr5-6Cu catalyst showed a thermo-reduction maximum in its H_2-TPR curve centered at 190 °C, while in the case of the SiZr5-3Cu catalyst the maximum hydrogen consumption appears to be centered at 230 °C. An easier reducibility of the copper species has the important influence of decreasing the temperature of the maximum conversion of catalysts [37]. On the other hand, the maximum activity of this catalyst was to be expected since the TPD-NO studies of the SiZr5-6Cu catalyst showed this to have the highest capacity to take up NO (figure 3). Thus, there seems to be a relationship between both the reducibility of Cu^{2+} to Cu^{+} and the ability to retain NO with the catalytic activity. This is in good agreement with the mechanism proposed for this catalytic reaction [38]. In fact, the SiZr5-1Cu sample with a broad band in its H_2-TPR curve and the maximum reduction peak at the highest temperature, *i.e.*, with Cu^{2+} strongly interacting with the support and hence difficult to reduce, together with the lower capacity to retain NO, is the less active in the SCR of NO. The observed catalytic behavior of the SiZr5-3Cu and SiZr5-6Cu catalysts in the SCR of NO is comparable with the best reported in the literature for CuO supported on high-surface-area oxides or zeolites, although this comparison should not be exhaustive because of the different experimental conditions reported in the literature [6,39–41]. In comparison with the catalyst Eurocat, our copper-based catalysts are more active at lower temperatures, although Eurocat exhibits a better performance at higher temperatures (350–400 °C). Moreover, these copper-based catalysts are very stable under experimental conditions, maintaining their activity during at least 8 h of time-on-stream. On the other hand, although the SCR of NO decays at reaction temperatures above 500 °C, their maximum activity is fully recovered when this reaction is again carried out at 200 °C.

For the most active catalysts and at temperatures ranging between 250 and 300 °C, the amount of N_2O found is almost negligible, being only of the order of 48 ppm; and only at temperatures higher than those corresponding to the maximum conversion did the formation of N_2O become more apparent, but never rising to values above 65 ppm at 400 °C (figure 5). The two reactions below, (2) and (3), are responsible for the production of N_2O, although the formation of N_2O according to reaction (3) implies the non-selective reduction of NO.

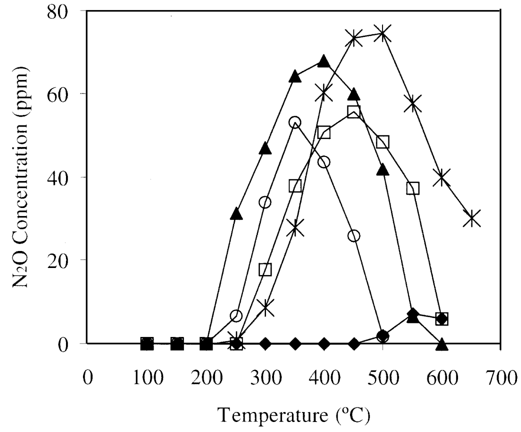

Figure 5. Formation of N_2O as a function of the reaction temperature for SiZr5-1Cu (◆), SiZr5-3Cu (□), SiZr5-6Cu (▲), SiZr5-12Cu (○) and Eurocat (✳) catalysts.

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \qquad (2)$$

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2O + 6H_2O. \qquad (3)$$

The selectivity of SCR reaction can be defined as

$$\text{selectivity}(\%) = 100[(NO)_{red} - (N_2O)]/(NO)_{red}$$

where $(NO)_{red} = (NO)_{initial} - (NO)_{final}$. The plot of selectivity as a function of the reaction temperature is shown in figure 6. At 250 °C, the selectivity is very high, being close to 100% for all the catalysts studied. Reaction temperatures higher than 300 °C produce a sharp decrease in the conversion of NO; however, the conversion of NH_3 remains more or less constant and above 80% (figure 7). Since the concomitant production of N_2 is higher than that expected on account of the stoichiometric reduction reaction of NO according to

