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CHARACTERIZATION OF HYDROTREATED Cu-ZSM-5 CATALYST FOR THE SELECTIVE CATALYTIC REDUCTION OF NO BY *n*-DECANE

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Abstract

The steam treatment of Cu-ZSM-5 prepared by solid ion exchange involves an important decrease of the NO conversion. Characterization of the solids by NO-TPD, H_2-TPR, ^{27}Al MAS NMR shows that the catalyst deactivation is mainly due to change in copper species rather than the collapse of the zeolite framework.

Keywords: Cu-ZSM-5, NO-SCR-$C_{10}H_{22}$, catalyst deactivation, hydrothermal treatment

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INTRODUCTION

The application of zeolitic materials for the selective reduction of NO with hydrocarbons (NO-SCR-HC), in highly oxidizing atmospheres has been an important research topic in recent years. Copper-exchanged ZSM-5 zeolite (Cu-ZSM-5) is one of the best catalysts for SCR-HC under dry conditions [1-5]. However, Cu-ZSM-5 deactivates in the presence of water vapor and at high temperatures, which are the typical conditions of engine exhaust gases. A number of causes of deactivation have been invoked which appear to be related to Cu modifications or zeolite structural changes [6-17]. Quincoces *et al.* [9] have

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reported that deactivation can be related to the sintering of Cu species, crystallinity losses in the zeolitic matrix. Tanabe *et al.* [14] have suggested that Cu ions migrate into inert sites (5-membered oxygen rings) under the deactivation process where gas molecules like nitrogen oxide and propene cannot reach them. Yan *et al.* [12] concluded that dealumination of the zeolite framework, formation of amorphous Al_2O_3 and inactive Cu/Al_2O_3 contribute to deactivation of the catalyst.

Literature data concerning the deactivation of Cu-ZSM-5 confirm that the presence of H^+ causes the deactivation of the catalysts [10,14]. Therefore, Cu-ZSM-5 catalysts become more stable when the Bronsted acidity decreases [10,14]. This can be achieved by increasing either the zeolite Si/Al ratio or copper content. Moreover, in all experiments dealing with Cu-ZSM-5 deactivation, copper ions were introduced in the host structure by ion exchange in solution. Therefore, this work was devoted to the study of the hydrothermal stability and structural changes accompanying deactivation of an overexchanged Cu-ZSM-5 catalyst prepared *via* solid ion exchange in the SCR of NO by *n*-decane.

EXPERIMENTAL

NH_4^+-ZSM-5 zeolite with an elemental Si/Al molar ratio of 15 was purchased from Zeolyst (CBV-3024 E, Lot 1822-56). The catalyst was prepared by solid ion exchange. 2 g of NH_4^+-ZSM-5 was intimately mixed with 0.12 g of CuCl in an agate mortar for 15 min. The mixture was then heated at 500°C for 2 h in dry nitrogen at a heating rate of 7.5°C min^{-1}. The resulting sample was cooled to ambient temperature under the same gas, washed chloride-free and finally dried overnight at 100°C. The resulting solid (wt.% Cu = 3.21 corresponding to an exchange level of 136 %) was labeled Cu1Za1.

Hydrothermal treatment of catalysts was carried out in a quartz fixed-bed microreactor. 1 g of catalyst was placed in the reactor and heated to the desired temperature in flowing air. Then water was injected by circulating the airflow through a bubbler containing deionized water for 24 h. All gas lines were heated to prevent water condensation. Two different hydrothermal procedures were used: (*i*) ht500: temperature: 500°C, water vapor pressure: 118 Torr (resulting in solid labeled Cu1Za1ht500) and (*ii*) ht750: temperature: 750°C, water vapor pressure: 32 Torr (resulting in solid labeled Cu1Za1ht750).

^{27}Al MAS NMR measurements were carried out on rehydrated samples. Spectra were recorded on a Brucker 300 MHz (AMX 300) at 78.2 MHz. The chemical shift in ppm was obtained with respect to $Al(H_2O)_6^{3+}$ as an external reference.

Temperature programmed reduction was carried out with a Micromeritics 2910 apparatus using H_2/Ar (3/97, v/v) gas at a total flow-rate of 30 cm^3 min^{-1} and by heating the samples from room temperature to 700°C (7.5°C min^{-1}). In each case, 103 mg of the catalyst was previously activated at 400 °C for 30 min under air, then cooled to room temperature under the same gas.

