

Decomposition of NO over Cu-AITS-1 zeolites

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Abstract

H-AITS-1 zeolite with Si/Ti = 50 and Si/Al = 50 was employed in preparing catalyst samples by ion-exchange and impregnation with a copper nitrate solution to obtain 0.24–1.15 wt.% and 1.5, 2 and 2.5 wt.% Cu loading, respectively. The catalytic properties for the NO decomposition were compared with that of Cu-ZSM-5 (Si/Al = 25 with 2 wt.% Cu loading) and similarity was found between the AITS-1 based samples and Cu-ZSM-5. Due to the higher acidity, the activity at 500°C per total copper atoms (an apparent turnover frequency, TOF) was significantly higher over Cu based AITS-1 samples being $2\text{--}3 \times 10^{-3} \text{ s}^{-1}$ as compared to $1 \times 10^{-3} \text{ s}^{-1}$ measured on Cu-ZSM-5. For the ion-exchanged Cu-AITS-1 there was an increase in TOF with increasing copper content, whereas on the impregnated samples a decrease in TOF was found. On all catalysts there was a maximum in the NO conversion at 500–550°C. The amount of NO per copper atom measured by temperature programmed desorption (TPD) was about the same as that on Cu-ZSM-5 and the features of the TPD were also similar. At the first contact of the catalyst at 500°C with the 2 vol% NO/Ar gas a transient N₂O formation and a considerable delay in the O₂ formation was observed. This could, however, be reproduced only on fresh catalyst, while all further transients showed different but reproducible features using the same sample. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: AITS; Zeolites; TOF

1. Introduction

Catalytic decomposition of NO is an attractive reaction to remove NO_x from exhaust gases. Until now only Cu-ZSM-5 catalysts have possessed activity high enough for any practical application, but their relatively low hydrothermal stability is a serious drawback

[1–3]. In a search for other catalysts for the NO decomposition Dedecek et al. reported considerable activity of Cu-MeAlPO-11 [4]. In a previous study [5] on Cu-ZSM-5 zeolite we assumed a reaction intermediate in which an acid site in the vicinity of the copper ion stabilized the adsorbed NO. As H-AITS-1 is known to have higher acidity than Cu-ZSM-5, but have the same structure as H-ZSM-5, there was a hope that the higher acidity might result in higher catalytic activity in NO decomposition. We continued to study NO decomposition [5–7] by preparing a series of Cu-AITS-1 catalysts by ion-exchange and impregnation and compared their catalytic properties with that of Cu-ZSM-5.

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2. Experimental

2.1. Catalyst preparation

NH₄-AITS-1 zeolite with Si/Al = 50 and Si/Ti = 50 was prepared from tetraethyl orthosilicate, aluminium isopropoxide and tetrabutyl orthotitanate using tetrapropyl ammonium hydroxide as template. The NH₄-AITS-1 was calcined in a stream of air at 550°C for 8 h to obtain the parent H-AITS-1. The Cu-AITS-1 catalysts with Cu = 0.24–1.15 wt.% were obtained by refluxing H-AITS-1 with 0.25 N Cu(NO₃)₂ at varying time periods. After reflux the sample was centrifuged, washed with deionized water, dried at 100°C and calcined at 500°C overnight in air. The copper exchanged catalysts thus obtained were of 0.24 wt.%, 0.33 wt.%, 0.44 wt.%, 0.52 wt.% and the maximum possible exchange of 1.15 wt.% corresponding to 100% exchange. Impregnation with calculated amounts of 0.25 N Cu(NO₃)₂ was used to obtain three of the so called over exchanged samples with 1.5 wt.%, 2 wt.% and 2.5 wt.% copper content. In these cases the water evaporated slowly while stirring at intervals on a steam bath to dryness. Finally the samples were calcined at 500°C overnight in air. All the copper concentrations were measured by atomic absorption.

2.2. Catalytic reactions

Catalytic studies were performed in a fixed-bed quartz tubular flow reactor with 4 mm I.D., described in [5]. About 0.15 g catalyst of 0.25–0.5 mm sieve fraction was placed between quartz wool plugs. The

pure argon and the 2 vol% NO/Ar as reactant gas were supplied by BOC England as N4.8 purity gas and used without further purification. The whole catalytic system was helium leak tested to avoid any contamination of the gases. MKS mass flow controllers were used to mix the gases and to form step function changes in NO concentration. A Spectramass PC2000 quadrupole mass spectrometer (QMS) in multiple ion detection mode was applied for analysis. A Spectramass gas inlet system consisting of a heated stainless steel capillary differentially pumped by a rotary pump, was linked via an orifice to the QMS and made the QMS signal proportional to the gas concentration in the effluent. By this arrangements a high stability of the QMS signal was ensured. The 2 vol% NO/Ar mixture and an analysed mixture of 0.9 vol% N₂ + 0.9 vol% O₂ in Ar was used to calibrate the $m/e = 30, 28$ and 32 signals, respectively.