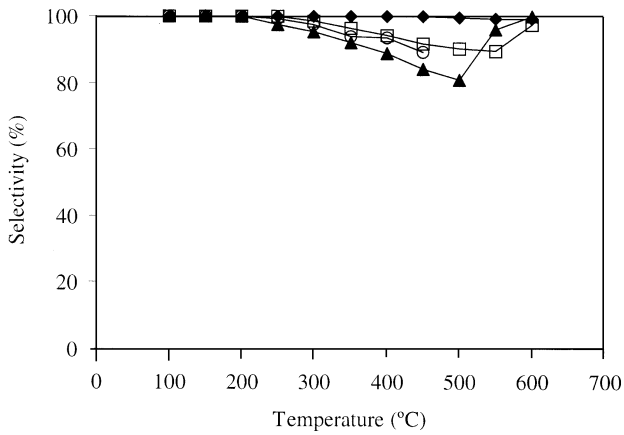

Figure 6. Variation of the selectivity (%) in the SCR reaction as a function of the reaction temperature for SiZr5-1Cu (◆), SiZr5-3Cu (□), SiZr5-6Cu (▲) and SiZr5-12Cu (○) catalysts.

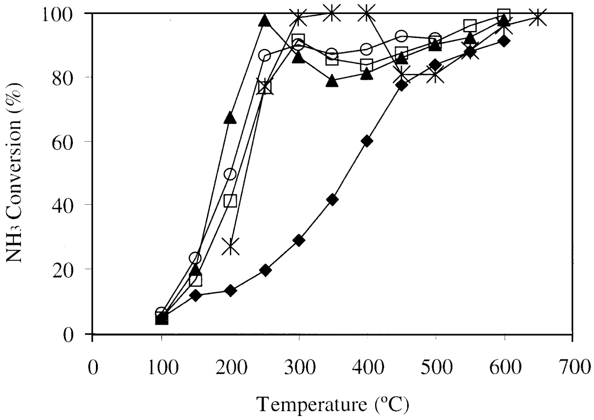

Figure 7. NH_3 conversion as a function of the reaction temperature for SiZr5-1Cu (◆), SiZr5-3Cu (□), SiZr5-6Cu (▲) and SiZr5-12Cu (○) catalysts.

reaction (1) (figure 8), it clearly indicates that the catalytic oxidation of ammonia according to the unselective reaction (4) occurs too, but only at temperatures higher than 350 °C.

$$2NH_3 + \tfrac{3}{2}O_2 \rightarrow N_2 + 3H_2O. \tag{4}$$

The influence of the space velocity on the NO conversion was studied by varying this parameter from 2000 to 12 000 h^{-1} and using one of the catalysts that shows a better performance, the SiZr5-3Cu catalyst. In figure 9, it can be observed that NO conversion is only affected for space velocities higher than 3300 h^{-1}, leading to a decrease in the NO conversion and moving the temperature of maximum conversion to higher values. At the same time, the selectivity of reaction shows a sharp decrease in contrast to the ammonia conversion which remains almost constant, indicating that the oxidation of ammonia to N_2 takes preference. The production of N_2O is very low and is almost unaffected by the space velocity, whereas the conversion of NH_3 and the selectivity to N_2 decreases in parallel with the NO conversion.

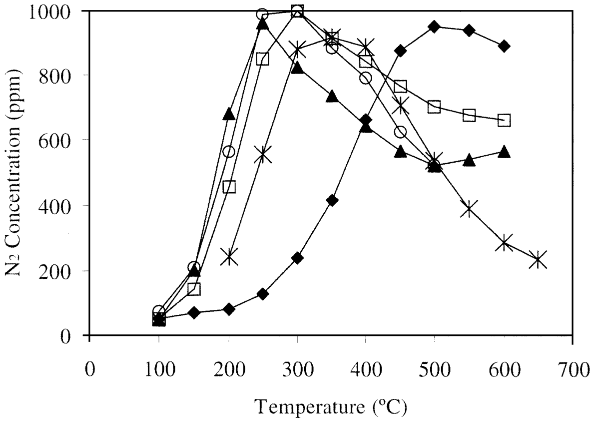

Figure 8. Formation of N_2 as a function of the reaction temperature for SiZr5-1Cu (◆), SiZr5-3Cu (□), SiZr5-6Cu (▲) and SiZr5-12Cu (○) catalysts.

