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Catalytic behavior and nature of active sites in copper-on-zirconia catalysts for the decomposition of N_2O

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Abstract

Copper-on-zirconia catalysts prepared by a sol-gel technique were found to have an activity in the decomposition of N_2O comparable to that of Cu-ZSM-5, but a higher stability at high N_2O concentrations. Zirconia promotes the activity of supported copper species and plays a catalytic role itself, but the tetragonal crystalline form of zirconia is more effective in the promotion than the monoclinic form. Characterization of the samples by ESR, IR (CO chemisorption) and oxygen thermodesorption suggests that during dehydroxylation of zirconia at temperatures in the 400–500°C range Cu^I species form which are stable against consecutive reoxidation, when the zirconia surface is not rehydroxylated. It is suggested that the good behavior of Cu-ZrO_2 catalysts in N_2O decomposition derives from the stabilization of Cu^I species by the support. Water in the feed inhibits the surface reactivity due to the modification of the redox properties of copper ions as well as competition with N_2O for chemisorption on copper ions.

Keywords: Copper-on-zirconia catalysts; Nitrogen oxide; Zirconia

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1. Introduction

Nitrous oxide (N_2O) is an important greenhouse gas with a long life time of about 150 years [1–3]. Nitrous oxide even has 270 times the greenhouse potential of CO_2 (on a weight basis and when calculated over a 100 year time span). Furthermore, it is broken down in the stratosphere by photolysis and oxidation, starting a chain reaction leading to stratospheric ozone destruction. Due to these effects, it is estimated [2] that a reduction of about 60%–90% in present N_2O EC anthropogenic emissions is necessary. The only emissions that can be reduced in the short term seem to be emissions associated with combustion (especially of sewage sludge or industrial wastes) and chemical processes (production and use of nitric acid). Catalytic decomposition of N_2O is the preferable technology, but notwithstanding the large number of studies and metal oxides tested [[4,5] and references therein], few data have been reported with significant relevance for industrial applications [5,6]. Recently Cu-ZSM-5 was shown to have superior performances over other catalysts [5] due to, probably, the easier spontaneous reducibility of copper in this zeolite. Copper oxide supported on zirconia also shows interesting redox properties and increasing attention has been given to this catalyst in recent years [7]. Recently,

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Cu, Co and Ni catalysts supported on monoclinic zirconia were tested and an interesting behavior was found; however the data are limited [8]. In this paper the properties and characteristics of copper-on-zirconia catalysts in N_2O decomposition are compared with those of Cu-ZSM-5 to show the interesting reactivity properties of this class of catalysts.

2. Experimental

ZrO_2 samples were prepared by a sol-gel method [base catalyzed hydrolysis of Zr(O–iso-C_3H_7)$_4$ diluted in a 1:5 vol. with ethanol]. Copper was added by incipient wet impregnation using an aqueous solution of $Cu(NO_3)_2$ on the ZrO_2 calcined at 550°C (tetragonal, 79 $m^2 g^{-1}$). ZrO_2 in the monoclinic form was prepared using the same methodology, but with a different aging time. Cu-ZSM-5 was prepared from the sodium form of the parent zeolite (Eka-Nobel) by ion exchange with an aqueous solution of copper acetate. The SiO_2/Al_2O_3 ratio of the zeolite is 49 and the copper content 3.8 wt.-% as CuO [9]. Other supports used were (i) commercial samples of silica and alumina, (ii) titania, prepared by the sol-gel technique and (iii) magnesia, prepared by the decomposition of the corresponding hydroxide. Their surface areas were as follows: SiO_2, 419 $m^2 g^{-1}$; TiO_2, 49 $m^2 g^{-1}$; γ-Al_2O_3, 279 $m^2 g^{-1}$; MgO, 22 $m^2 g^{-1}$.

Catalytic tests were carried out in a fixed-bed reactor equipped with an on-line mass-quadrupole system for the analysis of products. The data reported are corrected to consider overlap in the fragmentations in the mass intensities. FTIR spectra were obtained at 2 cm^{-1} resolution with a Bruker IFS 113V spectrometer equipped with a MCT cryodetector. Self-supporting disks were used. All thermal treatments were carried out using a quartz cell connected to a vacuum line. The spectra of gas phase components have been subtracted. ESR spectra were recorded at 77 and 293 K, respectivily, on a Varian E-109 spectrometer (X-band) equipped with a dual cavity. A conventional gas manipulation ramp was used for evacuation, reduction and reoxidation treatments.

