Selective catalytic reduction of NO by ammonia over Fe-ZSM-5 catalysts

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In the selective catalytic reduction (SCR) of NO by ammonia, over-exchanged Fe-ZSM-5 prepared by sublimation of $FeCl_3$ into H-ZSM-5, shows superior catalytic activity and stability in a wide temperature range; its activity is promoted by the presence of water in the feed while SO_2 is a weak poison at low but a promoter at high temperatures; its remarkable durability towards H_2O and SO_2 makes this zeolite catalyst a potential choice in Denox applications for stationary sources and heavy Diesel engines with ammonia or urea reductants.

In the selective catalytic reduction (SCR) of nitrogen oxides, metal-exchanged MFI-type zeolites, in particular Cu-ZSM-5, have received much attention due to their ability to catalyze the SCR not only by hydrocarbons,[1–3] but also by ammonia.[4] The insufficient stability of these catalysts has so far prevented their practical application in flue-gas abatement devices. Faced with the tail-gases of combustion engines containing high amounts of water, and often also SO_2, they suffer structural changes leading to deactivation. For the use of hydrocarbon reductants, water is also known as a reversible poison while it has been reported to promote the SCR activity with the reductant ammonia.[4]

In view of these problems, the recent discovery of the remarkable stability of over-exchanged Fe-ZSM-5 in the SCR of NO with isobutane[5] has been considered a breakthrough in flue-gas catalysis research. Further progress has to cope with a reproducibility problem in the preparation of these materials[6] and with the fact that the reductant isobutane that provides the highest reaction rates with these catalysts is impractical for any commercial purpose. We report here a superior catalytic performance of over-exchanged Fe-ZSM-5 in the SCR of nitrogen oxides with ammonia. The catalyst provides excellent activity and selectivity over a wide temperature range. It is promoted by water and, in certain temperature ranges, also by SO_2 (with or without water) and does not suffer any deactivation from these feed components on a time scale of 10–15 h.

The Fe-ZSM-5 was prepared on the basis of a Na-ZSM-5 (Si/Al ≈ 14, Chemiewerk Bad Köstritz, Germany). Iron was introduced by a modified sublimation technique derived from a route described in ref. 7 (sublimation of $FeCl_3$ vapour into the H-form of the zeolite under vacuum). Subsequently, the catalyst was calcined in air at 823 K without any washing step. Elemental analysis showed that this preparation provides an Fe/Al ratio of 1 : 1, which is a formal exchange degree of 300%. The sample will be, therefore, denoted as Fe-ZSM-5-14-300 indicating the Si/Al ratio and the formal exchange degree by the last two figures. A Cu-ZSM-5-14-220 prepared by the conventional ion-exchange method described by Iwamoto *et al.*[8] was also obtained from the same Na-ZSM-5 for use as a reference material.

The SCR of NO by ammonia was carried out in a microcatalytic flow reactor. A calibrated mass spectrometer and a combined non-dispersive IR/UV detector were employed to analyse the reaction product. The feed gas contained 1000 ppm NO, 1000 ppm NH_3, and 2% O_2 (balance He) and was loaded by 2.5% H_2O and/or 200 ppm SO_2 in the poisoning experiments. Under standard reaction conditions, 260 ml min^{-1} of this mixture were fed over 35 mg of catalyst, which results in a space velocity of 304 000 h^{-1}.

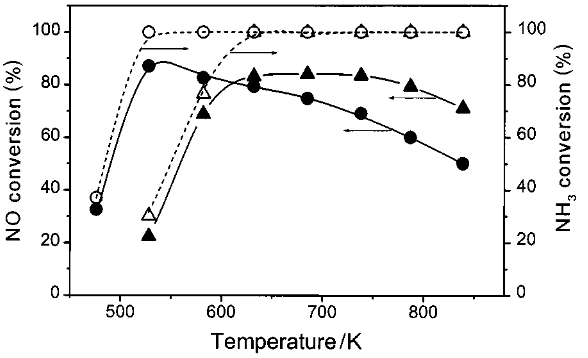

Fig. 1 Selective catalytic reduction of NO by NH_3 with over-exchanged Fe-ZSM-5 and comparison with over-exchanged Cu-ZSM-5. Dry condition: 1000 ppm NO, 1000 ppm NH_3, 2% O_2, balance He; 304 000 h^{-1}, (▲, △) Fe-ZSM-5-14-300, (○, ●) Cu-ZSM-5-14-220, filled symbols, NO conversion, open symbols, NH_3 conversion.

