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Enhancement of Hydrothermal Stability of Cu-ZSM5 Catalyst for NO Decomposition[1]

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Abstract—RECu-ZSM5 samples (RE = La, Sm or Ce) have been prepared by ion-exchange of H-ZSM5 with rare earth and copper ions in an aqueous solution both simultaneously and consecutively (RE before copper), and their physico-chemical and catalytic properties in NO decomposition have been compared with those of a Cu-ZSM5 with a similar copper content. The catalysts have been characterized by N_2 adsorption at 77 K (BET) and XRD before and after aging cycles under wet (2–2.5 vol % H_2O) conditions at 450–500°C. NO decomposition tests have been carried out in a fixed bed reactor at 450°C under dry or wet conditions on both fresh and aged catalysts. NO adsorption tests have been performed at 120°C on the same samples. The addition of RE does not affect the crystalline structure, surface area, and porosity but strongly enhances the catalytic activity and the hydrothermal stability of Cu-ZSM5, which, on the contrary, is completely deactivated under wet conditions. The two-step exchanged catalysts provide better performances likely due to the larger RE exchange level obtained with this method. A unique linear correlation between the amount of N_2O produced in the NO adsorption tests, related to the reoxidation of prereduced Cu^+ sites, and the TOF, estimated from the catalytic activity tests, has been found for both fresh and aged catalysts.

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INTRODUCTION

The catalytic decomposition of NO into N_2 and O_2 would be a very effective solution for nitrogen oxide abatement since no addition of a reducing agent is required [1, 2]. The breakthrough in the investigation of NO decomposition occurred when Iwamoto et al. found that copper-exchanged zeolites, in particular Cu-ZSM5, exhibit a rather high activity for this reaction [3, 4]. Later on, it was found that Cu-ZSM5 is also very active in other reactions of nitrogen oxide abatement, such as the selective reduction to N_2 with hydrocarbons in the presence of oxygen [2, 5] and the decomposition of N_2O [6, 7].

Since then, the Cu-ZSM5 catalyst has been the object of a lot of investigations mainly aiming to characterize its properties and/or understand the reaction mechanism, as recently reviewed [2, 8]. However, the strong limitation of Cu-ZSM5 as a potential catalyst for applications in de-NO_x processes is the very poor durability in the presence of steam at high temperature. The cause of the deactivation is still debated [9–17], being its phenomenology strictly related to the operating conditions of testing (temperature, water vapor pressure, time of exposition to wet mixtures). Kharas et al. [9], through a combined XRD, EXAFS, and catalytic analysis, concluded that the deactivation observed under real conditions was not due to the degradation of the zeolitic framework but to sintering of copper ions to form CuO and Cu_2O, which grow primarily inside the zeolite, with a partial loss of micropores volume. According to the findings of Yan et al. [12], highlighted by XRD and BET measurements, a significant destruction of the zeolite framework is not detectable even for a catalyst that underwent 50% deactivation. Nevertheless, they showed that the aging of a fresh catalyst containing Cu^{2+} ions in two different coordination environments resulted in the formation of CuO particles and the exchange sites, thus vacated by Cu^{2+}, were occupied by protons with consequently easier framework dealumination of H-ZSM5 [10].

The deactivation of Cu-ZSM5 in the presence of steam was also studied through TEM/EDX, XRD, and XPS by Zhang and Flytzani-Stephanopoulos [13], who suggested a twofold mechanism: (I) the reversible hydration of copper sites; (II) the irreversible migration and aggregation of copper sites to form inactive CuO crystallites. The migration of copper ions, responsible for the weak hydrothermal stability of Cu-MFI zeolites, was also investigated via DFT calculation by Rice et al. [18] who found that the genesis of CuO clusters is thermodynamically favored by the Madelung stabilization energy characterizing the formation of the bulk oxide phase. Moreover, they also demonstrated that the driv-

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[1] The text was submitted by the authors in English.

ing force for demetalation of $Cu^{+}Z^{-}$ and $Cu^{2+}(OH)^{-}Z^{-}$ is significantly greater than that of $Co^{2+}(OH)^{-}Z^{-}$, thus explaining the better stability of Co-ZSM5 with respect to Cu-ZSM5 experimentally observed in the HC-SCR of NO [19–21]. The migration of copper ions without the destruction of the zeolite lattice upon hydrothermal treatment was also proposed by Kucherov et al. [11, 14], Iwamoto et al. [15], Quincoces et al. [16] and Gomez et al. [17].

Further studies of Cu-ZSM5 in the NO decomposition were focused to improve the catalytic performances. The addition of a second cation seems to be one of the most promising ways to increase the catalyst activity under dry conditions [22–29], but among all these studies, only a few contributions were devoted to the enhancement of the hydrothermal resistance [11, 13, 29, 30]. A possible way to stabilize Cu-ZSM5 towards the deactivating effect of water vapor at high temperatures could be the insertion of large rare-earth cations [11, 13, 29] following an approach used to improve the resistance of Ni-Y zeolites in the cracking of PE-derived waste oil [31, 32]. As a matter of fact, Masuda et al. [32] demonstrated that the presence of RE elements resulted in constant activity during regeneration and reaction cycles over Ni-Y zeolite, while MFI zeolites are almost completely deactivated due to the dealumination.

