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Catalytic decomposition of N_2O over noble and transition metal containing oxides and zeolites. Role of some variables on reactivity

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Abstract

The catalytic behavior in the decomposition of N_2O of (i) Rh supported over Al_2O_3, ZSM5, TiO_2, ZrO_2 and Mg–Al oxide, (ii) Ni- and Cu-containing mixed oxides obtained from hydrotalcite-type anionic clays, and (iii) Cu/zeolites (ZSM-5 and Beta) with different characteristics is reported and some of variables which influence the activity are discussed. In particular, the following aspects of the reactivity are shown: (i) the effect of prereduction of the samples, (ii) the reversible or irreversible deactivation by O_2, NO, H_2O and SO_2, and (iii) the role of the ion-exchange method used to prepare the Cu/ZSM-5. The interesting catalytic behavior of Rh/TiO_2 and the comparison of its characteristics with those of Rh/ZSM-5 are also shown.

Keywords: Rh-supported catalysts; N_2O decomposition; Cu-zeolite; Deactivation

1. Introduction

The United Nations Framework Convention on Climate Change, signed in Rio de Janeiro in 1992, calls for the stabilization of greenhouse gas concentrations in the troposphere at a level that would prevent dangerous anthropogenic interferences [1]. As a first step towards achieving this objective, industrialized countries are required to bring their greenhouse gas emissions back to 1990 levels by the year 2000.

Nitrous oxide (N_2O), although present in relatively low concentrations in the troposphere (about 310 ppb), contributes significantly to global warming due to its 270 times higher greenhouse potential with respect to CO_2 (on a weight basis and when calculated over a 100 year time span) [1]. Furthermore it is broken down in the stratosphere by photolysis and oxidation, starting a chain reaction leading to stratospheric ozone destruction. N_2O emissions in the atmosphere derive from both natural and anthropogenic sources. Mathematical models on anthropogenic emissions of nitrous oxide indicate that in 1990, worldwide, human activities resulted in an estimated emission of 4.43 Tg N_2O-N/year with a rate of increase of about

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5–6% per year [2]. Assuming a climate goal of limiting total global warming to 0.1°C/decade during the next century and current trends in emissions of other greenhouse gases, the mathematical model indicates that worldwide anthropogenic N_2O emissions must be halved by the year 2000 [2]. Primary sources of anthropogenic N_2O emissions are, in decreasing order, cultivated soils, biomass burning, stationary and mobile combustion, and chemical production. However, the only emissions that can be reduced in the short term are those associated with combustion and chemical processes, with a reasonable goal of achieving about a 60–90% reduction by 2010 [2].

A survey of nitrous oxide emissions from combustion and industry [3] shows that two main areas of applications may be considered as real N_2O issues: (i) fluidized bed combustion especially of sewage-sludge or industrial wastes and (ii) chemical processes associated with the production and use of nitric acid. The two areas of application differ especially in composition (N_2O concentration, presence of deactivating agents), temperature and volumes of off-gas to be treated. N_2O emissions from mobile engines are also significant, especially in lean burn conditions and when using aged catalytic converters [3], but their treatment requires a modification of existing catalytic converters more than the development of a new cleanup technology as in the case of stationary sources.

Catalytic decomposition of N_2O is the preferable technology for stationary sources, because this method avoids the necessity of the addition of other chemicals. Various catalysts have been reported in the literature ([4–12] and references therein), but few of them were tested in conditions relevant for practical applications or that allow a good comparison with other literature data. For example, Ni-containing hydrotalcites [7] were claimed to have a superior activity to Cu/, Co/ and Rh/ZSM5, catalysts reported in a preceding paper as the most active [4]. Tests, however, were carried out only in a discontinuous reactor [7] without data on the stability of the catalyst in flow reactor conditions. Cu/ZSM5 was shown to have a rather stable activity using a N_2O concentration of about 0.1% v/v, but this catalyst deactivates rapidly when higher N_2O concentrations are used (about 30% v/v) [12]. There is thus a need for further studies on the development of catalysts for N_2O decomposition, especially (i) to select new classes of active samples, (ii) to understand the key factors responsible for their activity and stability towards possible deactivating agents (O_2, NO, H_2O, SO_2) and (iii) to tailor the behavior for optimum catalytic activity in the two areas of application indicated above. The objective of the present study was to contribute to a better understanding of the above topics by addressing some of the variables in the preparation and catalytic tests which influence the reactivity of three classes of catalysts selected from those reported in the literature as the more active (noble-metal based catalysts, catalysts from hydrotalcite-type precursors, and Cu/zeolite catalysts).

