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The catalytic activity of Cu-ZSM-5 and Cu-Y zeolites in NO decomposition: dependence on copper concentration

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NO decomposition was studied on Cu-ZSM-5 (Cu exchange extent from 23 to 210%) and Cu-Y (Cu exchange extent from 5 to 105%) catalysts at 773 K. The results show that the activity (NO molecules decomposed per gram of catalyst per second) increases by roughly 100-fold when the extent of exchange with copper in the ZSM-5 framework increases from 80 to 100%. This behaviour shows that not all Cu sites are equivalent in their decomposition activity. Cu-ZSM-5 samples prepared with either H-ZSM-5 or Na-ZSM-5 show the same activity pattern.

Keywords: NO_x abatement; Cu-ZSM-5; Cu-Y zeolite

1. Introduction

After Iwamoto and co-workers discovery (ref. [1] and references therein) of the high catalytic activity in NO decomposition of copper exchanged ZSM-5 systems, a large number of papers have been published on this topic. Valyon and Hall have recently given a comprehensive list of the aspects to be further investigated [2]. While several aspects still remain to be elucidated, two main points now appear to be widely accepted: (i) the unique role of the ZSM-5 host matrix, compared to other zeolites, in the production of highly active Cu-exchanged catalysts, and (ii) to obtain very active catalysts for the decomposition of NO, the Cu-ZSM-5 samples must be "excessively exchanged". It has been shown that the excess of Cu implies that extralattice oxygen is carried into the catalyst during the preparation of excessively exchanged samples [2,3]. These two facts have induced many scientists to focus their attention on the study of the catalytic behaviour of concentrated copper zeolites, in particular the "excessively exchanged" Cu-ZSM-5 catalyst. As a consequence, the activity of the Cu-ZSM-5 system in the lower copper concentration region and the activity of copper in zeolites other than ZSM-5, are two aspects that have received less attention.

To clarify the dependence of this activity on copper concentration, the present paper reports the catalytic activity of Cu-ZSM-5 and Cu-Y zeolites for the decomposition of NO. For this purpose, we prepared and tested a large number of Cu-ZSM-5 and Cu-Y samples with copper loading covering the full range of exchange extent, including the excessively exchanged Cu-ZSM-5 (23 to 210% for Cu-ZSM-5 and 5 to 105% for Cu-Y).

2. Experimental

2.1. CATALYST PREPARATION

The starting materials used were zeolites (i) Na-Y, obtained from Union Carbide (LZ-Y-54, lot No. 13923-55, Si/Al = 2.4), and (ii) Na-ZSM-5 and H-ZSM-5, prepared and characterised from Enichem Anic [4]. A distinctive feature of the ZSM-5 samples used in this work is their high external surface area and the limited crystal size (150 m^2 g^{-1} and 20–50 nm, respectively) [4]. The Si/Al ratios for Na-ZSM-5 and H-ZSM-5 determined in the Enichem Anic laboratories by bulk analytical methods were 14 and 17, respectively [4]. The same ratio was also measured by XPS (Leybold-Heraeus LHS-10 spectrometer) in our laboratory using the sensitivity factor method. By XRD (Philips PW 1725 diffractometer), we noted the presence of the analcime phase in the Na-ZSM-5 sample. The analcime was, however, removed by leaching with HCl 1 M during the preparation of H-ZSM-5 from Na-ZSM-5. During this process, some Al is extracted from the framework as demonstrated by the higher Si/Al ratio of H-ZSM-5. FT-IR investigations of CO adsorption at 77 K on H-ZSM-5 allow the presence of extraframework Al, as Al_2O_3 microparticles to be ruled out [4]. Slightly acidic extraframework $Al(OH)_x$ species were detected in the case of Na-ZSM-5 [4]. Before the copper ion exchange step, a few H-ZSM-5 samples were exchanged with a 0.04 M solution of $NaNO_3$. These samples therefore represent pure Na-ZSM-5 zeolites with Si/Al = 17 without the analcime phase and extraframework $Al(OH)_x$ species.