Among rare earths, the role of samarium as a promoter for Cu-ZSM5 has been deeply studied by Parvulescu et al. [25–27]. They found that Sm ions strongly enhance the catalytic activity of Cu-ZSM5 when co-exchanged in small amounts (below 0.20 wt %) with copper, increasing the T.O.F. (turnover frequency) of NO decomposition by 100% with respect to undoped CuZSM5. Their NO-DRIFT, O_2-TPD, and XPS results revealed that the presence of samarium improves the dispersion of copper ions during the ion exchange with consequent enhancement of both redox properties of Cu^{+} ions and mobility of extra-lattice oxygen whose release was proposed to be the rate-determining step in the decomposition of NO [33]. Nevertheless, the hydrothermal stability of the promoted catalyst was not investigated.

On the other hand, Zhang and Flytzani-Stephanopoulos [13, 29] first claimed that cerium prevents the migration of Cu^{2+}, which is responsible for the formation of inactive CuO clusters in the deactivated catalysts. It was also shown that cerium ions inserted in the zeolite provide a better copper dispersion, contributing to the enhancement of the catalytic performance. In agreement with these findings, the ESR results of Kucherov et al. [14] revealed that the effect of rare-earth cation as lanthanum or cerium resulted in a significant slackening of the coordination of Cu^{2+} ions after severe steam-aging treatments (20 vol % H_2O at 630°C for 17 h).

In order to improve the performances of Cu-exchanged ZSM–5 catalysts in NO decomposition, we have investigated the effect of three different rare-earth cations (Sm, Ce, and La) on ZSM5 in this work. The preparation method, the nature of rare-earth cations, the morphological features and the redox properties of copper sites before and after aging treatments were also studied in order to determine the influence of rare-earth cations on the catalytic activity and hydrothermal stability in the decomposition of NO.

EXPERIMENTAL

Preparation of Catalysts

The Cu-ZSM5 sample was prepared by ion-exchange of a commercial H-ZSM5 zeolite (Zeolyst CBU–5020, Si/Al = 25, and BET specific surface area = 400 m^2/g) in an aqueous solution at 50°C for 2 h with a 20 mM solution of copper(II) acetate monohydrate (Aldrich purity 99.8%). After ion exchange, the sample was centrifuged, washed twice with double-distilled water, and dried at 120°C overnight. Finally, the Cu-exchanged sample was calcined according to the following procedure: (a) heating under helium flow at 5 K/min up to 550°C, keeping this temperature for 2 h; (b) cooling to room temperature under He flow; (c) switching the gas flow to 1% O_2/He and heating 5 K/min up to 550°C, keeping this temperature for 4 h.

Two series of rare-earth containing Cu-ZSM5 were also prepared:

—**co-exchanged samples** were obtained by simultaneously exchanging the parent zeolite at 50°C with a solution containing both copper ($[Cu^{2+}]$ = 20 mM) and rare-earth cation with an atomic ratio of Cu/RE (RE = La, Sm, and Ce) equal to 12 as proposed by Pârvulescu et al. for Sm co-exchanged Cu-ZSM–5 catalysts [26]. Drying and calcination were performed as described above. These samples will be indicated as CuRE-Z (where Z = ZSM5 and RE = rare-earth cation);

—**two-step-exchanged samples** were obtained by first exchanging the rare-earth cation and subsequently the copper cation. The experimental conditions for the first ion exchange were chosen in order to maximize rare-earth loading according to literature data [25–28, 34–36]. More specifically, the samples containing lanthanum and samarium were exchanged at 95°C for 5 h in a 20 mM solution of the rare-earth salt, while the cerium-containing zeolite was obtained exchanging in a 8-mM solution for 3 h at 80°C. These catalysts will be indicated as RECu-Z. Lanthanum(III) nitrate hydrate (99.9%), cerium(III) nitrate hydrate (99.999%), and samarium(III) nitrate hexahydrate (99.9%), all supplied by Aldrich, were used as precursor salts for rare-earth exchange.

Catalytic Tests

A fixed-bed microreactor consisting of a 60-cm-long quartz tube (I.D. 1.0 cm), supplied with a porous disk supporting the catalyst particles (*d* = 200–

Table 1. Chemical composition, surface area, and pore volume (V_p, total; V_m, micropores) of fresh and aged samples

SAMPLE	FRESH					AGED			
	RE loading, wt %	Cu loading, wt %	BET surface area, m^2 g^{-1}	V_p, cm^3 g^{-1}	V_m, cm^3 g^{-1}	Cu loading, wt %	BET surface area, m^2 g^{-1}	V_p, cm^3 g^{-1}	V_m, cm^3 g^{-1}
Cu-Z	–	1.69	365	0.32	0.17	1.69	334	0.31	0.17
CuLa-Z	0.09	1.82	369	0.35	0.17	1.76	354	0.30	0.17
CuSm-Z	0.11	1.75	347	0.39	0.17	1.58	359	0.43	0.18
CuCe-Z	0.08	1.63	383	0.47	0.18	1.61	336	0.43	0.16
LaCu-Z	0.16	1.81	368	0.36	0.17	1.89	367	0.35	0.16
SmCu-Z	0.75	2.16	362	0.41	0.18	2.01	360	0.46	0.18
CeCu-Z	0.12	1.93	362	0.34	0.17	1.91	358	0.42	0.17