2. Experimental

Rh-based samples were prepared by incipient wet impregnation using an aqueous solution of $RhCl_3$. After impregnation, the samples were dried at 110°C overnight and calcined up to 600°C. The final rhodium content is 4 wt%. The oxide supports used were (i) commercial alumina (Rhône–Poulenc) or ZSM-5 (Eka Nobel; $SiO_2/Al_2O_3 = 49$; acid form), (ii) prepared by the sol–gel technique (titania, zirconia) and (iii) prepared by coprecipitation of nitrate salts (hydrotalcite-type precursor thermally decomposed at 650°C to form a Mg–Al mixed oxide). Further details on the preparation by the sol–gel method [13] and of the hydrotalcite-type precursor [14] have been reported elsewhere. The titania sample contains 10% alumina in order to increase its resistance to thermal sintering [13]. The surface areas of the oxide phases are as follows: TiO_2 (anatase phase, contains 10% wt alumina), 83 m^2/g; γ-Al_2O_3, 110 m^2/g; ZrO_2 (tetragonal phase), 79 m^2/g; Mg–Al oxide (spinel-type phase), 96 m^2/g.

Ni- and Cu-containing mixed oxides obtained from hydrotalcite-type precursors were synthesized by coprecipitation from nitrate salts and then calcined at 650°C (14 h). A complete characterization of the nickel samples and details on the method of preparation have been reported previously [14,15]. The following samples were prepared for the catalytic tests (indicated in brackets is the code used hereinafter in the text): Ni/Al = 71:29 [Ni–HT], Cu/Ni/Al = 33:33:34 [Cu–Ni–HT], Cu/Mg/Al = 10:61:29 [Cu–HT] and Mg–Al spinel-type mixed oxide further impregnated with 10% wt CuO followed by recalcination [HT impr. Cu].

Ion exchange with an aqueous solution of copper acetate was used to prepare Cu/zeolite samples from the sodium form of the parent zeolite (Z1: a commercial ZSM-5 from Eka-Nobel with $SiO_2/Al_2O_3 = 49$; Z2: a ZSM-5 zeolite synthesized hydrothermally with conventional methods and having $SiO_2/Al_2O_3 = 90$; B1: a Beta zeolite synthesized hydrothermally with conventional methods and having $SiO_2/Al_2O_3 = 30$). The ion-exchange was made at room temperature (Cu/Z1, Cu/Z2b and Cu/B1) or at 50°C (Cu/Z2a). After impregnation, the samples were recalcined up to 550°C in a flow of air (the temperature was increased at a rate of 50°C/h).

Catalytic tests were carried out in a quartz fixed-bed reactor equipped with an on-line mass-quadrupole system for the continuous analysis of the feed and of reaction products. Results are corrected to consider overlap in the fragmentations in the mass intensities. Tests were made using 0.1–1 g of catalyst in the form of particles with diameters in the 0.1–0.2 mm range and a space velocity of 1800 h^{-1}. The uniform axial temperature profile of the catalytic bed was monitored using a thermocouple. The standard feed composition used for the tests, if not otherwise indicated, was 1% N_2O in helium.

3. Results and discussion

3.1. Noble-metal based catalysts

Preliminary tests using Rh, Pd and Pt supported on alumina indicate a considerably higher activity of the Rh-based catalysts, in agreement with the results of Li and Armor [4]. Further experiments were thus made using only Rh as the active noble metal.