3. Results and discussion

3.1. Role of zirconia and of copper species

Reported in Fig. 1 is the comparison of the activity in N_2O decomposition of various copper supported samples containing 8 wt.-% copper oxide. The data shown in Fig. 1 clearly indicate the promotion effect of zirconia on the activity of the supported active copper component with respect to other oxide carriers. The activity of copper on tetragonal ZrO_2 compares well with that of the Cu-ZSM-5 sample, taking into account the lower copper content in the latter sample, but much greater possible dispersion.

However, while the amount of copper in ion-exchanged ZSM-5 cannot be further increased, the amount of copper deposited on zirconia can be easily increased. The activity of the catalysts obtained is not directly proportional to the copper content, but rather passes through a maximum for a copper loading of about 15% on a tetragonal ZrO_2 sample of 79 $m^2 g^{-1}$. Similarly, with constant copper content (4 wt.-% as CuO) and increasing surface area of the tetragonal ZrO_2, the activity passes through a maximum as shown in Fig. 2 which reports the rate constant of N_2O depletion at 350°C for Cu4–ZrO_2 samples using zirconia of different surface areas obtained by cal-

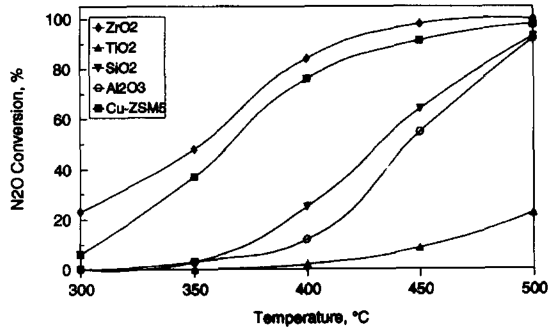

Fig. 1. Comparison of the activity in N_2O decomposition for various copper supported samples containing 8 wt.-% CuO (3.8 wt.-% in Cu-ZSM-5). Experimental conditions: 1% N_2O, GHSV 4000 h^{-1}.

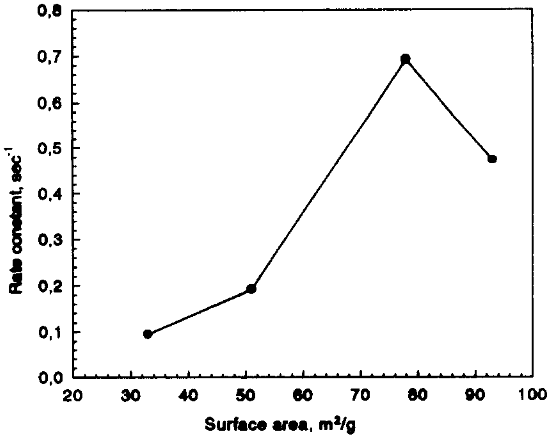

Fig. 2. Comparison of the rate constants of N_2O depletion at 350°C for Cu4–ZrO_2 samples with different surface areas of zirconia. Experimental conditions as in Fig. 1.

cination at increasing temperatures. On the basis of crystallographic parameters, it may be assumed that a $Cu^{II}O_4$ tetrahedral unit occupies an area of about 7 $Å^2$. A theoretical monolayer of copper thus corresponds to about 0.19 wt.-% CuO per m^2 g^{-1} of zirconia. For a 4 wt.-% CuO sample, the theoretical coverage is obtained for a surface area of about 20–25 m^2 g^{-1}. The data reported in Fig. 2 therefore indicate that the maximum in the specific activity per copper ion is reached for a copper loading corresponding to about one fourth of the amount required for complete monolayer coverage.

The activity of copper-on-zirconia samples in the decomposition of N_2O thus depends on the presence of copper ions on the surface, but their higher specific activity is obtained when a large fraction of the zirconia remains uncovered. This suggests a possible catalytic role of the zirconia surface itself. In agreement with this conclusion, it was observed that (i) the activity of pure ZrO_2 in the decomposition of N_2O is low, but not negligible and (ii) this activity may be significantly depressed when ZrO_2 is doped with Mg or Cr.

The crystalline form of zirconia also plays a significant role. This is shown in Fig. 3 which reports the comparison of the activity of two Cu4–ZrO_2 samples on tetragonal and monoclinic forms of zirconia. The tetragonal form of zirconia is more effective in enhancing the activity of the copper phase than the corresponding monoclinic form, even taking into account the lower surface area of the latter (59 vs. 79 m^2 g^{-1}). In fact, the specific rate constant at 400°C of N_2O depletion per m^2 of surface area in the tetragonal sample is about twice that for the monoclinic sample.