400 μm), inserted in an electrical furnace (LENTON) characterized by three heated and temperature-controlled zones, was used to perform the experiments. The temperature of the catalytic bed was measured by a Chromel-Alumel thermocouple placed in another quartz tube coaxially inside the reactor. Mass flow controllers (BROOKS 5850S) were used to control and measure the flow rates of high purity gases: 1 vol % NO/He (NO_2 impurity about 150 ppm) and pure He (99.995%). Before each experiment, the catalyst was treated under He (30 l/h) for 2 h at 550°C in order to reduce Cu^{2+} [33, 38–41]. The inlet and the outlet streams were analyzed by Hartmann and Braunn continuous analyzers specifically designed for NO, NO_2 (URAS 10 E), and O_2 (MAGNOS 6G), while the NO_2 concentration was indirectly evaluated through a NO_2 to NO catalytic converter (Hartmann and Braunn CGO-K). The standard conditions used for the activity measurements were $W/F = 0.09$ g s cm^{-3}, $T = 450°C$, and NO concentration = 5000 ppm. These conditions allowed the NO conversion to be enough low (<15% in all experiments) to assume a differential reactor behavior. Wet gas feed was obtained by saturating a helium stream at room temperature. The effect of water vapor on the catalytic activity was determined by measuring the activity under dry conditions after the two aging treatments reported below: (a) 80 min at 450°C by adding 2.0 vol % water to the reaction feed; (b) treatment (a) followed by the restoration of dry conditions and a further aging treatment under wet helium flow (2.5 vol % of water vapour) at 500°C for 15 h.

The catalytic performance is expressed as TOF (Turnover frequency = number of NO molecules converted to nitrogen per second per copper atom) in order to better compare samples with different copper contents.

Characterization Measurements

Elemental analysis of Cu, La, Sm, and Ce was performed by atomic emission spectroscopy with inductively coupled plasma atomization (ICP-AES) after drying the samples overnight at 100°C. The ion exchange level was calculated on the base of the atomic ratios of $Cu^{2+}/2Al^{3+}$ and $RE^{3+}/3Al^{3+}$, respectively, according to a procedure discussed elsewhere [37].

XRD patterns at room temperature were collected using a PW 1100 Philips XRD 6000 diffractometer with CuK_α radiation.

BET surface areas were measured by N_2 adsorption at 77 K with a Carlo Erba 1900 Sorptomatic.

In a typical NO adsorption experiment [41, 42], a 600 ppm NO/He gas mixture (20 l h^{-1}) was fed to the catalytic reactor at 120°C. The transient behavior of the system was recorded by analyzing the inlet and the outlet reactor gas composition (the concentrations of NO, N_2O, NO_2, and O_2 were continuously monitored). After each adsorption test, the reactor was purged under an He flow and then the TPD experiment was carried out by heating the reactor 9 K/min up to 550°C in flowing He.

RESULTS AND DISCUSSION

Effect of the Ion-Exchange

The chemical composition of the catalysts shows that the preparation procedure very strongly affects the amount of rare earth loaded in the samples (Table 1). However, it is worth noting that the catalysts prepared via a two-step exchange were exchanged under more favorable conditions (temperature, time of exchange, and concentration of rare earth salt in the solution) with respect to the co-exchanged samples (see experimental section). These conditions, together with the absence of copper ions in the first exchange step are probably responsible for the larger amount of rare earth loaded in the two-step-exchanged samples. Among the three rare earth cations investigated, samarium is the more easily exchanged ion, especially for the two-step preparation.

On the contrary, copper loading is only slightly dependent on the preparation procedure: all samples exhibit a copper content very similar to the unpromoted Cu-Z, which corresponds to a level of Cu exchange close to 100%, except for SmCu-Z, which contains an amount of Cu about 30% greater than CuSm-Z. The enhanced copper loading due to the large amount of samarium has been attributed by Pârvulescu et al. [26] to a better dispersion of Cu ions.