Reported in Fig. 1 is the comparison of the activity of samples of Rh/ZSM-5 and Rh supported over TiO_2, ZrO_2, Al_2O_3 and Mg–Al oxide. The change in the nature of the support influences the light-off temperature which shifts from about 300°C for the more active samples (Rh/ZSM-5 and Rh/TiO_2) to around 380–400°C for the less active sample (Rh/ZrO_2). However, notwithstanding the considerable change in the surface properties of the support, the change in the reactivity of the various samples is relatively limited. It is interesting to note that the change from 10 to 90% of N_2O conversion occurs in a temperature range of about 80°C in the more active samples and significantly broadens (up to 150°C) progressively with the decrease in activity. This broadening indicates that not only the number of active sites changes, but also that the apparent activation energy decreases. This suggests that the support

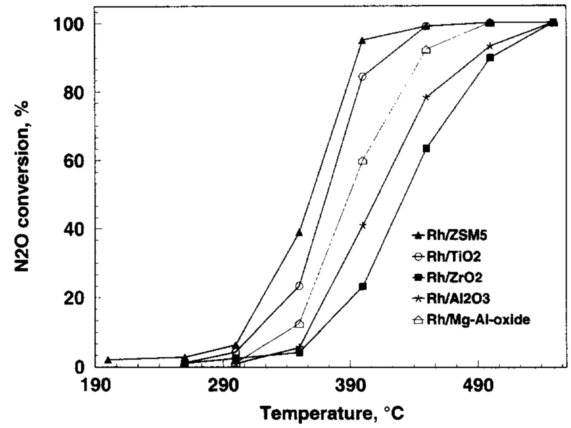

Fig. 1. Comparison of the activity in N_2O decomposition of Rh-based catalysts.

may influence not only the dispersion of Rh, but also the specific activity of the ions. It may be useful to note, however, that Rh in these catalysts is not present in the metallic form and thus the analysis of its dispersion by chemisorption methods does not give reliable information.

The activity of Rh/ZSM-5 in the decomposition of N_2O has also been reported also by Li and Armor [4] who found that complete conversion may be reached at reaction temperatures about 50°C lower than those indicated in Fig. 1. Their tests were made using a feed with a N_2O concentration one order of magnitude lower than the tests reported in Fig. 1, while higher concentrations are more representative of the application to emissions from chemical productions. Riley and Richmond [6] also noted that tests using very dilute N_2O concentration may give different results. Over Cu/ZrO_2 [12] the apparent reaction order is about zero for N_2O concentrations higher than about 1% due to saturation of the active sites. Therefore, the conversion decreases with increasing concentration of N_2O. The shift in the activity curve of Rh/ZSM-5 (Fig. 1) with respect to data reported by Li and Armor [4] probably derives from the higher concentration of N_2O used in the present tests, as well as from possible differences in the samples.

A second observation which derives from the results reported in Fig. 1 is that the activity of Rh/ZSM-5 is not unique as reported earlier [4], but rather comparable results may be obtained using Rh/TiO_2. The activity of the latter, furthermore, may be considerably promoted by a prereduction treatment (flow of 20% H_2 in He at 500°C for 30 min) differently from Rh/ZSM-5. The results of the effect of prereduction are shown in Fig. 2. After the prereduction treatment followed by cooling down from 500°C to 350°C, the feed containing 1% N_2O in He was sent to the reactor and the change in the conversion of N_2O was monitored as a function of time on stream. As a consequence of the prereduction, the initial activity of Rh/ZSM-5 and Rh/TiO_2 is complete, but progressively decreases due to the reoxidation by N_2O. After about 30 min, a stable activity is found (Fig. 2). However, while the activity of Rh/TiO_2 remains high (about 80% with respect to about 20% before prereduction), the activity of Rh/ZSM-5 returns approximately to the initial value (around 40%). A prereduction treatment may thus have a considerable influence on the activity, but different catalysts may have different sensitivities to this effect. The enhanced reactivity of Rh/TiO_2, however, is not a unique characteristic of this sample. Analogous behavior was also observed for Rh supported over Mg–Al oxide (Fig. 2).