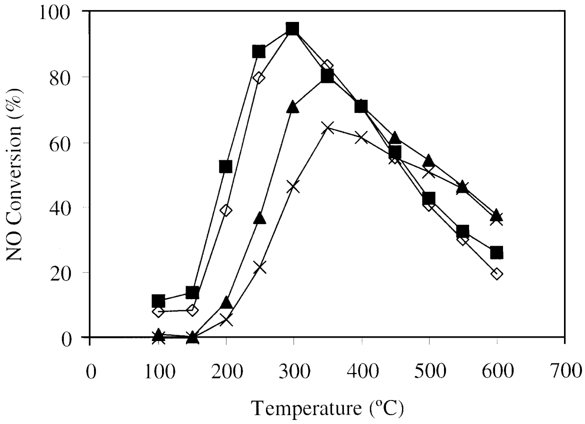

Figure 9. NO conversion at different temperatures on the supported copper oxide catalysts using different space velocities: 2124 (■), 3300 (◇), 7500 (▲) and 12012 h^{-1} ($\ast$).

Finally, the SCR of NO shows dependency on the partial pressure of ammonia when this parameter is varied between 500 and 3500 ppm. With a pressure of 500 ppm the NO conversion is only in the order of 45%, but at pressures higher than 1000 ppm conversion values are always above 92%, although the temperature of maximum conversion is shifted to higher values as the partial ammonia pressure is raised.

4. Conclusions

The family of catalysts based on copper oxide supported on a zirconium-doped mesoporous silica (Si/Zr molar ratio of 5), with copper loading of 3–6 wt%, is revealed to be very active in the SCR of NO with ammonia in excess of oxygen, with a stoichiometric NO/NH_3 ratio of 1000 ppm/1000 ppm, because they exhibit high conversion (close to 94%) at low temperatures (200–300 °C). At these temperatures, the N_2O formation is negligible but the selectivity is 100%, and as a consequence these catalysts are virtually ideal because in these conditions no slip of reactants takes place. The catalytic activity of these new catalysts seems to be related to the high dispersion of CuO attained on this support and the easy reduction of supported Cu^{2+} to Cu^{+}.

Acknowledgments

This research was performed under contract BRPR CT97 0545 of the European Union. We also wish to thank to CICYT (Spain), Project MAT97-906, for financial support.

References

[1] H. Bosh and F. Jansen, Catal. Today 2 (1988) 369.
[2] G. Busca, L. Lietti, C. Ramis and F. Beiti, Appl. Catal. B 18 (1998) 1.