3.2. *Stability of the catalytic behavior*

The stability of the catalytic behavior depends on various factors and, in particular, on the reaction temperature and N_2O concentration. For an N_2O concentration of about 1%, reaction temperatures above about 450°C are necessary for both Cu-ZSM-5 and Cu–ZrO_2 samples to obtain a stable activity. However, a further increase in the concentration of N_2O up to 20% leads to a rapid deactivation of the activity of the Cu-ZSM-5 samples, while the activity of the Cu–ZrO_2 sample remains nearly stable (Fig. 4).

The initial activation in the first hours of time-on-stream for Cu4–ZrO_2 is paralleled by desorption of water, as clearly detected by the mass quadrupole detector. Addition of water to the feed considerably decreases the stationary activity (Fig. 5). The effect, however, depends on the reaction temperature and becomes significant for temperatures below 500°C (Fig. 5). The inhibition effect of water, furthermore, is completely reversible after the elimination of water from the feed and thermal treatment at 500°C in an helium flow for about 30 min.

These results may suggest that the initial activation observed in Fig. 4 for Cu4–ZrO_2 derives

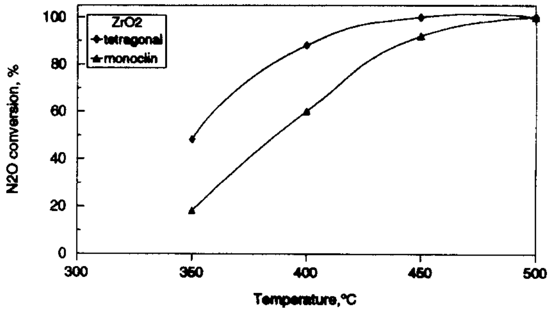

Fig. 3. Comparison of the activity in N_2O decomposition for Cu4–ZrO_2 samples with different crystalline forms of zirconia. Experimental conditions as in Fig. 1.

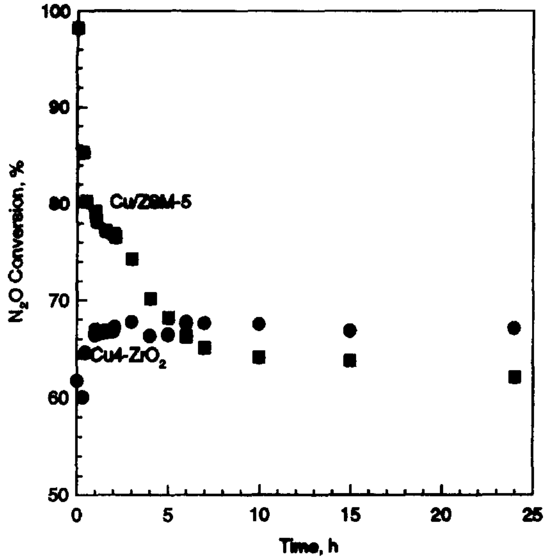

Fig. 4. Conversion of N_2O vs. time-on-stream for Cu-ZSM-5 and Cu4–ZrO_2 samples at 450°C using 20% N_2O. Other conditions as in Fig. 1.

from the initial shifting of chemisorbed H_2O by N_2O. Characterization data on the Cu–ZrO_2 catalysts, however, suggest a different possible interpretation.

3.3. Characterization of Cu–ZrO_2 catalysts

Fourier transform infrared spectra of the adsorption of carbon monoxide (CO) at room temperature onto 1 wt.-% Cu–ZrO_2 catalysts was employed to investigate which species is located at the surface of these systems in catalytic conditions. Two different situations are reported in Fig. 6; in particular, the solid-line and the broken-line spectra refer to the adsorption of 100 Torr CO onto samples that had been activated in vacuo at 773 and 473 K, respectively. Two main absorption peaks can be singled out, and the νCO allows us to distinguish between CO σ-complexes formed with coordinatively unsaturated Zr^{4+} (νCO in the 2180–2200 cm^{-1} range) and CO complexes formed with Cu^+ and due to an appreciable electron back-donation (νCO in the 2100–2130 cm^{-1} range). These latter species present different behaviors as a function of the degree of dehydration. On catalysts that have been treated at the lower temperature ($T = 473$ K) νCO lies at about 2110 cm^{-1}, whereas, at the higher temperature treatment ($T = 773$ K), νCO moves towards higher frequencies (2125 cm^{-1}).

