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Catalytic Removal of Trimethylamine, an Offensive-Odor Component, by Selective Oxidative Decomposition to N_2, CO_2, and H_2O over Copper-Exchanged Zeolites

Hiroki KUWABARA, Toshio OKUHARA,* and Makoto MISONO*
Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Copper-exchanged zeolites catalyzed the oxidative decomposition of $(CH_3)_3N$ to N_2, CO_2, and H_2O. The selectivity to N_2 was 92% and the formation of NOx was less than 5 ppm, when 8000 ppm of $(CH_3)_3N$ with O_2 (20%) was flowed over copper-exchanged Y zeolite at 573 K.

Development of technologies for removal of environmental pollutants such as NO, chlorofluorocarbons (CFC), and offensive-odor components is desirable. Recently, catalytic removal of NO$^{1)}$ or CFC$^{2)}$ has extensively been studied. For deodorization of offensive-odor components like amines, there are few reports on the catalytic combustion using solid catalysts.$^{3)}$ However, the formation of harmful gases, NO and NO_2 (these will be denoted by NOx), is a serious problem.

In the present study, we have studied various solid catalysts for the oxidative decomposition of $(CH_3)_3N$ to N_2, CO_2, and H_2O. We report here the novel catalysis of copper-exchanged zeolites for this reaction.

Ion-exchanged zeolites were prepared with Z-HY-4.8 (Y zeolite: Reference Catalyst of the Catalysis Society of Japan, abbreviated as Y), Z-M-20 (Mordenite: Reference Catalyst of the Catalysis Society of Japan, abbreviated as M), and ZSM-5 25H (Mobil Catalysts Corporation of Japan).$^{4)}$ 1.5wt%Pt-Y (from $[Pt(NH_3)_6]Cl_3$), 1.0wt%Pd-Y (from $Pd(OCOCH_3)_2$), 0.8wt%Ru-Y (from $[Ru(NH_3)_6]Cl_3$), 7.9wt%Cu-Y (from $Cu(OCOCH_3)_2$, exchange level; 81%), 4.7wt%Cu-ZSM-5 (exchange level; 120%), 8.4wt%Cu-M (exchange level; 80%), and 11.4wt%Ce-Y (from $Ce(OCOCH_3)_4$, exchange level; 79%) were used. The following Al_2O_3-supported metals were also used as catalysts; 1wt%Pt/Al_2O_3 (Engelhard, No. 50102), 2.7wt%Pd/Al_2O_3 (Engelhard, No. 8203), 2.5wt%Ru/Al_2O_3 (prepared from $Ru_3(CO)_{12}$ and γ-$Al_2O_3$$^{5)}$), and 5wt%Cu/$Al_2O_3$ (prepared by impregnation method with $Cu(OCOCH_3)_2$ and γ-Al_2O_3).

The reaction was performed in a flow reactor at 523 - 673 K under one atmospheric pressure after the catalysts were pretreated at 773 K in a flow of He. The feed gas (50 $cm^3 \cdot min^{-1}$) consists of $(CH_3)_3N$ (8000 ppm), O_2 (20%), and He (balance). The gas at the outlet of the reactor was analyzed by GC (Shimadzu GC-8A) using Unicarbon B-2000 ($(CH_3)_{3-x}H_xN$), Porapak Q (N_2O and CO_2), and Molecular sieve 5A (N_2, O_2, and CO), and by a NOx meter (Yanaco, ELC-11A) for NO and NO_2.

The catalytic activity was evaluated from the %-conversion of $(CH_3)_3N$ to CO_2 at 523 K after about 2 h, since no large changes of the conversion were observed for a few hours. The selectivity was measured at conversions higher than 70% and at temperatures higher than 573 K by the following reasons. Under these conditions, the N-balance in the gas phase was nearly 100% and independent of the conversion. At low conversion levels and low temperatures, the intermediate products with high boiling points such as $(CH_3)_3NO$ (sublimation temperature = 453 K) were formed and were deposited at the outlet of the reactor, resulting in the poor N-balance. The formation of $(CH_3)_2NH$ and CH_3NH_2 was less than 1%. It was observed that the conversion to CO_2 increased linearly with the W/F (catalyst weight/flow rate) at 523 K.