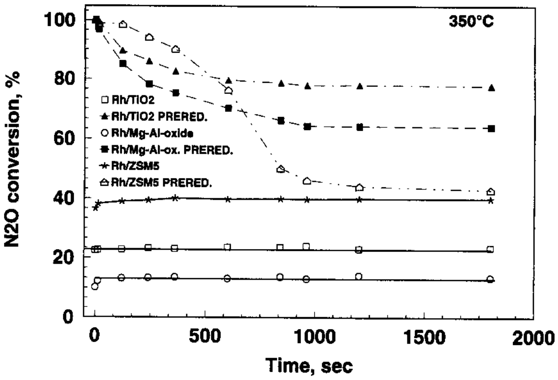

Fig. 2. N_2O conversion at 350°C as a function of time-on-stream after a pretreatment with 20% H_2 (500°C, 30 min).

Although present data do not allow us to clarify the reasons of the promotion effect of the pretreatment on the activity of Rh when deposited on some specific oxide supports, some hypotheses may be advanced. Dann et al. [16] comparing their catalytic results in the decomposition of N_2O with those of other authors [4,17] using also a $Rh–Al_2O_3$ catalyst, observed a considerable role of a pretreatment with H_2 on the activity of the sample. They observed that rhodium is present as Rh_2O_3 particles after calcination and during N_2O decomposition, but the treatment with H_2 reduces oxidized rhodium to metallic Rh [18]. It is also known that the dimension of Rh particles formed upon reduction may be significantly affected from the presence of transition metal oxides [19] and that Rh particles are reoxidized to Rh_2O_3 by N_2O [17].

In our case, the pretreatment with H_2 reduces Rh_2O_3 particles to metallic Rh, but TiO_2 or Mg–Al oxide promote the formation of smaller Rh particles. After reoxidation in mild conditions using N_2O, the dimension of Rh_2O_3 particles may remain smaller than the initial value after calcination with a promotion of catalytic behavior in the decomposition of N_2O. Instead, when the support do not promotes the dispersion of Rh upon reduction, the initial behavior returns to the value after the transient higher activity due to the reoxidation of metallic Rh by N_2O. Further data, however, are necessary to demonstrate this hypothesis.

Another difference in the behavior of Rh/ZSM-5 and Rh/TiO_2 was found regarding the formation of NO at high temperatures (above 500°C). In both cases the amount of NO formed is significantly lower than that reported for other catalysts (for example, values higher than 100 ppm were reported for Co–MgO [6]), but negligible amounts have been found for Rh/ZSM-5 and amounts of about 20–30 ppm were found for Rh/TiO_2.

Differences in the sensitivity of Rh/ZSM-5 and Rh/TiO_2 to various other possible gaseous components of real emissions were also noted. The results are summarized in Fig. 3, which reports in the upper part the change in conversion of N_2O at 400°C over Rh/ZSM-5 in a sequence of experiments using feed containing (or not) O_2, NO, H_2O and SO_2. The same type of experiments over Rh/TiO_2 are shown in the lower part of Fig. 3.

The following observations can be made: (i) O_2 and NO decrease the activity in a comparable manner and with an analogous effect on both catalysts; (ii) in the presence of NO the formation of NO_2 is also detected; its amount in Rh/ZSM-5 is about twice that in Rh/TiO_2; (iii) the presence of water in the feed also depresses the activity, although less than O_2 and NO; (iv) after removal of O_2, NO and H_2O from the gas phase, the activity returns to the initial value in about 30 min for both catalysts; these gaseous components have thus only a reversible effect, due to competitive chemisorption, but do not irreversibly deactivate the catalyst; (v) SO_2 has a strong deactivation effect on Rh/ZSM-5; treatment with H_2 at 500°C (upper Fig. 3) in order to reduce possible sulphate species does not lead to a regeneration of the activity; and (vi) SO_2 also irreversibly depresses the activity of Rh/TiO_2, but with a slower rate than for Rh/ZSM-5; the activity is also partially regenerable after switching-off the SO_2 from the feed.