Copper was introduced into the various zeolites by the ion-exchange method. To perform ion exchange we employed dilute aqueous solutions of cupric acetate or nitrate. This ion exchange was performed either for few minutes or several hours at room temperature; the pH values of the equilibrium solution after the exchange process are reported in table 1. Samples were subsequently equilibrated at ~ 79% relative humidity over a saturated solution of NH_4Cl. The copper content of these wet samples was determined by atomic absorption (Varian SpectrAA-30) and expressed as copper weight percent (Cu wt%) on a wet basis. The Cu-zeolites are labelled in the following fashion: Cu-(H or Na)-ZSM-5 (N or A), and Cu-Y (N or A), where N and A stand for copper nitrate or acetate (respectively), followed by a figure which gives the analytical copper content (Cu wt%). Cu-ZSM-5 were prepared with Cu loading from 0.66 to 5.64 wt% (100% exchange corresponds to Cu

Table 1
Catalysts and their main features

Catalysts	Si/Al	pH[a]	Cu content (wt%)	Exchanged sites[b] (%)	*n*[c]
Cu-Y (A)	2.4	7.45	0.50	5	1.8
Cu-Y (A)	2.4	7.30	1.00	10	1.8
Cu-Y (N)	2.4		2.97	29	1.8
Cu-Y (N)	2.4	5.80	5.06	50	1.7
Cu-Y (N)	2.4	5.70	8.12	81	1.5
Cu-Y (A)	2.4	7.00	10.43	105	1.5
Cu-H-ZSM-5 (N)	17		0.66	23	
Cu-H-ZSM-5 (A)	17		0.78	28	
Cu-H-ZSM-5 (N)	17		0.92	33	
Cu-Na-ZSM-5 (A)	17	4.86	1.13	34	
Cu-H-ZSM-5 (A)	17	5.90	1.34	48	1.2
Cu-Na-ZSM-5 (A)	17	5.64	1.86	57	1.3
Cu-Na-ZSM-5 (N)	14		1.96	60	1.2
Cu-Na-ZSM-5 (N)	14		2.02	62	1.3
Cu-Na-ZSM-5 (A)	14		2.60	80	1.1
Cu-Na-ZSM-5 (A)	14		3.17	97	1.1
Cu-Na-ZSM-5 (A)	14	5.92	3.74	115	1.2
Cu-Na-ZSM-5 (A) i[d]	14		4.81	149	
Cu-Na-ZSM-5 (A) i/w[e]	14		2.75	84	1.2
Cu-H-ZSM-5 (A)	17	6.88	5.64	210	1.2

[a] pH of the solution (±0.05) at the end of Cu exchange. In the case of the Y zeolite, the initial pH of the slurry (125–167 ml H_2O per gram of zeolite) is ~ 8.2.

[b] Percentage of zeolite sites exchanged with Cu (100% corresponds to 1 Cu^{2+} per 2 Al atoms).

[c] Reaction order with respect to NO.

[d] Sample prepared by impregnation with excess of copper acetate following the method described in ref. [4] (see also experimental).

[e] Sample prepared as in (d) but washed subsequently with H_2O at RT.

wt% = 3.2 and 2.8 for Na-ZSM-5 and H-ZSM-5, respectively). For the Cu-Y zeolites, Cu loading was from 0.5 to 10.43% (100% of exchange at about Cu wt% = 10). For the various samples, table 1 reports the analytical Cu wt% and the corresponding exchange extent, expressed as 200 (Cu/Al).

In addition to the ion exchange prepared Cu-ZSM-5 catalysts, a Cu-Na-ZSM-5 sample was prepared by impregnation, employing the method adopted by d'Itri and Sachtler [5]. Specifically, the Na-ZSM-5 zeolite (2 g, corresponding to 2.07 Na mmol) was contacted with 100 ml of a copper acetate solution (1.88 Cu mmol) before drying in a Büchi rotovapor at 303 K. After 2 h in vacuo, the sample dried out and the copper content amounted to 4.81 wt%. This sample is designated as Cu-Na-ZSM-5 (A) i 4.81. A portion of the latter sample was subsequently washed with H_2O at RT to eliminate excess copper acetate and sodium acetate. After washing, the copper content was 2.75 wt% (sample designated Cu-Na-ZSM-5 (A) i/w 2.75).