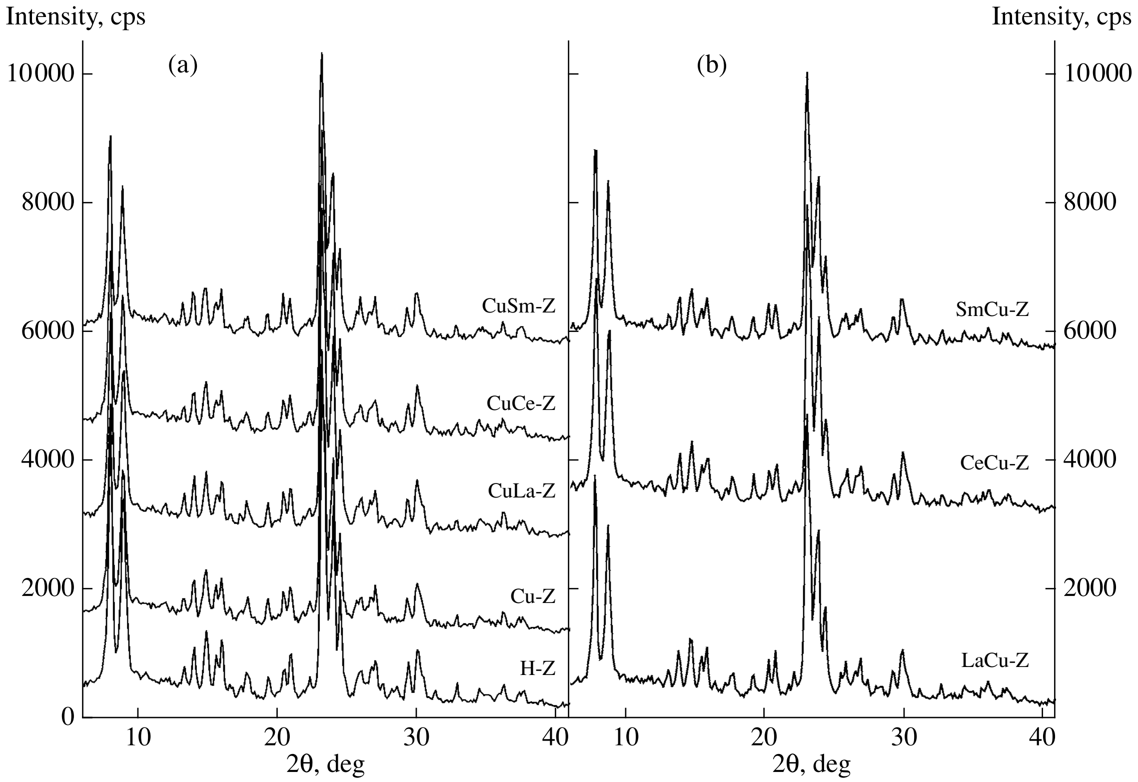

Fig. 1. XRD patterns of fresh co-exchanged (a) and two-step exchanged (b) samples in comparison with the parent H-ZSM5 zeolite.

Surface area measurements (Table 1) show that the insertion of a large rare earth cation does not result in any significant change of both specific surface area and porosity with respect to the unpromoted Cu-ZSM5. Also, the pore size distribution was almost unaffected by the presence of rare earth, which is in agreement with Parvulescu et al. [28] for Tl-promoted samples.

XRD patterns of the parent H-ZSM5 and all exchanged samples are shown in Fig. 1. In agreement with the BET textural analyses, the diffractograms reveal that all exchanged samples keep the MFI structure without appreciable loss of crystallinity with respect to the parent zeolite.

Catalytic Activity

Figure 2 reports the results of catalytic activity tests, as NO turnover frequency (TOF), evaluated for the two series of rare earth promoted Cu-ZSM5 samples compared with that of the unpromoted Cu-ZSM5.

The experiments clearly show that the samples containing rare earths show a higher activity in NO decomposition than the un-promoted Cu-ZSM5. In particular, the lanthanum two-step exchanged sample reaches a TOF of 1.23 mHz, corresponding to an increase of about 60% of intrinsic activity of copper in the unpromoted zeolite. Also samarium- and cerium-based samples are more active than the corresponding Cu-Z, although the promoting effect of the RE cation is slightly lower with respect to that of lanthanum (40 and 18%, respectively for cerium and samarium two steps exchanged samples).

As a general trend, the samples prepared via the two-step exchange procedure exhibit activity higher than that of the co-exchanged catalysts. This stronger promoting effect of rare earths for the two-step-exchanged samples could be simply related to the higher rare earth content. Nevertheless, the very close

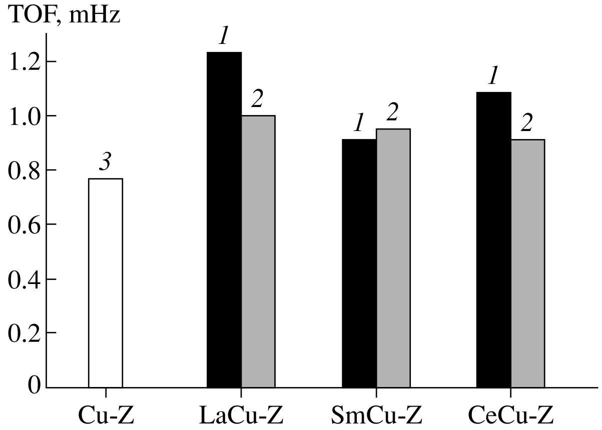

Fig. 2. NO decomposition rate (TOF) at 450°C evaluated under dry conditions for unpromoted and rare earth-promoted Cu-ZSM5. Two-step exchanged (*1*) and co-exchanged RE-containing zeolites (*2*), Cu-Z (*3*).