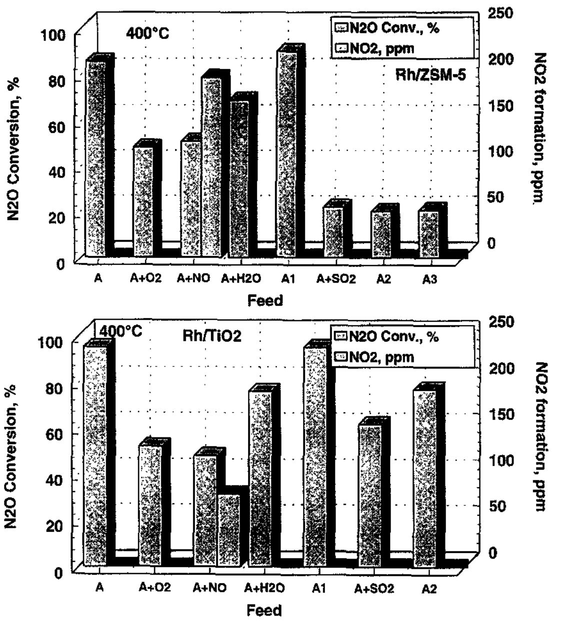

Fig. 3. Effect of gaseous additives on the conversion of N_2O at 400°C over Rh/ZSM-5 (upper) and prereduced Rh/TiO_2 (lower). Sequence of experiments from left to right. Feed: A 0.6% N_2O in helium; A+O_2: A and 0.7% O_2; A+NO: A and 0.6% NO; A+H_2O: A and 1% H_2O; A1: as A; A+SO_2: A and 0.3% SO_2; A2: as A; A3: as A, but after reduction with H_2 at 500°C for 30 min.

The difference in the rate of deactivation at 400°C by SO_2 of Rh/ZSM-5 and Rh/TiO_2 is reported in Fig. 4. The data clearly show that the latter catalyst has an enhanced resistance to deactivation by SO_2, even though on a timescale too short for applications. It should be noted, however, that the tests of Fig. 4 were made using a much higher SO_2 concentration than that actually present in typical cases of possible applications. They must therefore be

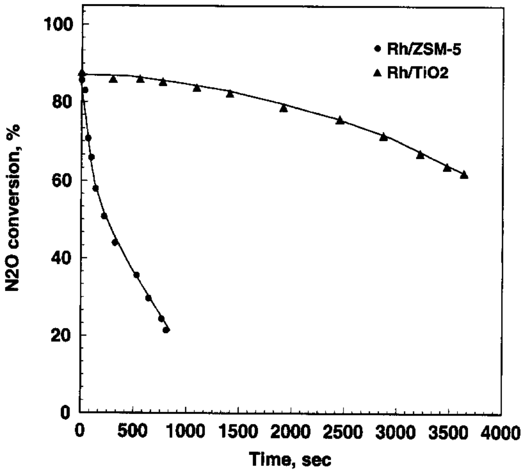

Fig. 4. Change in conversion of N_2O at 400°C as a function of time-on-stream for Rh/ZSM-5 and Rh/TiO_2 in the presence of 3000 ppm SO_2.

considered as accelerated tests of resistance to deactivation by SO_2.

Deactivation effect of SO_2 on the activity of Rh-supported samples may be interpreted by analogy with the effect of SO_2 on the activity in nitrogen oxides conversion of Cu- and V-based catalysts. For the latter samples, it is known that the deactivation must be attributed to the oxidation of SO_2 to SO_3 and the formation of relatively stable sulphate species [20]. However, in comparison with alumina, titania promotes the resistance to deactivation by SO_2 due to the formation of less thermally stable sulphate species and thus a consequent lower rate of accumulation on the surface of sulphate species around the active centers [20,21]. SO_3 readily reacts with Brønsted sites associated with Al ions in ZSM5 or on alumina surface to form stable sulphate, but the rate of SO_2 to SO_3 oxidation depends on the oxygen concentration and the catalytic effect of transition metal. The first factor, in absence of O_2 in the feed, depends on the conversion of N_2O and for this reason Dann et al. [16] found that apparently SO_2 has not deactivation effect on the activity of Rh–Al_2O_3 at low reaction temperatures where N_2O conversion is rather low. At high N_2O conversion, however, the deactivation effect depends on both the thermal stability of sulphate species and the temperature of reaction. Above 500°C Al–sulphate species tend to decompose, but at lower temperatures (400°C as in Fig. 4), Al–sulphate species are rather stable, whereas Ti–sulphate species have a low, but not negligible rate of decomposition. For this reason in the tests of Fig. 4 Rh-ZSM5 show a rapid rate of deactivation and Rh–TiO_2 a much lower rate of deactivation. In agreement with above discussion, the rate of deactivation by SO_2 may be considerably further reduced working at higher temperature (500°C) and using a lower SO_2 concentration in the feed.