2.2. ACTIVITY MEASUREMENTS

Before catalysis, all samples were given a standard pretreatment by heating in He at 823 K for 2 h. The catalytic experiments were carried out in an all-glass apparatus for flow catalytic experiments. The catalyst (0.05 to 0.2 g, powder) was placed in a silica reactor, whose temperature was controlled by a commercial device to ensure ± 1.5 K thermoregulation. The activity measurements were made at 773 K and at atmospheric pressure, using a reactant mixture consisting of 1–14% mixture NO in He. By adjusting the gas flow-rate and the mass of catalyst, N_2 conversion was limited to 20%. The same parameters were also adjusted to perform the kinetic experiments in the differential region. High purity NO (Alphgaz 99.9%), and He (Sol 99.998%) were used as such in flow experiments. The NO, N_2, O_2 and N_2O analysis was performed by a gas chromatograph (DANI 3400) connected to an integrator (Hewlett-Packard 3380) and equipped with a column composed of two concentric columns (Alltech, CTR 1): the inner one filled with Porapak Q and the outer one with molecular sieve 5A. The decomposition rates were calculated as molecules of NO converted to N_2 per gram of catalyst per second (R_g/molecules s^{-1} g^{-1}). In some cases, the turnover frequencies were also calculated, as specified below.

3. Results and discussion

In NO decomposition, over the whole range of copper concentration, it was observed that Cu-H(or Na)-ZSM-5 catalysts are active and stable with time on stream. A modest, albeit significant, decrease of catalytic activity with time on stream was observed on Cu-Y zeolites, whose activity decreases up to 20% after 2 h.

In addition to N_2 and small amounts of O_2, traces of N_2O were also observed on all catalysts. Taking into account the amount of NO consumed by oxidation with O_2 of undecomposed NO [6,7], the material balance with respect to total nitrogen atoms is almost 100%.

Fig. 1 (Cu-ZSM-5 and Cu-Y, respectively) illustrates the dependence of R_g at 773 K on the partial pressure of NO for Cu-ZSM-5 and Cu-Y at various copper loadings. Table 1 lists the order (n) with respect to the partial pressure of NO. Since n changes little within the Cu-ZSM-5 or Cu-Y catalysts as a function of the copper content ($n = 1.1$–1.3 and $n = 1.5$–1.8, respectively), a comparison of catalytic activities of the various samples gives the same activity pattern at any value of NO pressure taken in the 8–100 Torr range. The pressure dependence on both NO and O_2 and the kinetic analysis of the NO decomposition have been given by Li and Hall [7]. In the same paper, the authors show that the Arrhenius plot reaches its maximum at roughly 773 K and curves for samples at various Cu loadings are nearly parallel. Accordingly, the dependence of catalytic activity on the copper

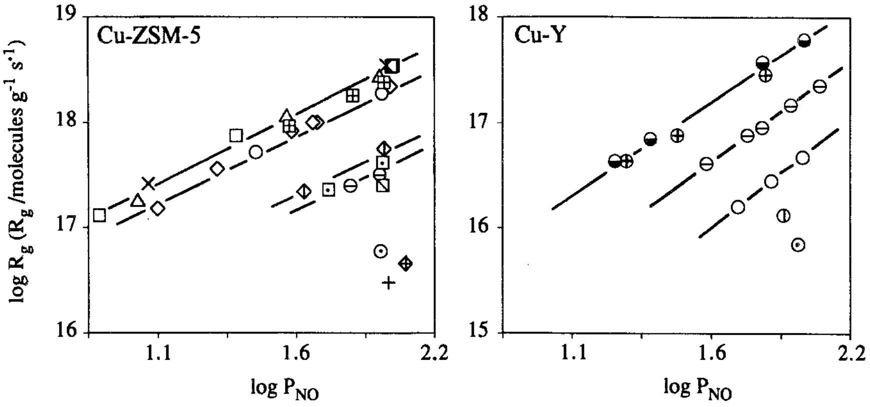

Fig. 1. The dependence of the catalytic activity at 773 K on the partial pressure of NO. A plot of log R_g (R_g/molecules of NO decomposed to N_2 per second per gram of catalyst) as a function of log P_{NO} (P_{NO}/Torr). *Cu-ZSM-5 catalysts*: (+) Cu-H-ZSM-5 (N) 0.66, (⊙) Cu-H-ZSM-5 (A) 0.78, (◈) Cu-H-ZSM-5 (N) 0.92, (⧄) Cu-Na-ZSM-5 (A) 1.13, (⟐) Cu-H-ZSM-5 (A) 1.34, (⊡) Cu-Na-ZSM-5 (A) 1.86, (○) Cu-Na-ZSM-5 (N) 1.96, (⊖) Cu-Na-ZSM-5 (N) 2.02, (⊞) Cu-Na-ZSM-5 (A) 2.60, (◇) Cu-Na-ZSM-5 (A) i/w 2.75, (□) Cu-Na-ZSM-5 (A) 3.17; (×) Cu-Na-ZSM-5 (A) 3.74, (△) Cu-H-ZSM-5 (A) 5.64. *Cu-Y catalysts*: (⊙) Cu-Y (A) 0.50, (⦶) Cu-Y (A) 1.00, (○) Cu-Y (N) 2.97, (⊖) Cu-Y (N) 5.06, (⊕) Cu-Y (N) 8.12, (◓) Cu-Y (A) 10.43.