Fig. 1 shows the conversions of NO and NH_3 at different reaction temperatures over Fe-ZSM-5-14-300 and Cu-ZSM-5-14-220. Cu-ZSM-5 is very active for the SCR with ammonia, and the conversions obtained with our preparation are at all temperatures well above those reported in the literature for a somewhat lower space velocity.[4] Fe-ZSM-5-14-300 provides the same conversions as Cu-ZSM-5-14-220 proving inferior only in the low-temperature region (⩽573 K). Over this catalyst, the temperature window for high NO conversion is significantly wider than over the Cu catalyst: NO conversions > 75% can be held between 573 and 823 K. The ammonia conversion is close to the NO conversion below 423 K, but is 100% at all temperatures above, which makes ammonia slip rather unlikely with such catalysts. Remarkably, the only oxidation product is nitrogen, neither NO_2 nor N_2O formation were detected in the whole temperature range. With Cu-ZSM-5-14-220, ammonia oxidation becomes significant already at 523 K, and since the NO conversion decreases steadily with increasing temperature, the copper catalyst is inferior in the ammonia utilization at almost all temperatures.

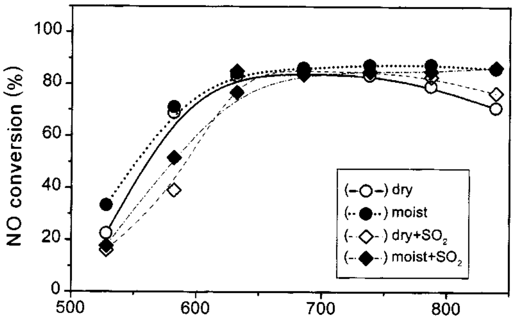

Fig. 2 Influence of water and sulfur dioxide on the NO conversion over Fe-ZSM-5-14-300. Space velocity, 304 000 h^{-1}, dry condition: 1000 ppm NO, 1000 ppm NH_3, 2% O_2, balance He. Moist condition: as dry, with 2.5% H_2O added, '+SO_2', with 200 ppm SO_2 added.

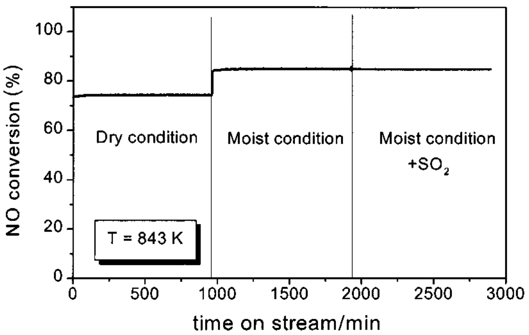

Fig. 3 Durability of Fe-ZSM-5-14-300 under the influence of water and SO_2: dry condition; moist condition; moist condition + SO_2 as in Fig. 2.

The impact of H_2O and/or SO_2 on the NO conversion over Fe-ZSM-5-14-300 is shown in Fig. 2. It is evident that SO_2 exerts a poisoning influence at low temperature both in dry and in moist feed. Remarkably, this effect is reversed at higher temperature: Above 700 K, the NO conversion is always higher with SO_2 present. On the other hand, water promotes the activity at all temperatures over our Fe-ZSM-5, which is similar to the behaviour found with Cu-ZSM-5.[4,9] This is most favourable at the upper end of the temperature range where an NO conversion of 85% (at *ca.* 300 000 h^{-1}) may be held up to a reaction temperature of 850 K in a moist feed stream.

The durability of Fe-ZSM-5-14-300 in various feed mixtures was tested at 840 K (Fig. 3). Under dry conditions, a slight increase of the NO conversion (by *ca.* 3% in 15 h) can be noted. Upon addition of 2.5% H_2O to the feed, a sudden increment in the NO conversion of *ca.* 10% is achieved. Addition of SO_2 into the wet feed does not lead to further changes. No deactivation of the catalyst is observed either in 15 h time-on-stream in moist feed or under the simultaneous action of H_2O and SO_2. It should be noted that such conditions would cause severe deactivation with the Cu-ZSM-5 system.[3]

The preparation of the Fe-ZSM-5 catalyst is critical also for its application to the SCR with ammonia. An Fe-ZSM-5 catalysts obtained by conventional aqueous exchange, which resulted in a formal exchange degree of $< 100\%$, was inferior to Fe-ZSM-5-14-300.[9] In a recent paper,[10] Fe-ZSM-5 prepared by aqueous exchange with subsequent precipitation provided NO conversions below 50%, with considerable N_2O formation at lower temperatures, at a space velocity of only 180 000 h^{-1}. Notably, in the SCR of NO by isobutane, our Fe-ZSM-5-14-300 sample could not compete with Cu-ZSM-5-14-220, and the NO conversions achieved[9] were much lower than those reported by Feng and Hall.[5] In addition, the air calcination step in the catalyst preparation (*vide supra*), which proved deleterious for the SCR with isobutane[9] in accordance with the literature,[6] had a slightly deactivating effect only in the low-temperature range but did not did not affect the peak conversion with ammonia.[9] This implies that the active sites required by the two reactions may be different.

In conclusion, over-exchanged Fe-ZSM-5 prepared by a sublimation technique shows highly promising catalytic performance in the SCR of NO by ammonia. Studies concerning the structure of the active sites in this catalyst and about its behaviour with respect to the oxidation of SO_2 are under way.

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Note and references

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