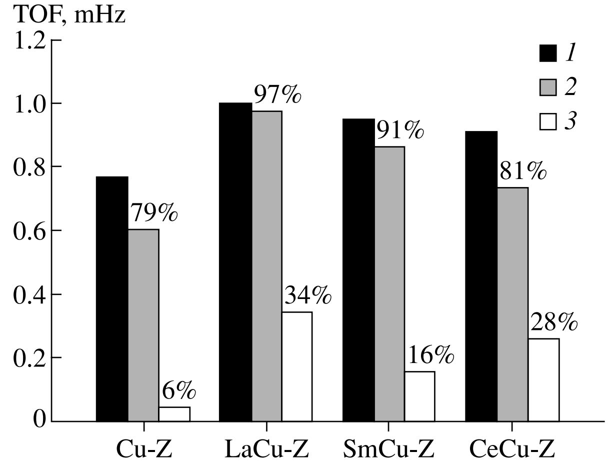

Fig. 3. Effect of the aging treatments on the TOF of NO decomposition evaluated under dry conditions at 450°C for CuRE-Z and Cu-Z samples. (Fresh sample (*1*), after 80 min under reaction mixture in the presence of 2 vol % of H_2O (*2*), after further 15 h in the presence of 2.5 vol % at 500°C (*3*). Numbers on corresponding bars represent the residual catalyst activity as percentage of that of the fresh sample).

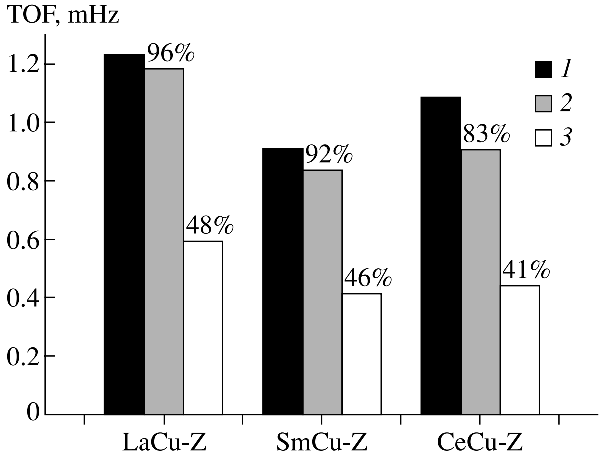

Fig. 4. Effect of the aging treatments on the TOF of NO decomposition evaluated under dry conditions at 450°C for RECu-Z samples. (Fresh sample (*1*), after 80 min under reaction mixture in the presence of 2 vol % of H_2O (*2*), after further 15 h in the presence of 2.5 vol % at 500°C (*3*). Numbers on corresponding bars represent the residual catalyst activity as percentage of that of the fresh sample).

values of TOF evaluated for the two Sm containing ZSM5, despite the very different Sm exchange level, could suggest that the promotion of the rare earth starts to decline at concentration levels that are too high, as in the case of the SmCu-Z sample.

Effect of Aging Treatments

Figures 3 and 4 report the TOF values measured under dry conditions after the two aging treatments carried out following the procedure described in the "Experimental" section. Lower values were obtained for all aged samples, indicating an irreversible partial loss of the original activity of the fresh catalysts. However, the presence of rare earth cations results in an enhancement of the hydrothermal stability of catalysts. Indeed, for Cu-Z, even the first and shorter aging treatment produces about a 20% irreversible loss of the original activity, whereas CuLa-Z and CuSm-Z retained almost the same activity measured before aging. Upon the second and more severe aging treatment, prolonged for 15 h at 500°C in the presence of water vapour (2.5 vol %), all samples were significantly deactivated. However, in this case as well, the values of TOF estimated at the end of the treatment are significantly higher for the rare earth-containing samples. The aged Cu-Z is about 20 times less active than the fresh one, while after the two aging cycles, the rare earth promoted catalysts still keep about 40–50% of the original activity. Nevertheless, unlike the findings of Zhang and Flytzani-Stephanopoulos [13, 29], the cerium-doped zeolite exhibits a lower hydrothermal stability. After the first aging treatment, the resistance of both CuCe-Z and CeCu-Z is similar to that of the undoped Cu-ZSM5, if compared on the base of percentage of residual activity of the fresh sample; however, after the second aging treatment, the Ce-containing catalysts are significantly more active than Cu-Z. This difference with Zhang and Flytzani-Stephanopoulos data can be likely attributed to the different preparation technique (ion exchange for 3 h instead of three subsequent ion exchanges) and lower rare earth content (≤1000 ppm in our samples vs. 1.7% in [13]).