First, the catalyst was heated in Ar to 500°C and when the QMS signal had been stabilized, the flow was switched to 20 cm³ min⁻¹ 2 vol% NO/Ar. On reaching steady state conditions the flow was switched back to Ar. These transients are called as the ‘first contact’ with NO. After this first cycle the flow was switched again for the 2 vol% NO/Ar. All components stabilized smoothly showing volume mixing only. The temperature was increased stepwise to 600°C and cooled to 200°C. After purging in Ar at 200°C, NO TPD up to 600°C was measured using 20 cm³ min⁻¹ flow rate and 10°C min⁻¹ heating rate. At 600°C the flow was switched again to 2 vol% NO/Ar and the cycle was repeated several times. The conversion and the TPD could be well reproduced. Above 400°C only N₂ and O₂ were the products. Using the calibration

Table 1
TOF at 500°C and TPD after cooling in NO to 200°C

Catalyst (wt.%)		TOF × 10 ³ (NO/Cu _{total}) s ⁻¹	TPD		
			NO (mmol/g)	NO/Cu	O ₂ (mmol/g)
2	Cu-ZSM-5 ion-exchanged	1.3	120	0.36	140
1.15	Cu-AITS-1 ion-exchanged	2.4	50	0.34	55
0.52	Cu-AITS-1 ion-exchanged	0.8	13	0.16	16
0.44	Cu-AITS-1 ion-exchanged	0.2	5.8	0.08	6.2
0.24	Cu-AITS-1 ion-exchanged	inactive	no NO desorption	n.a.	no O ₂ desorption
2.5	Cu-AITS-1 impregnated	1.9	116	0.30	129
2	Cu-AITS-1 impregnated	2.2	100	0.32	100
1.5	Cu-AITS-1 impregnated	2.9	84	0.36	89

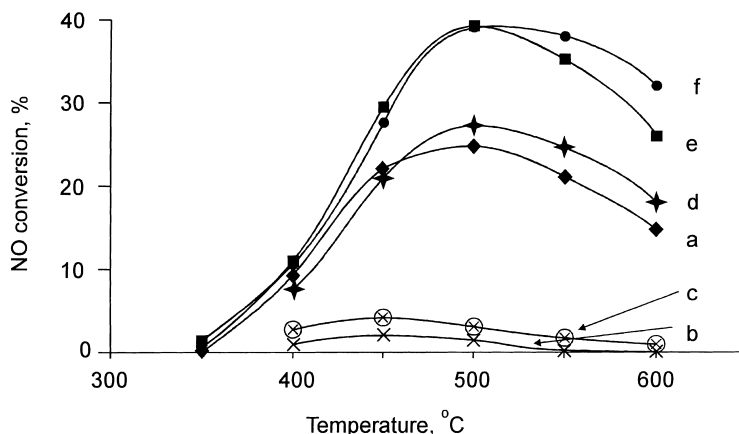


Fig. 1. NO conversions referenced to 0.15 g catalyst (a) 2 wt.% Cu-ZSM-5 ion-exchanged Si/Al = 25, (b) 0.44 wt.% Cu-AITS-1 ion-exchanged Si/Al = 50, (c) 0.52 wt.% Cu-AITS-1 ion-exchanged Si/Al = 50, (d) 1.15 wt.% Cu-AITS-1 ion-exchanged Si/Al = 50, (e) 1.5 wt.% Cu-AITS-1 impregnated Si/Al = 50, f) 2.5 wt.% Cu-AITS-1 impregnated Si/Al = 50.