content is examined for both Cu-ZSM-5 and Cu-Y at $P_{NO} = 100$ Torr and $T = 773$ K (fig. 2). In the whole copper concentration range, the data show that Cu-ZSM-5 zeolites are substantially more active compared to Cu-Y ones, as already found by other authors [1,7]. The dependence of the activity on the copper content is rather different with the two zeolites. A rather complex dependence is observed in the case of Cu-ZSM-5. Specifically, three activity regions can be envisaged: (i) a region below Cu wt% ≈ 2, where the activity is rather low, (ii) a region between Cu wt% ≈ 2–2.7, where the catalytic activity increases nearly 100-fold and (iii) a region above Cu wt% ≈ 3 (i.e., exchange extent $\approx 100\%$) where the activity remains almost constant. In the latter region, our result is at variance with what has been reported by other authors [7]. Specifically, a two-fold increase in the activity has been assessed by Li and Hall (table 2 in ref. [7]) on their Cu-ZSM-5 catalysts when Cu exchange extent increases from 76 to 166% (catalysts Cu-Z-24-76 and Cu-Z-26-166, respectively). Possible reasons for our failure to detect this activity increase are manyfold. Tentatively, we suggest segregation of Cu_xO_y microclusters on the external surface of our high external surface area H-ZSM-5, in the 210% exchanged Cu-H-ZSM-5 prepared at pH = 6.88. Since the Cu-ZSM-5 samples prepared with either H-ZSM-5 or Na-ZSM-5 fall on a same curve, we conclude that the acid nature of the zeolite, the presence of the analcime and extraframework $Al(OH)_x$ species have a minor role (if any) in the catalytic decomposition of NO. In the case of Cu-Y, the dependence of R_g on the copper content is relatively simpler (fig. 2). On these catalysts, for samples with copper content below Cu

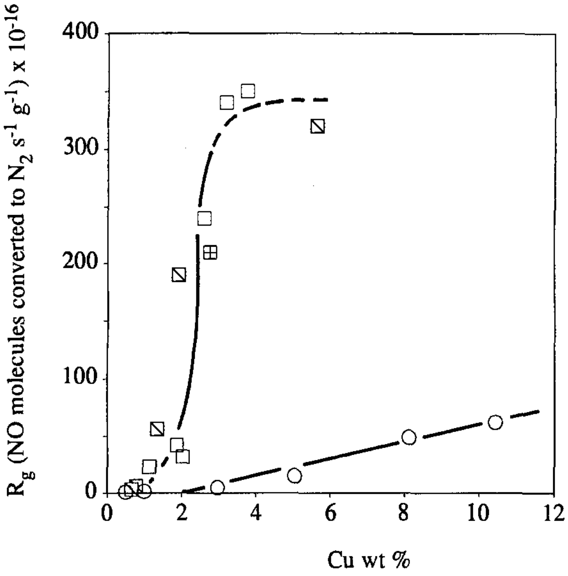

Fig. 2. The dependence of the catalytic activity on the copper content. A plot of R_g (R_g/molecules of NO decomposed to N_2 per second per gram of catalyst) as a function of the percentage of copper (wt%). R_g values are at 773 K and P_{NO} = 100 Torr. Catalysts: (○) Cu-Y, (▧) Cu-H-ZSM-5, (□) Cu-Na-ZSM-5, (⊞) Cu-Na-ZSM-5 i/w.

wt% ≈ 2, the activity is either absent or else extremely limited. When the Cu content increases up to Cu wt% ≈ 10, the activity rises linearly.