The results also show that the extent of deactivation of both co-exchanged (Fig. 3) and two-step exchanged samples (Fig. 4) is quite similar. For both classes of catalysts, the first aging treatment results in a weak deactivation of samples that are much more severely affected by the second longer treatment. Moreover, the two-step exchanged zeolites show not only a better activity of fresh samples but also a higher stability to severe wet treatments (Fig. 4). The recovery of activity after the first aging treatment is almost similar for the two classes of catalysts, but a significant enhancement of catalyst stability is clearly shown by the RECu-Z samples at the end of the second aging treatment. Therefore, the preparation procedure and, above all, the higher rare earth loading promote not only a better distribution of copper and a higher activity of the catalysts but also their hydrothermal resistance. At the end of the second cycle, the following scale of stability among all catalysts investigated can be given:

LaCu-Z > SmCu-Z > CeCu-Z > CuLa-Z > CuCe-Z > CuSm-Z > Cu-Z

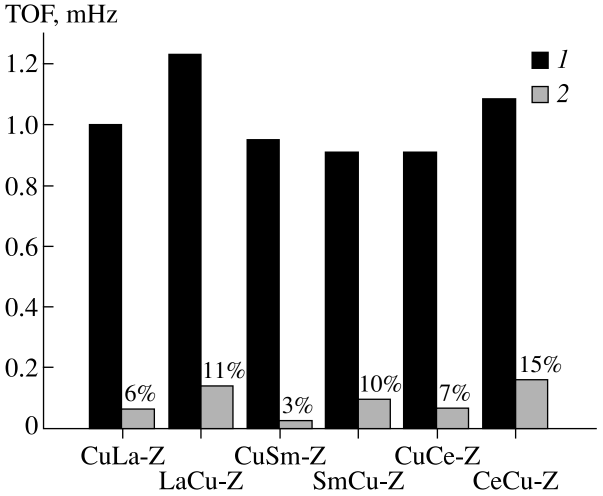

Fig. 5. TOF of NO decomposition evaluated at 450°C in the presence of water for rare earth-promoted Cu-ZSM5 (*2*) compared with those of fresh samples under dry conditions (*1*). (Numbers on corresponding bars represent the residual catalyst activity as percentage of that of the fresh sample.)

Catalyst Performance under Wet Conditions

The activity of catalysts was also measured under wet feed conditions. Cu-Z does not have any detectable activity in the presence of steam, but the samples containing rare earth metals (two-step exchanged samples) show stable residual activity, although the reduction of TOF with respect to dry conditions is quite large (Fig. 5). This dramatic reduction of activity in the decomposition of NO can be attributed either to an irreversible deactivation of catalysts, as evidenced by the subsequent tests under dry conditions (Figs. 3 and 4), or to a reversible effect of competition between water and nitric oxide for the adsorption on the same active Cu sites.

Also in the presence of water, the two-step exchanged samples were more active than coexchange catalysts, as observed under dry conditions. However, the effect of the kind of rare earth cation on the activity under wet conditions is slightly different compared to that observed for the corresponding dry tests. In fact, under the wet conditions explored, CeCu-Z is the most active catalyst.

Characterization of the Aged Samples

The deactivation of the Cu-ZSM5 and of the rare earth-containing samples upon water addition to the feed was preliminarily investigated through structural and chemical characterization. Data reported in Table 1 clearly show that the hydrothermal aging did not cause any noticeable loss of surface area or micropore occlusion. Moreover, XRD patterns of the steam-aged catalysts, shown in Fig. 6 in comparison with the corresponding fresh samples for Cu-Z and LaCu-Z, do not reveal any significant difference, neither in the range $2\theta = 35°–40°$, where the presence of segregated phases of copper oxides could be evidenced [13, 16, 43]. However, the absence of these peaks cannot exclude the formation of very small particles of copper oxides with sizes smaller than 40 Å [43].

Likewise, the results of elemental analysis of the aged samples (Table 1) indicate that the copper content remains quite unchanged with respect to the fresh samples, suggesting that no copper is washed up under wet experimental conditions.

Therefore, all these results suggest that the catalyst deactivation is not caused by the collapse of the MFI framework, as proposed by Yan et al. [12] and Iwamoto et al. [15], but could be better attributed to some modi-

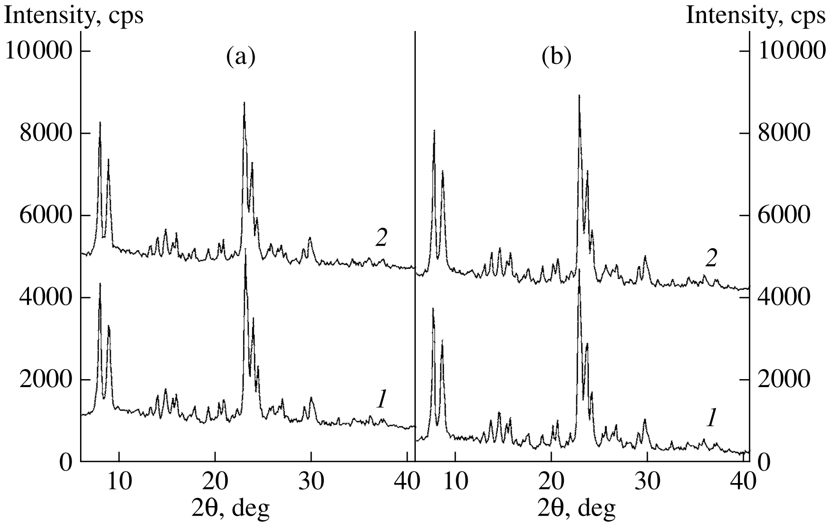

Fig. 6. XRD patterns of fresh and aged Cu-Z (a) in comparison with LaCu-Z (b).