3.2. Catalysts from hydrotalcite-type precursors

The activity of some mixed oxides containing Ni and/or Cu and derived from thermal decomposition (650°C, 16 h) of hydrotalcite-type precursors is reported in Fig. 5. Data on the characterization of the hydrotalcite-type precursor phase and on the nature of the mixed oxides obtained after the thermal decomposition have been reported previously [14,15].

Analogous catalysts obtained by thermal decomposition of Ni–Al and Cu–Al hydrotalcite samples were indicated as highly active in N_2O decomposition by Kannan and Swamy [7], but only on the basis of tests in a static, discontinu-

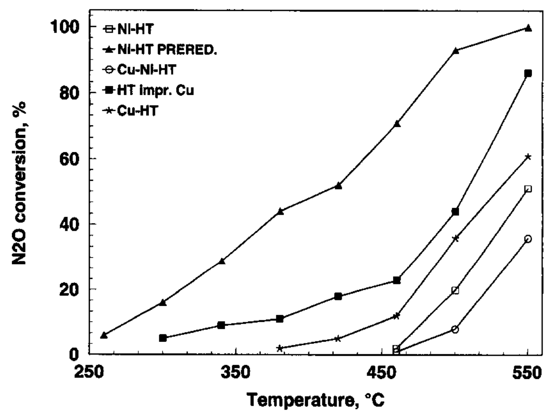

Fig. 5. Comparison of the activity in the conversion of N_2O for various Ni- and Cu-containing mixed oxides derived from hydrotalcite-type anionic clays.

ous reactor. In flow reactor conditions both Ni–HT and Cu–HT were found instead to have a very low activity, with appreciable conversion only above 500°C, especially in the former catalyst. A sample containing both Ni and Cu (Ni–Cu–HT) was found to have even worse performances, whereas the impregnation with copper of the mixed oxide obtained from the thermal decomposition of the hydrotalcite precursor (HT impr. Cu) resulted in a higher activity, even though still relatively low.

However, when the Ni–HT sample is prereduced analogously to Rh/TiO$_2$ and Rh/Mg–Al oxide and then reoxidized with N$_2$O before beginning the catalytic tests, considerably higher activity is observed (Ni–HT PRERED in Fig. 5). The temperature of 50% conversion shifts to temperatures about 150°C lower with respect to the catalyst before prereduction, indicating that the considerable increase in activity is a consequence of the prereduction treatment. The sample shows an appreciable activity also below 300°C, but complete conversion of N$_2$O may be reached only at temperatures of about 550°C. In comparison with the catalytic behavior of Rh/ZSM-5 and Rh/TiO$_2$ (Fig. 1), where the change from 10 to 90% conversion occurs in a narrow range of temperatures (about 80°C), using the Ni–HT PRERED sample a much broader temperature range is necessary (about 200°C).

Ni- and Cu-containing mixed oxides derived from hydrotalcite-type precursors thus do not have a reasonable activity in flow reactor conditions. A prereduction treatment leads to a considerable improvement in activity especially at low temperatures. However, the very broad range of temperatures necessary to obtain complete conversion means that their use is without interest.

