

Nitrogen-containing Compounds as a Reductant for the Selective Catalytic Reduction of NO

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When acrylonitrile and other nitrogen-containing compounds are passed over Cu- and H-ZSM-5, they can act as efficient reductants in the selective catalytic reduction of NO by forming NH₃ and carbonaceous deposits through hydrolysis.

New techniques for decreasing the amount of reductants that are required in the selective catalytic reduction of NO (SCR) are needed for its economical operation. Although SCR with NH₃ is a practical reaction, equivalent amounts of NH₃ and NO are necessary because of the stoichiometry of the reaction. In the case of SCR with hydrocarbons, one hydrocarbon molecule can react with two NO molecules.¹ The rate of NO conversion, however, is competitive with the rate of hydrocarbon oxidation by O₂. We focused on certain nitrogen-containing compounds (NC), such as acetonitrile (AN), acrylonitrile (ACN), and *N,N*-dimethylformamide (DMF) for use as reductants. These NCs are expected to exhibit dual character as reductants, because they contain both a nitrogen atom and carbon atoms in a reducing state in one molecule. Miyadera reported high reactivities of AN and HCN with NO_x over Ag/Al₂O₃.² We report here high performances of Cu- and H-ZSM-5 for the reduction of NO_x with NCs, which have a bifunctional role as a reductant.

Cu-exchanged ZSM-5 was prepared by aqueous ion exchange (IE) using Cu(CH₃COO)₂. These catalysts were denoted by the format Cu-ZSM-5-57, where the suffix number indicates the ion exchange ratio. The catalytic reactions were carried out under conventional flow reactor conditions with a flow rate of 160 mL min⁻¹. The NCs were introduced into the reactant gas by passing a predetermined flow rate of He through liquid samples of the NCs, which were maintained at 273 K for AN and DMF and 255 K for ACN. The feed gas was composed of ca. 200 ppm NC, 1150 ppm NO, 0.5% H₂O, and 5% O₂. Temperature-programmed desorption of NH₃ (NH₃-TPD) was carried out for some zeolite materials. The details of the procedure are described elsewhere.³

Figure 1 shows the activity for SCR with ACN over Cu-ZSM-5-57. The reaction proceeded above 400 K, and the conversion of ACN reached 100% at 623 K. N₂ was a dominant nitrogen-containing product, and a small amount of N₂O, HCN, and HNCO were observed as byproducts. HCN and HNCO were produced only below 623 K. The ratio of NO_x consumption and N₂ formation to ACN consumption was greater than unity above 623 K.

Table 1 lists the activity for SCR of various NCs over Cu- and H-ZSM-5. The temperature where NO/NC was a maximum decreased as the IE ratio of the Cu increased. AN and ACN exhibited higher NO/NC and N₂/NC ratios than DMF. However, it was noted that Cu-ZSM-5-165 exhibited the most significant decline in NO/NC at higher temperature. The highest N₂/NC ratio

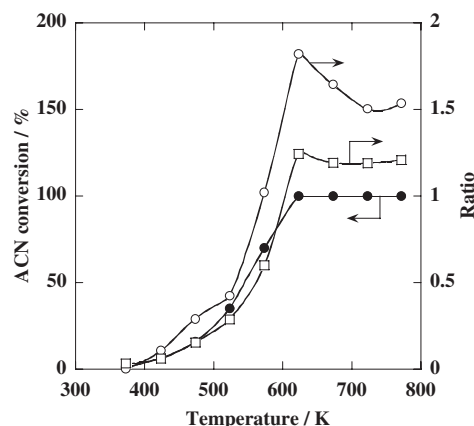


Figure 1. Temperature dependence of the activity of Cu-ZSM-5-57 for NO reduction by ACN. The weight of catalyst was 0.1 g. The feed gas composition was ca. 200 ppm ACN, 1150 ppm NO, 0.5% H₂O and 5% O₂. The total flow rate was 160 mL min⁻¹. The symbols indicate ACN conversion (●) and the ratios of NO_x consumption (○) and N₂ formation (□) to ACN inlet.

was obtained with ACN over H-ZSM-5.

The formation of acrylic acid was observed over H-ZSM-5 during SCR with ACN, and the formation of NH₃ was observed during the reaction of ACN + O₂ + H₂O. These results clearly suggest that ACN was hydrolyzed to acrylic acid and NH₃. The occurrence of SCR with NH₃ over Cu-ZSM-5 and H-ZSM-5 has been reported^{4,5} and it has been suggested that NH₃ adsorbed on H-ZSM-5 exhibits selective reduction activity at temperatures as low as 373 K.⁶ Consequently, it is suspected that the NH₃ formed during the hydrolysis of ACN might act as a reductant.

We examined SCR with acrylic acid over Cu- and H-ZSM-5 by using a feed gas containing 1180 ppm NO, 150 ppm acrylic acid and 5% O₂. The maximum amounts of NO that were con-

Table 1. Activity for SCR with nitrogen-containing compounds

Catalyst	Reductant	Activity			
		Temp./K ^a	NC Conv./%	NO/NC ^b	N ₂ /NC ^c
Cu-ZSM-5-165	AN	623	100	1.7	1.2
	ACN	573	100	1.5	1.2
	DMF	523	99	1.2	1.1
Cu-ZSM-5-57	AN	623	100	1.7	1.2
	ACN	623	100	1.8	1.2
	DMF	673	100	1.5	1.3
H-ZSM-5	AN	673	97	1.9	1.2
	ACN	723	99	1.7	1.4
	DMF	773	100	1.3	1.0

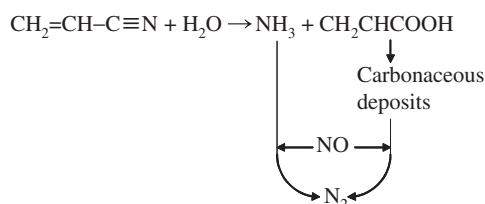
^aAt the temperature for the highest ratio of NO_x consumption/NC consumption.