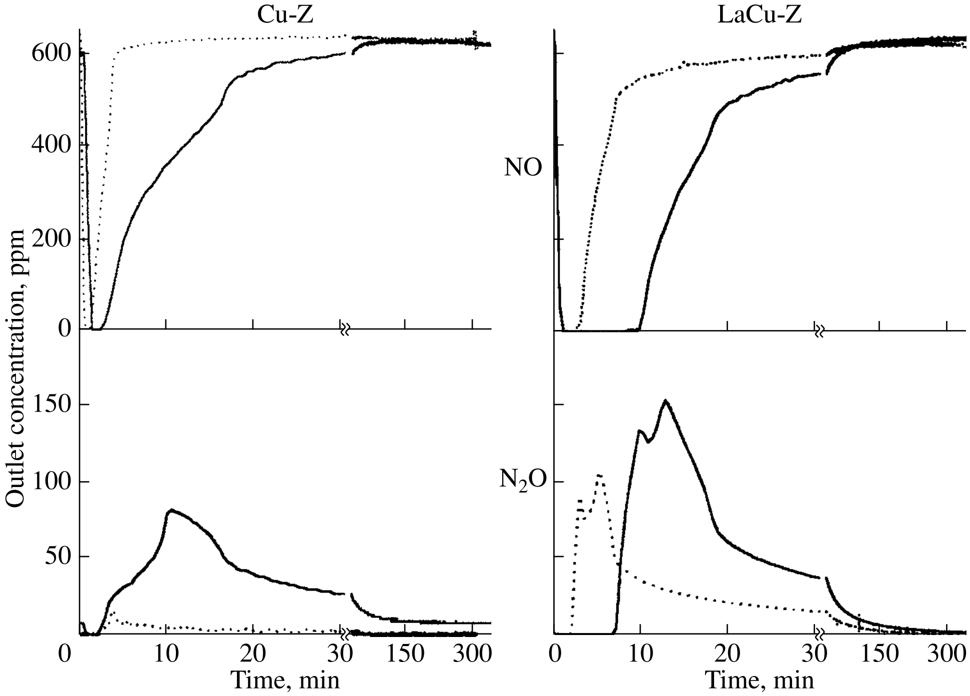

Fig. 7. NO and N_2O outlet concentrations as functions of elapsed time after the addition of NO (600 ppm) at 120°C on pre-reduced Cu-Z and LaCu-Z. (Continuous lines represent the signals of the fresh samples, dotted lines of the aged ones.)

fication of copper properties as proposed by Kucherov [14]. These modifications should be associated to the migration of active species to inactive positions and to the subsequent segregation of small CuO clusters in the zeolite channels, as already proposed by others [13, 15, 16], copper content in the catalyst being unchanged.

NO Adsorption Measurements

In previous works [41, 42], we showed that the study of the interaction between NO and over-exchanged Cu-ZSM5 at temperatures low enough to completely inhibit a steady-state activity was a very useful tool to investigate the redox chemistry of these systems. In particular, we demonstrated that NO adsorption experiments at low temperatures can be used to titrate those copper ions that are "self-reduced" at high temperature under inert flow or vacuum through the evaluation of Cu sites selectively re-oxidized by nitric oxide that are supposed to be active. The re-oxidation of Cu^+ sites at low temperatures was reported to occur via the transient formation of gaseous N_2O during NO adsorption [33, 38–41, 44–49]. In the present work, the experiments of NO adsorption on the pre-reduced catalyst were hence carried out with the aim to correlate the enhancement of the hydrothermal stability induced by rare earths with the amount of these copper sites.

NO adsorption tests on both fresh and aged catalysts were performed at 120°C after a standard reducing pretreatment in He flow (see experimental section). The results of this experiment for the unpromoted Cu-Z and the lanthanum-containing LaCu-Z samples, chosen as representative of all investigated catalysts, are reported in Fig. 7 showing the outlet reactor concentrations of NO and N_2O during the transient NO adsorption.