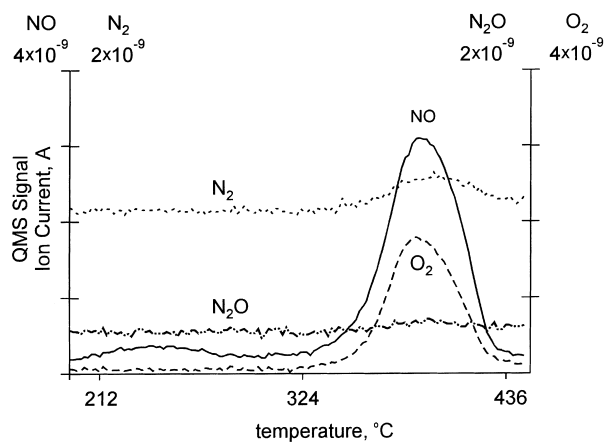


Fig. 2. TPD into Ar starting at 200°C, 1.15 wt.% Cu-AITS-1 ion-exchanged.

described in the previous section the mass balance could be closed to 10%. In the transient kinetic studies the catalyst was heated in argon to the desired temperature, typically to 400°C, and the gas flow was then switched several times for the NO/Ar mixture and back to argon. Contrary to the first contact with NO, these transients could be well reproduced.

3. Results and discussion

Although the results obtained on the 2 wt.% Cu-ZSM-5 catalyst have already been published [5–7], for the sake of easier comparison they are inserted into

the figures and Table 1. In Fig. 1 the stabilized conversions referenced to 0.15 g catalyst are shown. The maximum in NO conversion on the ion-exchanged catalysts increased on increasing copper loading, while it was independent of that measured on impregnated samples. The 0.24 wt.% Cu-AITS-1 was practically inactive. Even on increasing the amount of the catalyst to 0.65 g the conversion was below the detection limit (1% conversion). The conversion below 500°C was practically the same on the three impregnated catalysts. There was a slight difference in the descending side of the temperature-conversion curve above 500°C, where the higher copper loading resulted in higher conversions. In Table 1 apparent

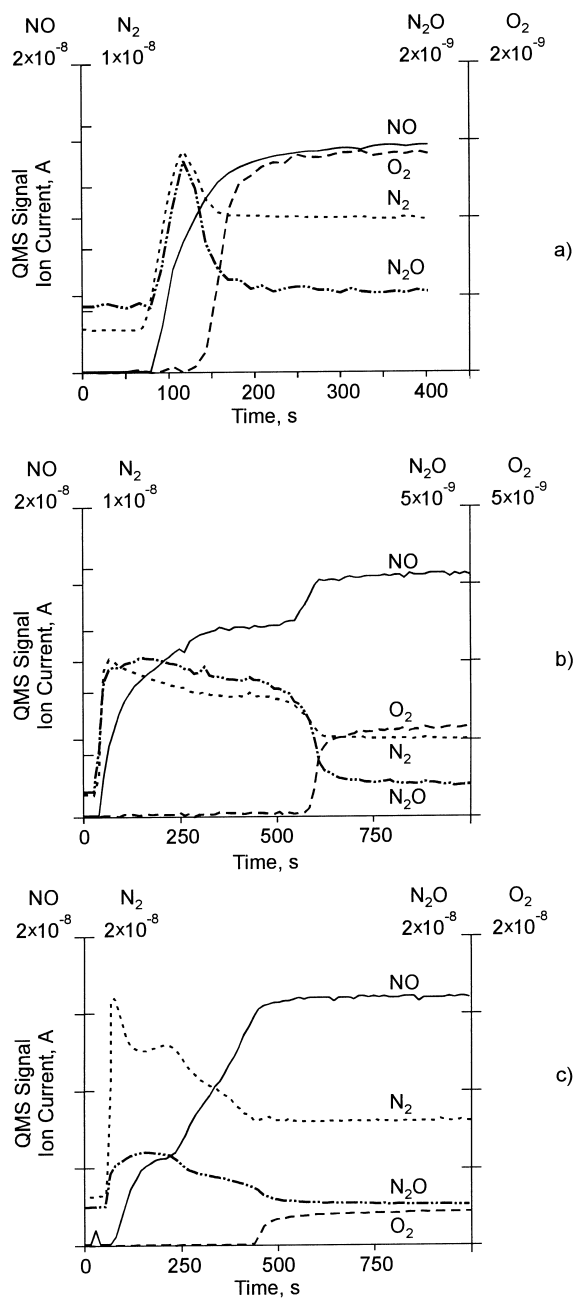


Fig. 3. First contact with NO at 500°C, (a) 2 wt.% Cu-ZSM-5 ion-exchanged, (b) 1.15 wt.% Cu-AITS-1 ion-exchanged, (c) 2.5 wt.% Cu-AITS-1 impregnated.