The TPD experiments were performed in a pyrex U-reactor with 104 mg of catalyst in the same apparatus as SCR. The sample was pretreated under air flow (100 cm^3 min^{-1}) at 500°C for 30 min and then cooled to room temperature. After flushing with He until no oxygen was detected in the effluent, NO was adsorbed at room temperature using a flow of NO/He mixture (0.1/99.9, v/v) at a total flow-rate of 50 cm^3 min^{-1} for 30 min. Afterwards, the system was purged with He (100 cm^3 min^{-1}) until no NO was detected in the effluents. Thereafter, the TPD run was started from room temperature to 500°C at a heating rate of 7.5°C min^{-1}, in He flow (50 cm^3 min^{-1}).

The selective catalytic reduction of NO by *n*-decane (NO-SCR- $C_{10}H_{22}$) was carried out at atmospheric pressure in a fixed bed flow reactor with 0.104 g of catalyst. The flow-rates were adjusted using Brooks mass flow controller units. The composition of the effluents was monitored continuously by sampling in line to a quadrupole mass spectrometer (Pfeiffer Omnistar QMS 200) equipped with SEM detector (0-200 amu) and following the masses 28, 30, 44, 46, 57. The reaction gas containing 1000 ppm of NO, 300 ppm of *n*-decane and 9 % O_2 diluted with He was switched on. The total flow rate was 120 cm^3 min^{-1} and the temperature ramped from 25 to 500°C (7.5°C min^{-1}). At 170°C, *n*-decane was introduced to prevent its pre-adsorption [18].

RESULTS AND DISCUSSION

The conversion profiles of the NO-SCR-$C_{10}H_{22}$ of the fresh and steamed catalysts are shown in Fig. 1. During these 3 catalytic tests, no formation of NO_2 and N_2O was observed. The NO conversion of the fresh catalyst begins at 260°C, passes through a maximum of 85 % around 366°C and then decreases slowly to reach 41 % of NO conversion at 500°C. After the hydrothermal treatment ht500, the conversion of NO is delayed and the maximum of NO conversion of 72% is obtained at 375°C. Above this temperature the NO conversion strongly decreases in comparison with the fresh sample and no more activity is observed above 490°C. By increasing the temperature of the hydrothermal treatment to 750°C, the maximum of NO conversion is divided by 2 and appears at a higher temperature: 390°C. Above 390°C, the NO conversion also drops to 0 % at 500°C. On the other hand, the conversion profiles of *n*-$C_{10}H_{22}$ to CO_2 were nearly the same over fresh and hydrotreated catalysts. Total oxidation of *n*-decane was reached at a temperature close to the maximum of NO conversion and was not affected by steaming.
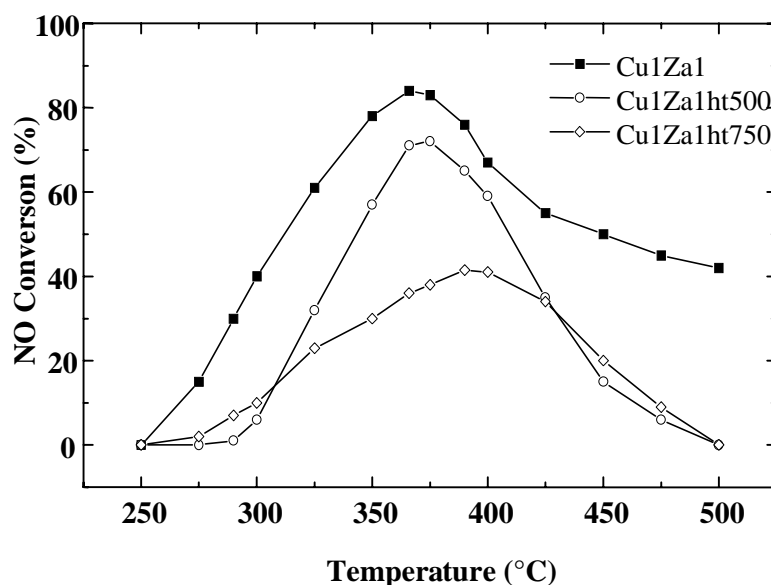
Fig. 1. NO conversion of fresh catalyst (Cu1Za1); hydrotreated   at 500°C (Cu1Za1ht500); hydrotreated at 750°C (Cu1Za1ht750)

^{27}Al NMR spectroscopy allows to differentiate lattice and extra-lattice aluminium in the zeolite samples due to the difference in chemical shifts of tetrahedral (50 ppm) and octahedral aluminium (~0 ppm) [19-22]. Both the ^{27}Al MAS NMR spectra of fresh and deactivated Cu-ZSM-5 samples show the presence of only one peak at around 50 ppm (Fig. 2). The peak related to octahedral aluminium is not observed in any spectrum.