The case of Cu-Y catalysts is discussed first. The absence of catalytic activity below Cu wt% ≈ 2 can be accounted for as follows. After a thermal treatment at high temperature of low copper content ($\leqslant$2 wt%) Cu-Y zeolites, Cu^{2+} ions are preferentially located in S_I sites. Both IR and ESR (see ref. [1] and references therein) show that, ions in the S_I sites, namely Cu^{2+} ions located in the centre of hexagonal prisms of the Y-zeolite, are inaccessible to NO molecules and these Cu^{2+} ions are therefore inactive in NO decomposition. At higher copper loading, some of the Cu^{2+} also occupy the more accessible S_{II} and S_{III} sites in the supercage where NO decomposition takes place. The progressive and almost linear increase of the catalytic activity in the region from Cu wt% = 2 to about 10 shows that all Cu ions, or a constant fraction of the total Cu, are active in this region. This result suggests that active sites Cu-Y catalysts consist of mononuclear copper species. Based on the facts illustrated above, a turnover frequency for NO decomposition on Cu-Y catalysts (N_{Cu} calculated as NO molecules decomposed to N_2 per second per Cu atom) can be calculated by normalising the rates with respect to the active copper (total copper atoms minus those corresponding to Cu wt% ≈ 2, i.e. the copper ions in the S_I sites). Since, as mentioned above, only a fraction of total Cu is possibly active, the N_{Cu} values thus obtained are lower limits for the true turnover frequency. Fig. 3 shows the log N_{Cu} values for Cu-Y zeolites (Cu wt% = 2–10) as a

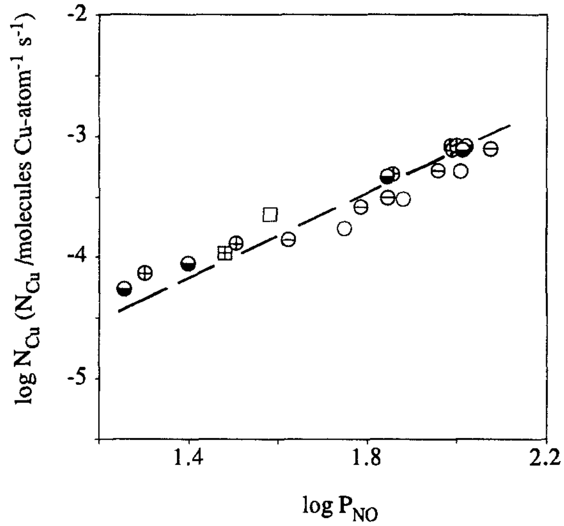

Fig. 3. The turnover frequency on Cu-Y catalysts. A plot of log N_{Cu} (N_{Cu}/molecules of NO decomposed to N_2 per second per Cu atom, the number of Cu atoms used for the calculation is specified in the text) as a function of log P_{NO}/Torr). Catalysts: (○) Cu-Y 2.97, (□) Cu-Y 2.9 calculated from ref. [8], (⊖) Cu-Y 5.06, (⊕) Cu-Y 8.12, (⊞) Cu-Y 9.9 calculated from ref. [7], and (◒) Cu-Y 10.43.

function of log P_{NO}. For the purpose of comparison, fig. 3 reports also representative data obtained previously in other laboratories with similar Cu-Y catalysts. Specifically, N_{Cu} values were calculated from the data reported by Iwamoto et al. [8] and by Li and Hall [7] where we adopted the same calculation procedure as we did with our own data (i.e., for the calculation of N_{Cu} the inactive fraction of copper was subtracted from the total Cu). Thus, at a given NO pressure, a turnover frequency value almost independent of the Cu content can be assessed for all Cu-Y samples with loading in the Cu wt% = 2–10 range. The comparison clearly shows the close agreement with data from other laboratories [7,8].

As regards Cu-ZSM-5 catalysts, the first noteworthy feature is the very sharp increase of catalytic activity observed above Cu wt% ≈ 2. This increase in the catalytic activity is almost 100-fold and it is brought about by increasing the copper loading from Cu wt% ≈ 2 to roughly 2.7; this increase enables us to calculate an upper limit for that fraction of total copper endowed with this high catalytic activity for NO decomposition. Since Na-ZSM-5 Cu wt% = 3.2 corresponds to ~ 100% exchange, the upper limit for the active fraction of copper is given by $(2.7 - 2.0)/3.2 \approx 0.2$. Because of the S-shaped curve observed when R_g-values are plotted as a function of the copper content (fig. 2), N_{Cu} values, calculated by normalising the rates with respect to the total copper, must be regarded with great caution. With this reserve, N_{Cu} values relative to some of our Cu-ZSM-5 catalysts (selected in the region of higher copper loading, as specified in the caption to fig. 4) can then be examined. For the purpose of comparison, fig. 4 also reports the data obtained on similar catalysts in other laboratories [1,7]. With one exception (vide

