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Influence of operating protocol in the temperature-programmed reaction of NO with decane on Cu/mordenite

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A Cu/mordenite catalyst was prepared by ion exchange and characterized by N_2 sorption, XRD, TPR by H_2 and TPD by NO. The catalyst was evaluated in the selective catalytic reduction of NO by decane in O_2-rich atmosphere under temperature-programmed reaction from 293 to 773 K. Two NO reduction profiles at 590 and 650 K occur under these conditions. By testing different operating protocols and different alkanes as reductants, it was concluded that the low temperature peak (590 K) is due to alkane condensed in the porosity of mordenite.

Keywords: nitric oxide; selective reduction; Cu/mordenite

1. Introduction

In order to meet the environmental regulations, the selective catalytic reduction (SCR) of NO_x from automotive exhaust of diesel engines will be a necessity in the near future. For that goal the most interesting reductant, from a practical point of view, would be the fuel itself (C_{10}–C_{20} alkanes in diesel fuels), which is easier to handle in the vehicle. However, in most studies low molecular weight alkanes ($\leqslant C_3$) have been used, hence there is a demand for studying the efficiency of higher alkanes ($\geqslant C_{10}$). Indeed, some specific and intricate behaviours seem linked to their use [1]. It was the aim of this work to investigate the properties of a Cu/mordenite catalyst for the SCR of NO by decane.

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2. Experimental

The parent NH_4^+ form of mordenite (PM-1H from Zeocat, Si/Al = 7.5) was first exchanged by NaCl for 1 h at 383 K, three times, then the Cu/mordenite catalyst (CuMOR) was prepared by exchanging Na-MOR with copper acetate in water, for 24 h at room temperature. The resulting solid was washed, dried, then calcined under dry air at 773 K for 6 h (ramp: 10 K min^{-1}, flow: 100 cm^3 min^{-1} g^{-1}). The Cu content in the final catalyst is 3.38 wt% which corresponds to a 64% Cu^{2+} exchange.

The catalyst was characterized by N_2 sorption at 77 K (Micromeritics ASAP200), X-ray diffraction (CGR Theta 60 instrument using Cu Kα monochromated radiation), temperature-programmed reduction by H_2 (H_2 TPR) and temperature-programmed desorption of NO (NO TPD).

The reducibility and the amount of copper species were determined by H_2 TPR of Cu-MOR as described in detail elsewhere [2]. 100 mg of the catalyst were activated at 673 K for 1 h under air, then cooled to room temperature under high purity He flow. Helium is then replaced by the reducing H_2/Ar gas (3/97, vol/vol, purity of both gases >99.995%), the linear temperature programme was then started from 293 to 873 K (ramp: 5 K min^{-1}, flow: 20 cm^3 min^{-1}).

The accessibility to Cu sites was determined by NO TPD [2]. 200 mg of the catalyst were pretreated in an air stream at 673 K for 1 h, then cooled to room temperature and the air stream switched to a helium stream until no oxygen was detected in the effluent. NO was then adsorbed at room temperature in a flow of NO/He (1/99, vol/vol, purity of NO >99.95%) for 30 min. NO in the gas phase was then flushed with helium until no NO was detected in the effluent. TPD experiments were performed from room temperature to 873 K at a heating rate of 10 K min^{-1}. The gas desorbed from the solids was monitored by using a quadrupole mass spectrometer (Balzers QMS421) calibrated on pure standard mixtures. The amount of NO held on the catalyst surface was determined from the peak area of the TPD curves.

The selective catalytic reduction of NO by decane (SCR NO) was studied in a flow reactor operating at atmospheric pressure. 50 mg of the catalyst were activated in situ at 773 K for 1 h under air and then cooled to 298 K under He. The reaction gas containing 0.1 vol% NO, 0.1 vol% *n*-decane (12 000 ppmC, purity >99.5%), and 9 vol% O_2 (purity >99.995%) diluted with He, was switched on. The flow rate was 60 cm^3 min^{-1} (space velocity: 70 000 h^{-1}) and the temperature ramped from 298 to 750 K (ramp: 5 K min^{-1}). The composition of the effluents was monitored continuously by sampling on-line to a quadrupole mass spectrometer Balzers QMS421 equipped with the Faraday detector (0–200 amu). This apparatus allows us to monitor 64 masses simultaneously. We have followed 10 masses characteristic of NO (14, 15, 30), N_2 (14, 28), N_2O (14, 15, 30, 44), NO_2 (14, 30, 46), CO (12, 28), CO_2 (12, 22, 44, 46), H_2O (18) and $C_{10}H_{22}$ (57). The intensity I^x of the peak of x amu is given by