The as-prepared Cu–ZrO_2 samples exhibit an intense EPR spectrum due to cupric ions. The spectrum actually results from the overlap of two distinct signals, the first one being unstructured and due to interacting copper species (species A), while the second one is due to isolated cupric ions with $g_{par} = 2.30$ and $A_{par} = 150$ G (species B).

Evacuation at increasing temperature, with progressive dehydration of the sample, causes a decrease in the spectral intensity which eventually ($T = 773$ K) vanishes. The trend of the spectral intensity for a 1 wt.-% CuO sample as a function of the annealing temperature is reported in Fig. 7 (solid-line data). By reoxidation of the same sample in an oxygen atmosphere at 773 K, an EPR spectrum due to cupric ions reappears, but it is different from that of the as-prepared sample, since (i) its intensity is definitely lower and (ii) the trace of two distinct isolated Cu^{2+} species is present in the spectrum (not shown, for the sake of brevity). The first one is the above-mentioned species B, while the second (new species, C) is characterized by $g_{par} = 2.24$ and $A_{par} = 155$ G, and probably originates from the migration of a fraction of the originally present copper ions during the thermal treatment in vacuum. The effect of a second run of evacuation is also reported in Fig. 7 (broken-line data). It can be easily seen that the decrease in intensity in the Cu^{2+} spectrum is lower than that observed in the case of the hydrated

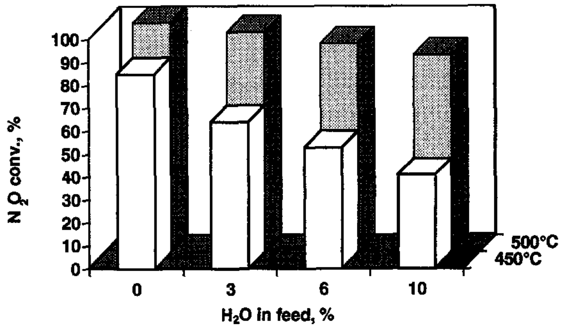

Fig. 5. Effect of water concentration in the feed on the activity of Cu8–ZrO_2 (tetragonal) in the decomposition of N_2O at 450 and 500°C. Other, experimental conditions as in Fig. 1.

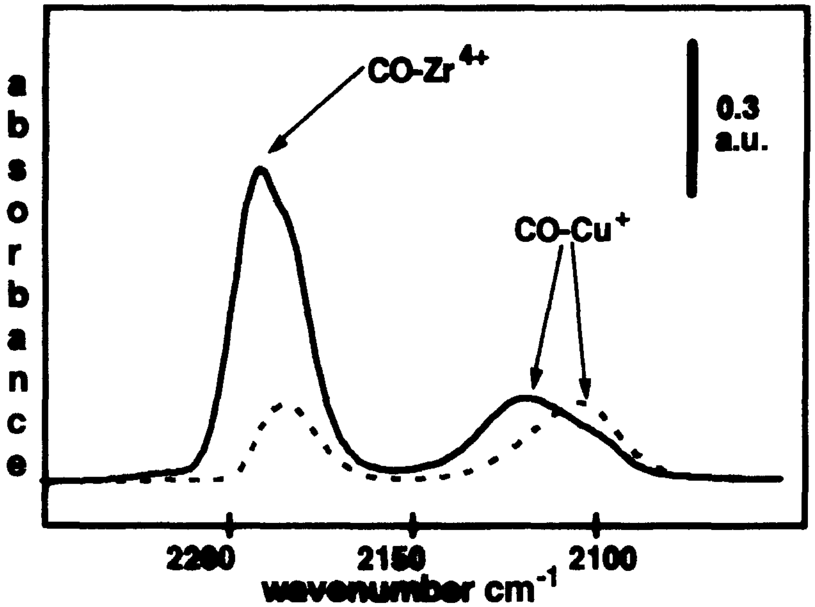

Fig. 6. FTIR spectra of CO adsorbed onto 1 wt.-% Cu–ZrO_2 activated at 473 K (broken-line spectrum) and at 773 K (solid-line spectrum).