The TPR profiles of fresh and hydrotreated catalysts at 500 and 750°C are presented in Fig. 3. The fresh sample exhibits three reduction peaks at 174, 224, and 374°C. The first and second temperature peak are assigned to the reduction of Cu^{2+} to Cu^{+} and to one step reduction of CuO particules in Cu^{0}, respectively. The last one corresponds to the reduction of Cu^{+} to Cu^{0} [23]. From the surface of the latter peak, the proportion of copper ions in compensation charge of the zeolite has been estimated to be 70%. Taking into account that the exchange level of this sample is 136%, this TPR result shows that copper ions occupy firstly the accessible exchange sites of ZSM-5. For the hydrotreated sample, the reduction of Cu^{2+} ions is shifted to higher temperatures and occurs in the same

temperature range as the reduction of CuO aggregates. On the other hand reduction of Cu^+ ions is shifted to low temperature. The appearance of a broad peak centered around 390°C for Cu1Za1ht750 should be noticed, which is attributed to the reduction of copper aluminate as already proposed by Yan *et al.* [12,24]. The proportion of Cu^{2+} ions in compensation charge of the zeolite seems to remain the same in the sample treated at 500°C but drastically decreases in the sample treated at 750°C. A value close to 15-20% was assessed. As for copper aluminate, it represents 64 % of the copper present in the solid. Therefore, the formation of copper aluminate may imply the presence of extra-lattice aluminium but no NMR signal due to octahedral aluminium was observed. As suggested by Grinsted *et al.* [25], Cu-Al oxide is probably present as small aggregates of low symmetry (amorphous), which is not easily tracked by NMR. H_2/Cu ratio close to unity were found for the three solids showing thus that all the copper is reduced to the metallic state at the end of the TPR experiments.
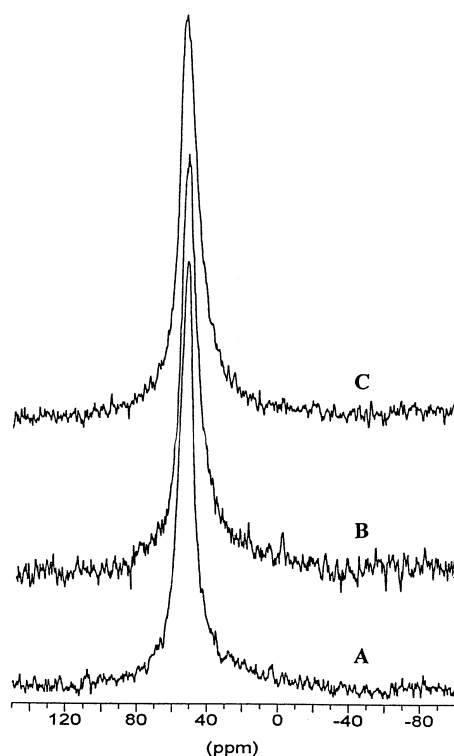

Fig. 2. ^{27}Al NMR signals of (A) fresh catalyst (Cu1Za1); (B) hydrotreated at 500°C (Cu1Za1ht500); (C) hydrotreated at 750°C (Cu1Za1ht750)
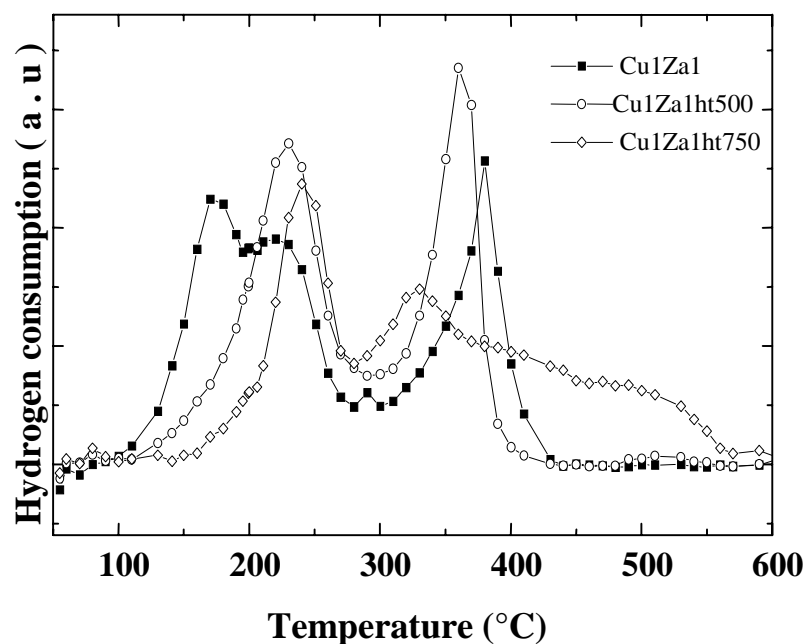
Fig. 3. H$_2$-TPR profiles of fresh catalyst (Cu1Za1);   hydrotreated   at 500°C
(Cu1Za1ht500); hydrotreated at 750°C (Cu1Za1ht750)