[3] H. Mishima, K. Hashmoto, T. Ono and M. Anpo, Appl. Catal. B 19 (1998) 119.
[4] K.A. Bethke, M.C. Kung, B. Yang, M. Shah, D. Alt, C. Li and H.M. Kung, Catal. Today 26 (1995) 169.
[5] M. Iwamoto, H. Yahiro, Y. Mine and S. Kaguwa, Chem. Lett. (1989) 213.
[6] G. Centi and S. Perathoner, Appl. Catal. A 132 (1995) 179.
[7] D.J. Parrillo, J.P. Fortney and R.J. Gorte, J. Catal. 153 (1995) 190.
[8] D. Pietrogiacomi, D. Sannino, S. Tuti, P. Ciambelli, V. Indovina, M. Occhivzzi and F. Pepe, Appl. Catal. B 21 (1999) 141.
[9] B. Montanari, A. Vaccari, M. Gazzano, P. Käbner, M. Papp, J. Aasel, R. Dziembaj, W. Makowski and T. Lojewski, Appl. Catal. B 13 (1997) 205.
[10] G. Diaz, R. Perez-Hernandez, A. Gomez-Cortes, M. Benaissa, R. Mariscal and J.L.G. Fierro, J. Catal. 187 (1999) 1.
[11] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kesge, K.D. Schmitt, C.T.W. Chu, D.H. Olsen, E.W. Sheppard, S.B. McCullen, J.B. Higgins and J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
[12] A. Sayari, Chem. Mater. 8 (1996) 1840.
[13] A. Corma, Chem. Rev. 97 (1997) 2373.
[14] L.Y. Chen, S. Jaenicke and G.K. Chuah, Microporous Mater. 12 (1997) 323.
[15] R.T. Yang, T.J. Pinnavaia, W.B. Li and W.Z. Zhang, J. Catal. 172 (1997) 488.
[16] A. Jentys, W. Schiesser and H. Vinek, Chem. Commun. (1999) 335.
[17] W. Schiesser, H. Vinek and A. Jentys, Catal. Lett. 56 (1998) 189.
[18] S.C. Shen and S. Kawi, Catal. Today 68 (2001) 245.
[19] W. Schiesser, H. Vinek and A. Jentys. Appl. Catal. B 33 (2001) 263.
[20] A. Jiménez-López, E. Rodríguez-Castellón, P. Maireles-Torres, L. Díaz and J. Mérida-Robles, Appl. Catal. A 218 (2001) 295.
[21] J. Santamaría-González, J. Mérida-Robles, M. Alcántara-Rodriguez, P. Maireles-Torres, E. Rodríguez-Castellón and A. Jiménez-López, Catal. Lett. 64 (2000) 209.
[22] J. Santamaría-González, J. Luque-Zambrana, J. Mérida-Robles, P. Maireles-Torres, E. Rodríguez-Castellón and A. Jiménez-López, Catal. Lett. 68 (2000) 67.
[23] J.P. Chen and R.T. Yang, J. Catal. 125 (1990) 411.
[24] S. Perathoner and A. Vaccari, Clay Minerals 32 (1997) 123.
[25] D.J. Jones, J. Jiménez-Jimenez, A. Jiménez-López, P. Maireles-Torres, P. Olivera-Pastor, F. Rodríguez-Castellón and J. Rozière, Chem. Comm. (1997) 431.
[26] B. Solsona, J.M. Lopez-Nieto, M. Alcántara-Rodriguez, E. Rodríguez-Castellón and A. Jiménez-López, J. Mol. Catal. 153 (2000) 199.
[27] L.P. Haack and M. Shelef, in: Proceeding of the Symposium on Catalytic Reduction of NO, ACS Spring Meeting (Denver, March 1993).
[28] W. Grünert, N.W. Hayes, R.W. Joyner, E.S. Shepiro, M. Rafiq, H. Siddiqui and G.N. Baeva, J. Phys. Chem. 98 (1994) 10832.
[29] C.M. Millar, A. Canning, G. Rose, B. Woof, L. Trewartha and D.R. Mackinnon, J. Catal. 183 (1999) 169.
[30] P.W. Park and J.S. Ledford, Appl. Catal. B 15 (1998) 221.
[31] G. Delahay, B. Coq and L. Broussous, Appl. Catal. B 12 (1997) 49.
[32] R. Hernández-Huesca, J. Santamaría-González, P. Braos-García, P. Maireles-Torres, F. Rodríguez-Castellón and A. Jiménez-López, Appl. Catal. B 29 (2001) 1.
[33] C. Torre-Abreu, H.F. Ribeiro, C. Henriques and G. Delahay, Appl. Catal. B 14 (1997) 261.
[34] Y. Li and J.N. Armor, Appl. Catal. 76 (1991) LI.
[35] S.C. Larsen, A.W. Aylor, A.T. Bell and J.A. Reimer, J. Phys. Chem. 98 (1994) 11533.
[36] J.F. Moulder, W.F. Stickle, P.E. Sobol and K.D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, ed. J. Chastain (Perkin-Elmer, Minnesota, WI, 1992).
[37] C. Torre-Abreu, M.F. Ribeiro, C. Henriques and G. Delahay, Appl. Catal. B 12 (1997) 249.
[38] G. Ramis, Y. Li, G. Busca, M. Turco, E. Kortur and R.J. Willey, J. Catal. 157 (1995) 523.
[39] T. Iizuka, H. Ikeda and S. Okazaki, J. Chem. Soc., Faraday Trans. I 82 (1986) 61.
[40] G. Centi, C. Nigro, S. Perathoner and G. Stella, Catal. Today 17 (1993) 103.
[41] G. Centi, S. Perathoner, D. Biglino and F. Giamello, J. Catal. 151 (1995) 75.