Various oxides catalyzed this reaction. The activity (per unit surface area) was in the following order; Co_3O_4 > Mn_2O_3 > Cr_2O_3 > CuO > Fe_2O_3 > NiO, which is in agreement with that for oxidation of propene.[6)] The main product over these oxides was N_2O (43 - 85% at 673 K), except for CuO which produced mainly N_2 (56%). NOx was considerably formed (1.3 - 26%)

Table 1. Activities and Selectivities for Reaction of $(CH_3)_3N$ + O_2 over Various Solid Catalysts

Catalyst	Activity[a)]	Selectivity[b)]/%			Conversion[b)]/%
		N_2	N_2O	NOx	
1.0wt%Pt/Al_2O_3	4.9	11.5	86.8	1.7	100
2.7wt%Pd/Al_2O_3	34.6	47.5	50.6	1.9	100
2.5wt%Ru/Al_2O_3	4.1	72.3	25.6	2.1	100
5.0wt%Cu/Al_2O_3	12.1	85.2	14.6	0.2	100
1.5wt%Pt-Y	35.0	18.5	80.9	0.6	100
1.0wt%Pd-Y	35.0	45.4	52.9	1.7	100
0.8wt%Ru-Y	2.1	87.1	11.0	1.9	69
7.9wt%Cu-Y	5.3	92.6	7.3	0.1	80

a) Unit: 10^{-4} mol g^{-1} h^{-1} at 523 K. b) On the basis of N atom. The selectivity was measured at 573 K, at which the N-balance was nearly 100% (see text).

over these oxides.

Catalytic activities and selectivities of Al_2O_3-supported metals and ion-exchanged zeolites are summarized in Table 1. With both types of catalysts, the selectivity to N_2 decreased in the order of Cu > Ru > Pd > Pt. It is noteworthy that Cu-Y was highly selective for the N_2 formation (92.6% at 573 K) and the formation of NOx was suppressed to 0.08%, which corresponds to about 5 ppm.

The selectivities of ion-exchanged zeolites at 673 K are shown in Fig. 1. The selectivity to N_2 over Cu-Y was high even at 673 K and the concentration of NOx formed was very low (about 7 ppm), while NOx was considerably formed over Pt-Y, Pd-Y, and Ru-Y. Besides Cu-Y, 4.7wt%Cu-ZSM-5, 8.4wt%Cu-M also exhibited the high selectivity to N_2. The activities of Cu-ZSM-5 and Cu-M were similar to that of 7.9wt%Cu-Y. Furthermore, it was observed that 11.4wt%Ce-Y was also highly selective to N_2; the products were N_2 (98.1%), N_2O (1.8%), and NOx (0.1%).

The typical time course of %-conversions to CO_2, N_2, and N_2O over Cu-Y are shown in Fig. 2. The conversions were nearly constant for at least 7 h at 673 K, indicating that this catalyst was stable under these reaction conditions.

The reaction order with respect to the pressure of $(CH_3)_3N$ was about 0.7 over 7.9wt%Cu-Y. The reaction order was similar for less selective Pd/Al_2O_3. The order in the O_2 pressure was 0.6 in the range of 2 - 5% and