$$I^x = \sum_i K_i^x P_i .$$

P_i is the partial pressure of compound i and K_i^x the response coefficient of this compound at x amu, the partial pressure of each compound is given by solving a linear system of equations.

3. Results and discussion

The isotherm for N_2 sorption on CuMOR is of the type I, which provides evidence that more than 90% of the surface is in the micropores. The volume of these micropores, 0.218 ml g^{-1}, is very close to that of NaMOR; this shows that there is not any blocking by CuO aggregates to the access at the porosity. Moreover, the X-ray diffraction pattern shows neither loss of crystallinity of MOR after the Cu exchange process, nor the occurrence of large CuO clusters (dp > 3 nm).

The thermogram of Cu/MOR reduction by H_2/Ar (3/97) is presented in fig. 1. Two reduction peaks occur at about 480 and 590 K. The hydrogen consumption during the reduction process is very close to that required for the stoichiometric reduction of Cu^{II} to Cu^0, and the respective surface area between the two peaks is about 55/45. By studying the reducibility of Cu in Cu/MOR, it was previously shown that these two peaks correspond to the reduction of Cu^{2+} to Cu^+ and CuO to Cu^0 aggregates for the low temperature reduction peak, while the second peak corresponds to the reduction of isolated Cu^+ to Cu^0 [2,3]. The respective areas of these two peaks allow us to conclude that Cu is in the form of isolated Cu^{2+} species (90%) and CuO aggregates (10%). This respective amount of Cu^{2+} and CuO species is in good agreement with the values found for a similar Cu exchange level of 60%

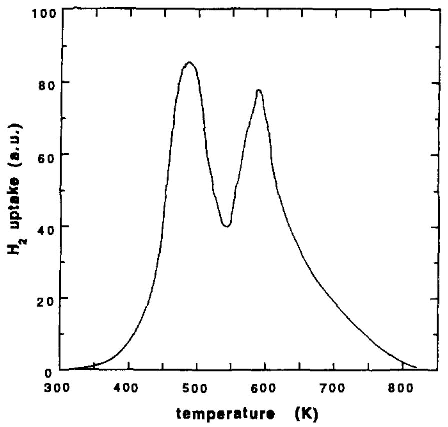

Fig. 1. Temperature-programmed reduction profile of Cu/MOR; $m = 0.1$ g, gas: H_2/He (3/97, vol/vol), flow: 20 cm^3 min^{-1}, ramp: 5 K min^{-1}.

in Cu/HMOR [2]. We could just notice that a shift to lower temperature of 20 and 40 K for the first and second reduction processes respectively occurs for Cu/NaMOR, in the present study, with respect to Cu/HMOR [2]; this behaviour can be accounted for by the lower acidity of NaMOR which facilitates the Cu reduction in mordenite as found for X and Y zeolites [4].

Two peaks appear, at 378 and 523 K respectively, during the NO TPD (fig. 2), in agreement with previous studies [2,5–7]. These two NO desorption peaks were ascribed to Cu^{2+}(NO) species for the low temperature peak and to bidentate nitrate species bonded on CuO clusters for the high temperature peak. The monitoring of NO release during the TPD allows one to determine the number of Cu^{II} sites accessible to NO, i.e. the Cu dispersion in Cu/MOR which is very close to 1.

In conclusion, the Cu/MOR catalyst is mainly constituted of Cu^{2+} isolated species (90%), with some small CuO clusters (10%); there is an excellent accessibility, near one, to these Cu sites for the NO molecule.