The accessibility of Cu to NO has been probed by TPD of NO adsorbed at
room temperature. The NO TPD profiles are reported in Fig. 4. The NO TPD
profile of the fresh catalyst (Cu1Za1) can be divided into two parts. At low
temperature the broad NO desorption peak is ascribed to the decomposition of
Cu$^+$-NO$^+$ species leading to Cu^{2+} and NO (gas) with a maximum at 129°C and a
shoulder at around 210°C occurs. The second peak of NO desorption
accompanied by oxygen desorption appears at 360°C and is attributed to the
decomposition of nitrate (NO$_3^-$), nitrite (NO$_2^-$) or NO$_2^+$ adsorbed species on both
isolated Cu sites and CuO aggregates [26,27]. For the fresh solid the quantity of
N$_2$O and NO$_2$ analyzed during the desorption is negligible in comparison with
the quantity of NO desorbed (Table 1). Assuming that the NO/Cu stoichiometry
at the surface is unity whatever the adsorbed species, an accessibility of 0.43
has been estimated. After the hydrothermal treatment at 500°C, the shape of
the NO TPD profile remains quite the same. It should be noticed that the high
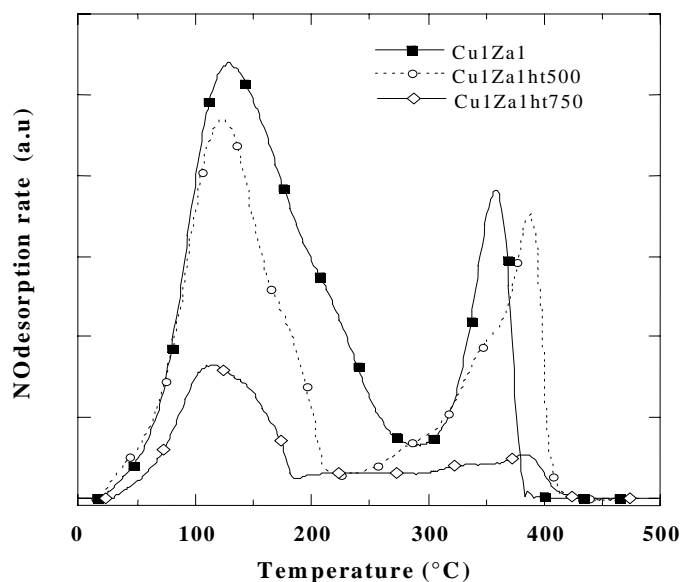
Fig. 4. NO-TPD profiles of fresh catalyst (Cu1Za1); hydrotreated at 500°C (Cu1Za1ht500); hydrotreated at 750°C (Cu1Za1ht750)

Table 1

Amounts of desorbed species from fresh and hydrotreated catalysts (µmol/g)

Catalyst	NO			O_2	N_2O	NO_2	NO/Cu	NO/Cu
	total	[a]LT peak	[b]HT peak	HT	total	total	total	[b]HT
Cu1Za1	217	174	43	55	3	3	0.43	0.09
Cu1Za1ht500	142	110	32	40	5	49	0.34	0.06
Cu1Za1ht750	57	37	20	6	2	26	0.12	0.04

[a] low temperature peak, [b] high temperature peak

temperature peak is shifted of 30°C towards higher temperatures. The key point is the important desorption of NO_2 accompanying the latter peak. The hydrothermal treatment causes a decrease of the NO adsorption capacity. This phenomenon is enhanced after the hydrothermal treatment at 750°C. In this case no NO desorption occurs at high temperature but desorption of NO_2 is observed only, and the peak of NO desorption at low temperature is much more smaller. This change of the nature of the NOx molecule desorbing at high temperature

may be related to the presence of a new species induced by the hydrothermal treatment: aluminate. Moreover if we consider the quantity of NO desorbing at low temperature which we may attribute essentially to Cu^{2+} ion species, it is obvious that the quantity of these Cu^{2+} ions decrease with the hydrothermal treatment and therefore explains the lower copper accessibility of the hydrothermally treated samples. The decrease of the NO/Cu ratio confirms the occurrence of clustered cationic copper species and/or CuO aggregates which explain the very low SCR activity observed.

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