^bRatio of NO consumption (ppm) to NC consumption (ppm).

^cRatio of N₂ formation (ppm N) to NC consumption (ppm).

verted were 46 ppm (579 K), 132 ppm (723 K) and 82 ppm (723 K) for Cu-ZSM-5-165, Cu-ZSM-5-57, and H-ZSM-5, respectively. Although the conversion of acrylic acid was 100% at the same temperatures, the conversion rates of acrylic acid to CO_x ($= \text{CO}_2 + \text{CO}$) remained at 98, 98, and 78%, corresponding to ratios of 0.3, 0.9, and 0.7 for the conversion of NO with respect to the conversion of acrylic acid to CO_x . The low carbon balance for H-ZSM-5 indicates that significant carbonaceous deposition occurred. Considering the high activity of H-ZSM-5, carbonaceous deposits might be involved as reductants for SCR. One of the co-authors has suggested that carbonaceous deposits can be an active species for NO reduction.⁷

These results suggest that ACN has a bifunctional role as a reductant, i.e., it works for conversion to NH_3 and it works for producing active carbonaceous deposits derived from acrylic acid. A speculative reaction pathway is shown in Scheme 1. The fact that the NO/NC ratios are above unity suggests that the bifunctional role is exhibited by all of the NCs, though there should be differences in the rate of formation of NH_3 and in features of the carbonaceous deposits.



Scheme 1. Speculated reaction pathway.

Figure 2 shows the temperature of 50% ACN conversion, T_{50} , under various conditions. All of the catalysts exhibited a decrease in T_{50} after the addition of H_2O and $\text{H}_2\text{O} + \text{NO}$ to the feed gas. It is suggested that H_2O and NO enhanced the reactivity of the ACN by promoting hydrolysis and by the clearance of acid sites that were covered with NH_3 , respectively. We have

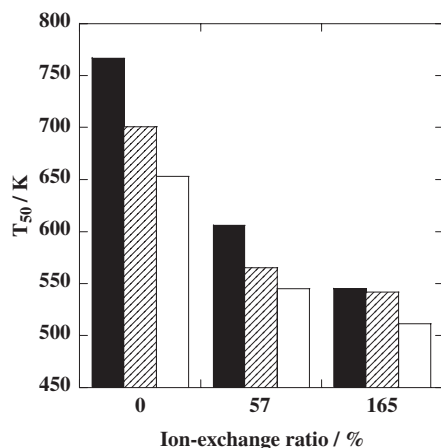


Figure 2. The effect of co-existing gas and ion-exchange ratio on the temperature for 50% ACN conversion. The weight of catalyst was 0.1 g. The feed gas composition was ca. 200 ppm ACN, 5% O_2 , 0 or 0.5% H_2O and 0 or 1150 ppm NO. The total flow rate was 160 mL min^{-1} . The shaded patterns indicate the gas composition: ACN + O_2 (heavy shading), ACN + O_2 + H_2O (light shading), and ACN + O_2 + H_2O + NO (no shading).

previously reported a promotion effect due to the clearance of NH_3 in the decomposition of nitroethene over H-ferrierite.⁸ The differences in T_{50} for each reaction condition decreased as the Cu loading increased, probably as a result of improvements in the oxidation activity. Too much Cu loading may result in an increase in the oxidation activity and a decrease in the active carbonaceous deposits. On the other hand, a lack of Cu loading may result in the rapid accumulation of carbonaceous deposits and the covering of the active sites. An appropriate loading of Cu, probably an IE ratio of ca. 50%, is thought to be the most favorable for achieving a bifunctional role of reductant.

Table 2 lists the NH_3 -TPD results and the activities of three H-form zeolites. H-ZSM-5 showed the highest activity, whereas it is mid-range in terms of the NH_3 -TPD results. It may be necessary to establish the relationship between the acid properties and the carbonaceous deposits to clarify the role of the acid sites in this reaction.

Table 2. NH_3 -TPD results and activity of H-form zeolite for SCR with ACN

Catalyst	Si/Al ratio	NH_3 desorption ^a		Activity ^b			
		amount mmol g^{-1}	Temp. K	Temp. K	Conv. %	NO/ACN	N_2/ACN
H-FER	17	0.57	698	648	63	1.3	0.9
H-ZSM-5	23.8	0.28	637	723	99	1.7	1.4
H-MOR	18.7	0.17	743	748	67	1.3	1.2

^aThe amount of NH_3 desorption for a higher peak.

^bCalculated in the same manner as those in Table 1.

AN is better than ACN as a reductant in terms of their relative toxicities.⁹ However, we confirmed that Cu-ZSM-5 can completely convert ACN in the reaction of $\text{ACN} + \text{O}_2 + \text{H}_2\text{O}$ at 623 K and can run for 100 h without any change in selectivity. Furthermore, there will be no release of NH_3 as a by-product, due to the strong acidity of ZSM-5 and the rapid reaction with NO. The NCs used in this study are disposed of at ca. 21000 t/year into the atmosphere and in waste-treatment sites in Japan. The incineration of these compounds induces almost an equivalent amount of NO_x formation. The work in this paper implies that these wastes could be utilized in the NO_x abatement process. Studies in widening the active temperature range, especially toward lower temperature, are in progress.

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