During the temperature-programmed reaction of NO with decane from 293 to 750 K, two distinct features can be separated. Firstly, NO is adsorbed between 293 and 333 K, then it desorbs between 373 and 473 K in agreement with TPD results. In parallel, a large uptake of decane by CuMOR occurs, 0.08 cm^3 g^{-1} as determined by gravimetry. Secondly, above 523 K the NO reduction starts (N_2 selectivity $>96\%$) with two maxima at about 590 and 650 K (fig. 3). During the first NO reduction wave, there is CO_2 formation but the gas phase concentration of decane remains surprisingly constant. By contrast, in the course of the second NO reduction wave the expected behaviour is found with a parallel decrease of decane concentration in the gas phase and an increase of CO_2 formation. This behaviour is unaffected by the method used to prepare the CuMOR catalyst. Such a phenomenon was previously observed during the SCR of NO by n-$C_{16}H_{34}$ on BEA zeolite exchanged with H^+, Ga^+, Ni^{2+} and Fe^{3+} [1].

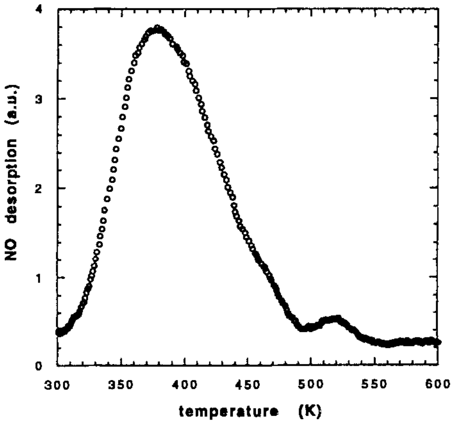

Fig. 2. Temperature-programmed desorption profile of NO from Cu/MOR catalyst; $m = 0.1$ g, gas: He, flow: 50 cm^3 min^{-1}, ramp: 10 K min^{-1}.

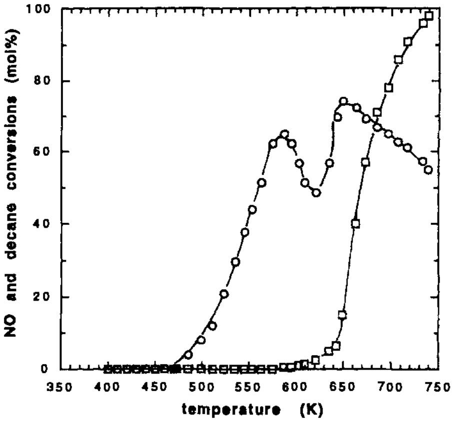

Fig. 3. Selective catalytic reduction of NO by decane over Cu/MOR as a function of temperature. (○) NO conversion, (□) decane conversion; gas: 1000 ppm NO, 1200 ppm decane, 9% O_2, balance He, flow: 60 cm^3 min^{-1}, ramp: 5 K min^{-1}.

On the other hand, there is some effect of the alkane nature on this phenomenon (fig. 4). At the same hydrocarbon concentration (12000 ppmC), the use of *n*-heptane as reductant reproduces a very similar NO reduction profile as found with *n*-decane. The first reduction waves are identical and there is only a shift of the second wave to higher NO conversion for *n*-heptane. This shows the higher reducing power of *n*-heptane under these conditions. In contrast, with propane the low temperature NO reduction profile has disappeared. Moreover, propane is less efficient as reductant. Therefore, an hypothesis can be formulated for the assignment of the two NO reduction profiles. The high temperature peak (650 K) would correspond to the steady state regime where the adsorption/desorption equilibrium of decane with the surface is reached:

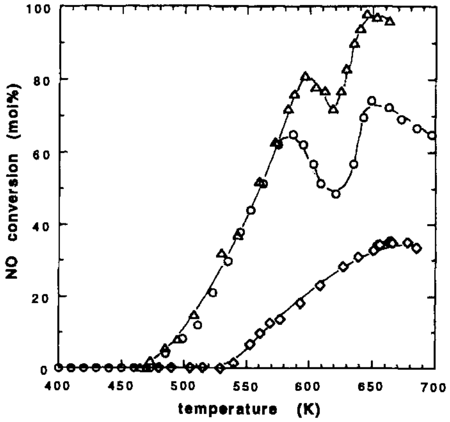

Fig. 4. Selective catalytic reduction of NO by different alkanes over Cu/MOR as a function of temperature. (○) Decane, (△) heptane, (◇) propane; gas: 1000 ppm NO, alkane concentration: 12000 ppmC, 9% O_2, balance He, flow: 60 cm^3 min^{-1}, ramp: 5 K min^{-1}.