For all samples, a transient evolution of N_2O was observed during NO adsorption. Moreover, both the fresh and aged rare earth-containing samples show a larger NO adsorption capacity with respect to the unpromoted zeolite. Since no modification of the microporous structure occurred upon rare earth exchange and the total copper content was the same for either unpromoted and promoted catalysts, the enhancement of NO adsorption capacity should be attributed to modifications induced to copper by rare earth cations. A better distribution of copper species in the zeolite promoted by the presence of rare earth, as already suggested for other rare earth cations [26], could be responsible for this phenomenon. In addition, it should be noticed that the transient production of N_2O, associated to NO adsorption, is significantly larger for rare earth-containing zeolites than for unpromoted Cu-ZSM5, both as fresh and as aged samples, as shown in Table 2 where the amount of N_2O produced, evaluated from the integration of the area of N_2O signal, is reported for each catalysts. In a previous paper [41], we proposed that under these conditions, NO is partially reduced to N_2O leaving one oxygen atom per two reacted NO molecules on the surface. The stoichiometry of this gas-solid reaction is not very trivial, depending on the different hypotheses made on the

Table 2. Amount of N_2O produced during the adsorption of NO at 120°C for fresh and aged pre-reduced samples

SAMPLE	N_2O produced			
	FRESH		AGED	
	mmol g^{-1}	molecules/ Cu atom	mmol g^{-1}	molecules/ Cu atom
Cu-Z	62	0.23	3	0.01
CuLa-Z	89	0.31	29	0.10
CuSm-Z	84	0.30	14	0.05
CuCe-Z	71	0.28	21	0.08
LaCu-Z	100	0.35	49	0.17
SmCu-Z	82	0.24	40	0.12
CeCu-Z	91	0.30	28	0.09

redox chemistry of copper in Cu-ZSM5 [45–51] and can be expressed according to the following equation:

$$2NO + \sigma_{red} \longrightarrow N_2O + \sigma\text{-}O,$$

where σ_{red} indicates the general form of copper in the reduced state and σ-O, the same site in the oxidized form.

An oxygen atom is then available for reoxidizing the pre-reduced copper sites. As a consequence, if Cu^+ containing sites are supposed to be the active centers, the amount of N_2O formed should be proportional to the catalytic activity. The dramatic decrease of the amount of N_2O formed over Cu-Z after the aging treatment is in agreement with the hypothesis. This indicates that the redox properties of Cu^+ sites, or the nature itself of these sites, are significantly modified by the aging treatment. This effect is less marked for rare earth-containing catalysts, as expected from the lower reduction of activity after the aging treatments. Thus, the presence of even small amounts of lanthanum, cerium, or samarium (see Table 1) not only enhances the number of self-reducible copper ions and, consequently, the catalytic activity in the decomposition of NO under dry conditions, but also partially preserves these features in the action of water at high temperature.

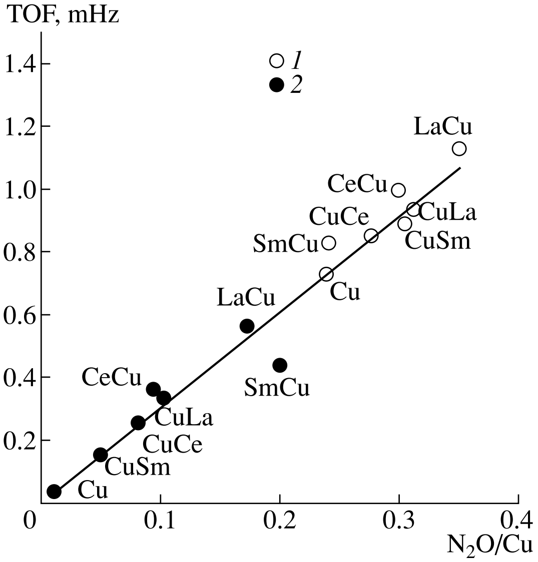

Fig. 8. TOF of NO decomposition as a function of the amount of N_2O produced during the NO adsorption over pre-reduced CuRE-Z and RECu-Z catalysts. (Fresh samples (○), aged samples (●)).

In order to quantitatively demonstrate that the nature of active copper sites does not change upon both rare earth addition in the zeolite and aging treatment but that only the number of these sites is affected, in Fig. 8, the values of TOF estimated for all samples investigated in this work (fresh and aged) is reported as a function of the N_2O/Cu ratio calculated from the NO adsorption experiments on pre-reduced catalysts. A very good linear correlation between the amount of nitrous oxide evolved during the NO adsorption and the catalytic activity has been obtained. Moreover, it is noteworthy that such correlation passes through the origin, further suggesting that the catalytic activity in the decomposition of NO is directly related to the presence of Cu^+ ions involved in the redox cycle.

CONCLUSIONS

The effect of the addition of small amounts of rare earth cations (lanthanum, samarium, and cerium) on the catalytic properties of copper-exchanged ZSM5 in the decomposition of nitric oxide results in a significant enhancement of both catalytic activity and catalyst hydrothermal stability. Catalysts prepared by two-step exchange show better performances compared to those prepared by simultaneous exchange of copper and rare earth cations, likely due to the higher rare earth content obtained using the former method. The enhanced activity has been associated with a better copper dispersion promoted by the rare earth cations, which leads to an increase of copper reducible sites involved in the redox mechanism of NO decomposition. The partial or total deactivation of the catalysts upon aging treatment under wet conditions at high temperatures has been attributed to the migration of active copper into inactive positions, likely forming CuO micro-clusters. This phenomenon is highly inhibited by the presence of rare earth cations which significantly preserve active copper by limiting its mobility in the presence of water, thus improving the hydrothermal stability of the catalyst.

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