TOF values at 500°C are presented as converted NO per second and per total copper atoms. Since for the impregnated catalysts the conversion was the same, the apparent TOF decreases on increas-

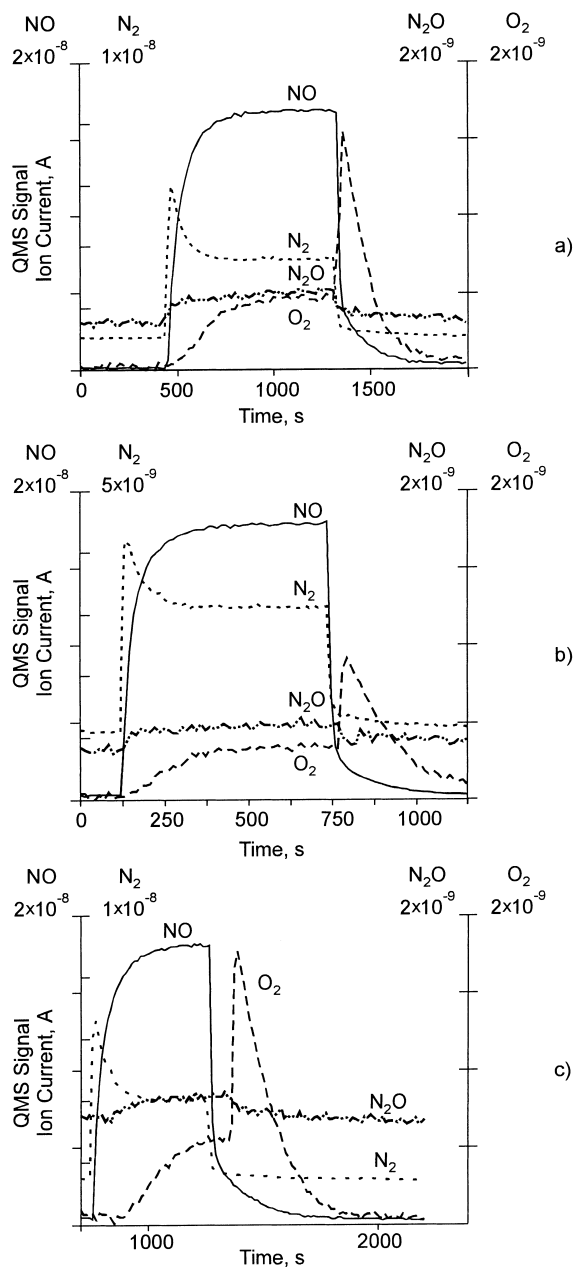


Fig. 4. Isothermal transients at 400°C, (a) 2 wt.% Cu-ZSM-5 ion-exchanged, (b) 1.15 wt.% Cu-AITS-1 ion-exchanged, (c) 2.5 wt.% Cu-AITS-1 impregnated.

ing copper content, but in all the cases it is higher than that measured on Cu-ZSM-5. The apparent TOF on the 100% ion-exchanged Cu-AITS-1 (1.15 wt.%) is about twice of that on the 100% ion-exchange

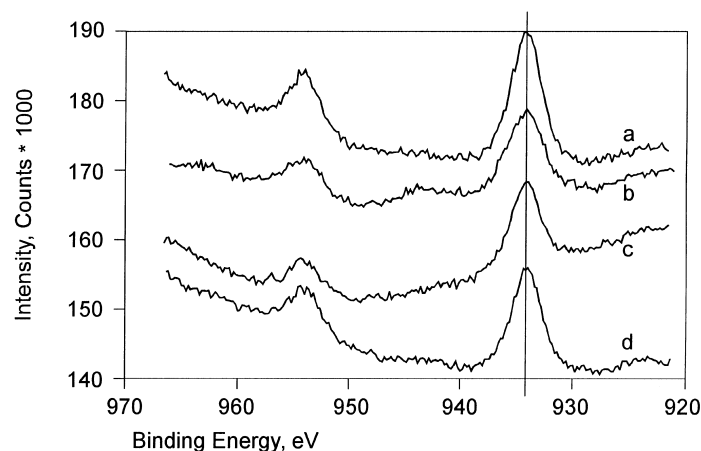


Fig. 5. Typical Cu 2p_{3/2} XPS, (a) 1.5 wt.% Cu-AITS-1 impregnated, fresh, (b) 1.5 wt.% Cu-AITS-1 impregnated, spent, (c) 1.15 wt.% Cu-AITS-1 ion-exchanged, fresh, (d) 1.15 wt.% Cu-AITS-1 ion-exchanged, spent.