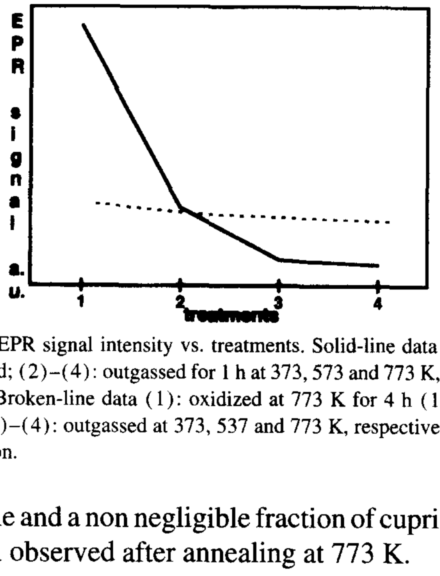

Fig. 7. EPR signal intensity vs. treatments. Solid-line data (1): as prepared; (2)–(4): outgassed for 1 h at 373, 573 and 773 K, respectively. Broken-line data (1): oxidized at 773 K for 4 h (100 Torr O_2); (2)–(4): outgassed at 373, 537 and 773 K, respectively, after oxidation.

sample and a non negligible fraction of cupric ions is still observed after annealing at 773 K.

In order to analyze further the effect of the degree of hydroxylation of zirconia on the reducibility of copper, oxygen thermodesorption experiments (O_2-TPD) were made. The results are summarized in Fig. 8. The as-prepared Cu–ZrO_2 samples desorb oxygen in a flow of helium above about 400°C due to spontaneous reduction of copper ions, in agreement with the ESR and IR results. The maximum in the oxygen desorption is found at about 500°C (Fig. 8). The total of mol O_2 desorbed per g sample (case A) are reported in the inset of Fig. 8. After the TDP run the sample was treated in a flow of oxygen at 500°C for 15 min and then cooled in an oxygen flow up to 200°C. After removal of gaseous oxygen, a second thermodesorption run was made in a flow of oxygen. The total amount of oxygen desorbed in this second case is also reported in the inset of Fig. 8 (case B). The oxygen desorbed in the second case is about 1/3 of that desorbed from the initial sample. On the contrary, if the reoxidation treatment is made in the presence of water in the feed, the initial oxygen thermodesorption behavior (case

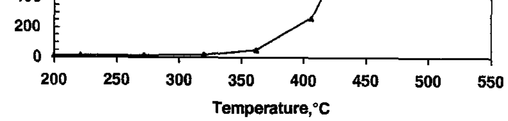

Fig. 8. Oxygen thermodesorption in a flow of helium from as-prepared Cu4–ZrO_2; temperature ramp 20°C min^{-1}. In the inset, mol oxygen desorbed per g sample from the sample as prepared (A) and after dehydroxylation at 500°C followed by oxygen treatment at the same temperature (B).

A) is obtained. O_2-TPD data thus confirm the ESR indications (Fig. 7) and indicate that the enhanced deactivation effect of water for temperatures below 500°C (Fig. 5) is probably due to a different degree of surface hydroxylation of zirconia at the two reaction temperatures with a consequent different effect on the redox and catalytic properties of supported copper ions.

In agreement with the role of hydroxyl groups of zirconia in the modification of the redox properties of supported copper ions a maximum in specific activity per copper ion for a surface coverage much below monolayer coverage (Fig. 2) and a desorption of water during the initial transient change of activity in N_2O decomposition of copper-on-zirconia samples (Fig. 4) were observed. In the latter case chemisorbed water was completely removed during pretreatment of the sample at 450°C in a helium flow and, therefore, the desorption of water must be attributed to sample dehydroxylation induced by the redox reaction between copper ions and N_2O. This transformation is accomplished by an increase in the surface reactivity (Fig. 4).

The combination of IR, ESR and O_2-TPD data thus suggests that the spontaneous reduction of copper ions at high temperature is favored by the hydroxyl groups of the zirconia forming stable Cu^+ species that are not easily reoxidized and which are characterized by a different environment as shown by the IR data (Fig. 6). O_2-TPD data suggest also that a rehydration of the surface is necessary to improve redox properties of supported copper ions, even though further studies are necessary to clarify the reasons for this effect. This suggests the hypothesis that in the absence of water in the feed, the reaction mechanism of N_2O decomposition does not involve a redox reaction at copper centers, but rather the initial reduction of Cu^{2+} to Cu^+ ions which then act as the sites for N_2O decomposition. When water is present in the feed, however, reoxidation of Cu^+ to Cu^{2+} assisted by hydroxyl groups of the zirconia occurs faster thus probably the reaction mechanism of N_2O decomposition also changes and partial inhibition of the surface reaction occurs. Water, therefore, has a more complex effect on the surface reactivity of copper-on-zirconia samples than that of only acting as a competitive adsorbent.

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