3.3. Cu/zeolite catalysts

Reported in Fig. 6 is the comparison of the catalytic behavior of four Cu/zeolites. Samples Cu/Z1 and Cu/Z2a have an analogous copper ion-exchange level (Cu/2Al = 110), but different SiO$_2$/Al$_2$O$_3$ ratios (49 and 90, respectively). The amount of copper in the Cu/Z1 sample is thus about twice that in the Cu/Z2a sample. The Cu/Z2a and Cu/Z2b samples were instead prepared from the same parent zeolite, but making the ion-exchange at 50° and 25°C, respectively. The copper ion-exchange level in the latter is slightly lower than in the former (112 and 90, respectively). Cu/B1 was prepared instead using a zeolite with a different structure with respect to the Cu/Z series (Beta and ZSM-5, respectively). Although the level of copper exchange of Cu/B1 is lower than that of Cu/Z2a (55 and 112, respectively) the amount of copper is higher due to the higher SiO$_2$/Al$_2$O$_3$ ratio (30 and 90, respectively).

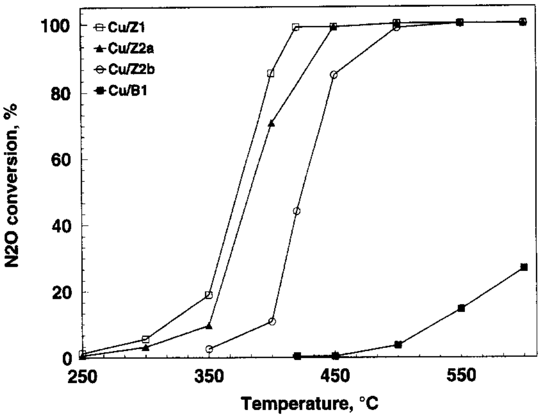

Fig. 6. Comparison of the activity in the conversion of N$_2$O of Cu-based zeolites.

The results reported in Fig. 6 show that these parameters have a considerable effect on the reactivity of the samples in the decomposition of N$_2$O. The activity of Cu/B1 is very poor, whereas the three Cu/Z samples show an appreciable activity in the 300–450°C temperature range. However, significant differences in the activity may be noted. The comparison of Cu/Z2a and Cu/Z2b (same parent zeolite, but different temperature of ion-exchange) shows that a relatively small change in this factor does not change significantly the ion-exchange level (112 and 90, respectively), but may have a considerable effect on the activity. The specific rate constant at 400°C per mole of copper is

2.4×10^3 s^{-1}(mol Cu)$^{-1}$ in Cu/Z2a and 0.34 $\times 10^3$ s^{-1}(mol Cu)$^{-1}$ in Cu/Z2b, thus about a one order of magnitude increase. In Cu/Z1 the specific rate constant at 400°C per mole of copper is 2.0×10^3 s^{-1}(mol Cu)$^{-1}$ and thus slightly lower than in CuZ2a. Both the SiO_2/Al_2O_3 ratio and the procedure of ion-exchange therefore affects the activity of Cu/ZSM-5 samples in the decomposition of N_2O. The differences may be related to the different distribution of copper species in the three samples which is a function of both the ion-exchange procedure and the Si/Al ratio. UV–Vis–NIR diffuse reflectance spectroscopy shows small, but significant differences in the distribution of the copper species between the Cu/zeolite samples, but further, more thorough studies on this problem are beyond the scope and limits of the present work. The structure of the zeolite is another factor which may influence the catalytic behavior, as shown by the very poor activity of Cu/Beta zeolite.

4. Conclusions

The comparison of the catalytic behavior of three classes of catalysts for N_2O decomposition chosen from those indicated in the literature as the more active shows that several factors may influence the reactivity. It is thus quite difficult to establish a significant order of reactivity per class of samples which may be useful for the selection of the preferable samples for a practical application. For example, it was shown in this work how small changes in the preparation of Cu/ZSM-5 may lead to considerable differences in the activity. The sensitivity of the catalysts for N_2O decomposition to other components of real emissions, such as O_2, NO, H_2O and SO_2, is another factor of clear importance for the selection. Catalytic performances in N_2O decomposition may be considerably depressed in the presence of these other components, especially at temperatures below 500°C.

The results of this work also have shown the interesting catalytic behavior of Rh/TiO_2, especially after a prereduction treatment. This catalyst is promising for future applications, but its resistance to irreversible deactivation by SO_2 must be enhanced and its sensitivity to reversible deactivation by O_2, NO and H_2O must be reduced.

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