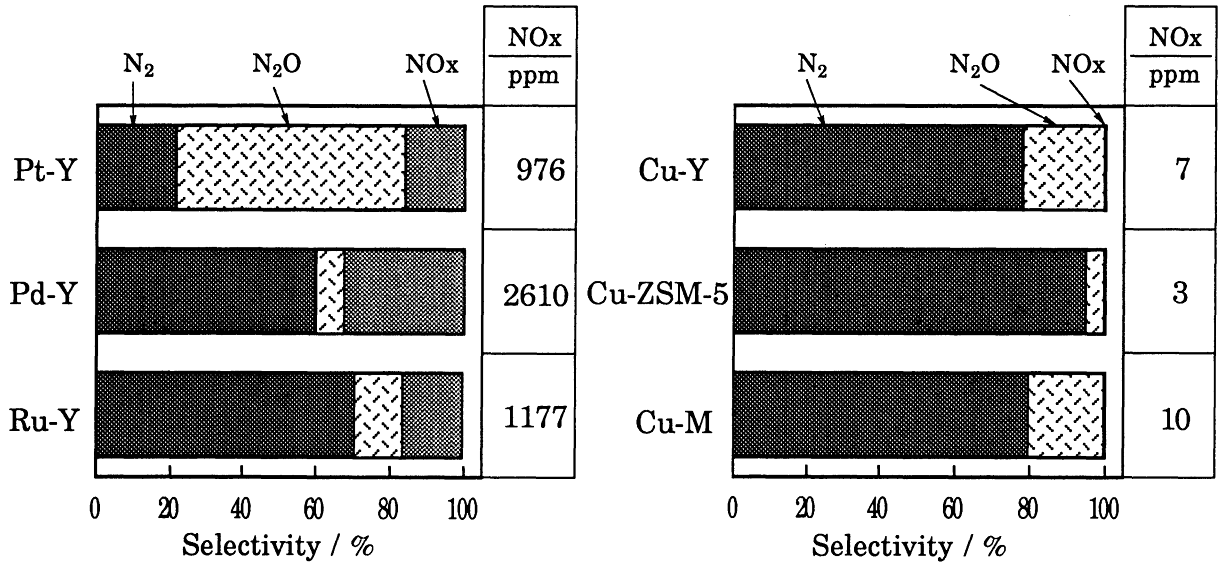

Fig. 1. Selectivities of metal-exchanged zeolites for $(CH_3)_3N + O_2$ reaction at 673 K. $(CH_3)_3N$; 8000 ppm, O_2; 20%. Conversions were 100% for all catalysts. The concentration of NOx was shown in the right frames.

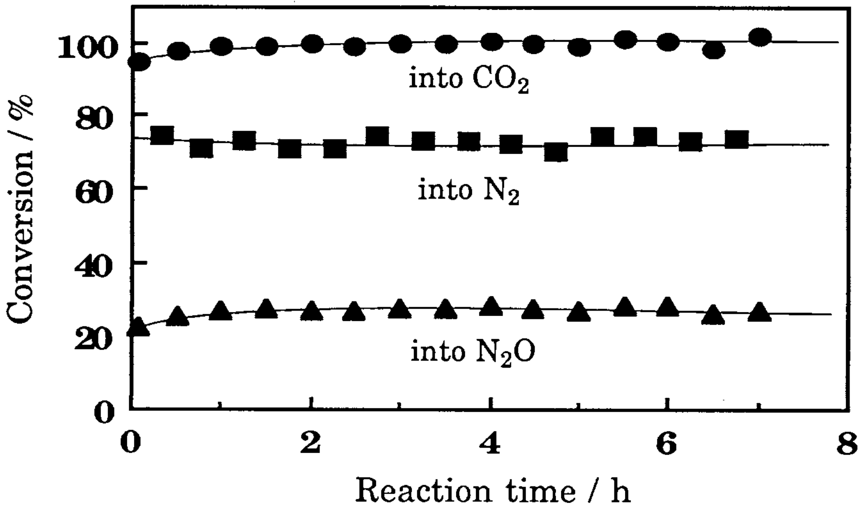

Fig. 2. Typical time course of $(CH_3)_3N$ + O_2 reaction over 7.9wt%Cu-Y at 673 K. Catalyst; 1.0 g, $(CH_3)_3N$; 8000 ppm, O_2; 20%.

zero order above 10% of O_2 over Cu-Y, while it was zero for Pd/Al_2O_3 in the range of 2 - 20% O_2. This suggests that the adsorption of oxygen is weak on the Cu ion. This may be one reason for the selective formation of N_2 in the oxidative decomposition of $(CH_3)_3N$.

Since copper-exchanged zeolites are known to be active for selective catalytic reduction of NOx with hydrocarbons in the presence of O_2,1) the reduction of NO by $(CH_3)_3N$ in the presence of O_2 was examined over 7.9wt%Cu-Y. When NO (500 ppm) was added to the feed ($(CH_3)_3N$; 3000 ppm and O_2; 20%) at 673 K, the nitrogen-containing molecules at the outlet of the reactor were N_2 (83%), N_2O (17%), and NOx (0.1%). This fact shows that this catalyst is also efficient for the removal of the mixture of NOx and $(CH_3)_3N$.

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