Cu-ZSM-5 (2 wt.%). On decreasing the degree of the ion-exchange apparent TOF drops drastically.

NO TPD into Ar carrier gas after cooling the catalyst from the reaction temperature to 200°C in 2 vol.% NO/Ar and purging in Ar is shown in Fig. 2. The TPD was similar for all the catalysts studied except the 0.24 wt.% Cu containing sample, on which no desorption was found. It is typical that a surface complex of NO₃ composition decomposes at about 400°C into nearly equal amounts of NO and O₂ with some traces on N₂, but without any N₂O formation. When the catalysts were cooled from 600°C in air instead of NO, no O₂ desorption was observed during TPD even if the catalysts were cooled to room temperature. Quantitative data are given in Table 1. Including Cu-ZSM-5, the amount of NO formed per total copper is the same for high copper loadings, but below 100% exchange it decreases. This decrease is reflected also in apparent TOF. The difference in apparent TOF with the same amount of the surface complex per copper atoms for the 100% ion-exchanged Cu-AITS-1 and Cu-ZSM-5 indicates that not the number, but the activity of the available copper sites is different. As the crystalline structure of the two zeolites is the same, we assume that the higher activity of Cu-AITS-1 is related to the higher acidity. In a previous study on bimetallic Cu-Pt-ZSM-5 we already observed a decrease in NO decomposition activity on reducing the acidity by sodium exchange [8].

First contacts with NO at 500°C are given in Fig. 3. Rather complicated transients were observed with transient N₂O formation, overshoot in N₂ and delay in O₂ formation, respectively, and steps in the NO QMS signal. In all cases the O₂ signal was delayed until N₂O had been formed. In a preliminary quantitative evaluation no correlation was found between the missing O₂ and the copper content. Similar transients were reported for other copper zeolites [7]. It seems that these transients indicate structural changes in the catalysts and the final catalyst forms in the reaction itself. These transitions were observed only in the very first contact with NO. Any further stepwise change in the NO concentration between 350 and 450°C resulted in transients given in Fig. 4. In the Ar-NO/Ar transient there was an overshoot in N₂ and a delay in O₂ and NO with practically no N₂O formation. At the NO/Ar-Ar transient an overshoot in O₂ and tailing in NO were observed. A semi-quantitative estimation of the adsorbed and desorbed amounts was in agreement with the formation of Cu(O) (NO) (NO₂) intermediate proposed in [5], suggesting the same reaction intermediates in Cu-AITS-1 and Cu-ZSM-5. As in these transients a surface complex is formed, they could be observed only in a relative narrow temperature window. Below 350°C its formation and decomposition is too slow, above 450°C it decomposes (see TPD).

Cu 2p XP spectra shown in Fig. 5 were recorded before and after extensive use in NO decomposi-

tion. In each case the Cu 2p_{3/2} binding energy was 934 ± 0.2 eV, being slightly above 933.6 eV (characteristic of CuO species). In the spent catalysts a shake-up satellite indicative of CuO species, also appeared at 943 eV, indicating a change in the structure of the copper environment. The same time there was a slight increase in the Cu/Si ratio from 1.1% and 0.73% to 1.2% and 0.83% for the 1.5 wt.% Cu impregnated and 1.15 wt.% Cu ion-exchanged catalysts, respectively. This copper enrichment in the reaction is in line with the previous findings, showing changes in the structure of the catalysts in the NO decomposition reaction.

4. Conclusions

The mechanism of the NO decomposition on Cu-AITS-1 catalysts seems to be similar to that on the Cu-ZSM-5 ones, probably because their structures are similar. A possible explanation for the higher apparent TOF on the Cu-AITS-1 at 100% ion exchange might be the higher acidity, which stabilizes a higher fraction of the Cu ions in catalytically active positions. This conclusion is based on the similar NO/Cu values which involves that not the amount but the rate of the decomposition of the complex is different. The

apparent TOF on the impregnated catalysts is also higher, probably also because of the higher acidity.

The NO decomposition itself initiates irreversible changes in the structure of the catalysts. Further research is needed to understand details of these changes.

Acknowledgements

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