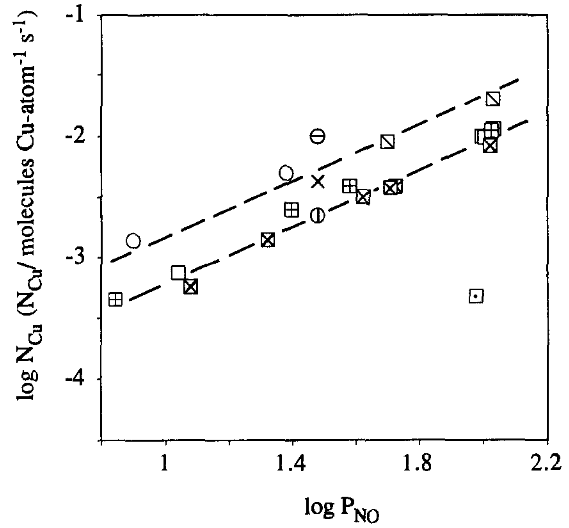

Fig. 4. The turnover frequency on Cu-ZSM-5 catalysts. A plot of log N_{Cu} (N_{Cu}/molecules of NO decomposed to N_2 per second per total Cu atoms) as a function of log P_{NO} (P_{NO}/Torr). Catalysts: (⊞) (⧅) two distinct portions of Cu-Na-ZSM-5 (A) 3.17 (0.2077 and 0.0502 g, respectively), (□) Cu-Na-ZSM-5 (A) 3.74, (⊠) Cu-Na-ZSM-5 (A) i/w 2.75, (⊡) Cu-Na-ZSM-5 (A) i 4.81, (⊖) Cu-Na-ZSM-5 (A) 3.10 (Si/Al = 14) from ref. [7], (⦶) Cu-Na-ZSM-5 (A) (76% exchange) (Si/Al = 24) from ref. [7], (○) Cu-Na-ZSM-5 (A) (Si/Al = 26) (166% exchange) from ref. [7], (×) Cu-Na-ZSM-5 (A) 1.60 (Si/Al = 26) from ref. [1].

infra), all N_{Cu} data tend to lie on two activity levels (slope $n = 1.1$, order with respect to NO) characterised by the weight of the sample employed. The upper activity level corresponds to experiments performed on small weight samples ($\leqslant 0.05$ g), whereas those close to the lower level involve experiments on larger ($\geqslant 0.15$ g) samples (in fig. 4, compare the activity of Cu-Na-ZSM-5 (A) 3.17, 0.0502 g, with that of a larger portion of the same sample, 0.2077 g). Once this mass effect has been considered, the activity level of Cu-ZSM-5 can then be satisfactorily assessed. The only experimental point indicating a much lower activity is that corresponding to the impregnated sample, Cu-Na-ZSM-5 (A) i 4.81. When the excess of copper is removed from this sample by washing with H_2O, it is, however, observed that the resulting Cu-Na-ZSM-5 (A) i/w 2.75 catalyst is as active as those prepared by the ion exchange procedure.

4. Concluding remarks

The high catalytic activity of Cu-ZSM-5 samples in NO decomposition is due to the very last fraction of the copper exchanged in the zeolite framework (20% of the total copper at most) immediately below 100% exchange. Turnover frequencies on both Cu-ZSM-5 and Cu-Y prepared in our laboratory are in fair agreement with those measured in other laboratories [1,7,8]. However, we find no evidence of any special activity on the part of "excessively exchanged" Cu-ZSM-5 samples. This aspect, therefore, deserves further investigation to assess the possible role of the ZSM-5 starting material and/or preparation method adopted to obtain the excessively exchanged Cu-ZSM-5.

The importance of the preparation method in obtaining samples that are active for the NO decomposition can be envisaged from the following fact. In a recent investigation of the selective NO catalytic reduction with propane in the presence of oxygen (SCR), d'Itri and Sachtler [5] concluded that one effective technique for preparing active Cu-ZSM-5 catalysts consists of impregnation. In the present investigation we found that a catalyst prepared according to the method given in ref. [5] is only one-tenth as active for NO decomposition as ZSM-5 catalysts ion-exchange prepared. Since different copper sites are active for SCR and NO decomposition, as also suggested by Iwamoto et al. [9], this discrepancy is not surprising. We found that, provided that the excess copper is removed by H_2O washing after impregnation (a procedure not adopted in ref. [5]), the impregnated catalyst becomes as active for NO decomposition as ZSM-5 catalysts ion-exchange prepared.

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