$$n\text{-}C_{10}H_{22(gas)} + \text{site}* \rightleftharpoons n\text{-}C_{10}H_{22}* \quad (*\text{: adsorption site})$$

In contrast, the first reduction wave at 590 K would correspond to a transient kinetic situation where the local decane partial pressure is strongly enhanced due to the capillary condensation of decane in the pores of mordenite which has occurred under 493 K. Under these conditions, the surface coverage by decane is close to unity. As soon as the first Cu active sites become free after decane desorption (500 K), all NO molecules which can adsorb are immediately reduced owing to the local superconcentration in decane.

In order to check the validity of this hypothesis, two kinds of experiments were carried out:

(i) the direct decomposition of NO in the absence of decane in the gas phase, on Cu/MOR with and without pre-adsorption of decane at low temperature,

(ii) the temperature-programmed reaction in an increasing ramp starting from 493 K, and in a decreasing ramp starting from 693 K. These protocols will prevent the capillary condensation of decane in the mordenite micropores.

The first series of experiments (fig. 5) show that this free Cu/MOR, without proton, exhibits little efficiency for NO decomposition in agreement with reported studies [8,9]. But the NO conversion shows a sharp reduction peak at 575 K when the NO decomposition is carried out on Cu/MOR pre-adsorbed with decane. The position of this reduction profile fairly corresponds with the NO reduction wave in the SCR by decane. The second series of experiments (fig. 6) put in evidence on the one hand that the low temperature NO reduction has disappeared during the increasing ramp when started at 473 K, on the other hand, that there is a nice fit between NO reduction profiles on both increasing and decreasing ramps.

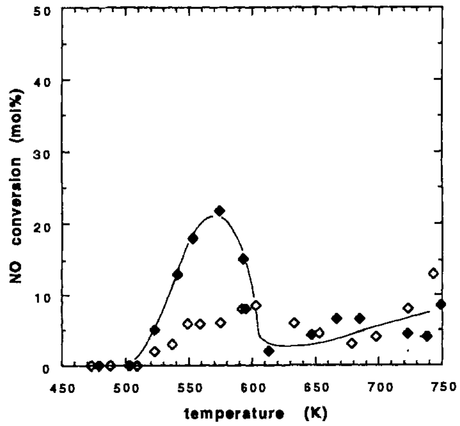

Fig. 5. Conversion of NO over Cu/MOR as a function of temperature. (◇) Without decane, (◆) with pre-adsorbed decane under 473 K; gas: 1000 ppm NO, 9% O_2, balance He, flow: 60 cm^3 min^{-1}, ramp: 5 K min^{-1}.

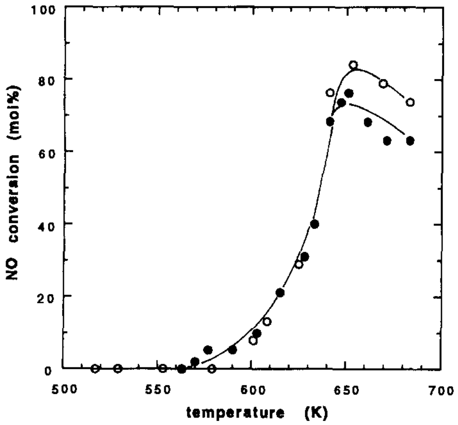

Fig. 6. Selective catalytic reduction of NO by decane over Cu/MOR as a function of temperature and started from 473 K; (●) increasing ramp, (○) decreasing ramp; gas: 1000 ppm NO, 12000 ppmC decane, 9% O_2, balance He, flow: 60 cm^3 min^{-1}, ramp: 5 K min^{-1}.

These two sets of experiments confirm the hypothesis about the effect of decane preadsorbed under 473 K when the SCR is started at room temperature.

In conclusion, decane is a better reducing agent than propane, and can be used for DeNOx on Cu/MOR, but its condensation in the microporosity at low temperature introduces no steady state peaks which appear as artefacts in the kinetics of the reaction.

Acknowledgement

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