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Approach to De-NOx-ing Photocatalysis. Photocatalytic Decomposition of NO on Cu^+/SiO_2 Catalyst Prepared via Ion-exchange Method

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Cu^{2+} ions supported onto SiO_2 (Cu^{2+}/SiO_2) prepared by an ion-exchange method are reduced to Cu^+ ions when the Cu^{2+}/SiO_2 sample is evacuated above 573 K. Cu^+/SiO_2 catalyst decomposes NO photocatalytically and stoichiometrically at 275 K. The excited state of the Cu^+ ions plays a significant role in the photocatalytic decomposition of NO on the Cu^+/SiO_2 catalyst.

The reduction of global air pollution caused by NOx is currently an urgent and demanding challenge. Ion-exchanged Cu^+/zeolite catalysts have attracted a great deal of attention as potential catalysts for the direct decomposition of NOx into N_2 and O_2.[1,2] On the other hand, utilization of photocatalytic processes in gas-solid systems also seems promising.[3] We now report that Cu^{2+} ions supported on SiO_2 (Cu^{2+}/SiO_2) prepared by an ion-exchange method are reduced to Cu^+ when Cu^{2+}/SiO_2 samples are evacuated at the temperatures above 573 K, and thus prepared Cu^+/SiO_2 catalysts decompose NO photocatalytically and stoichiometrically at 275 K.

Cu^{2+}/SiO_2 samples were prepared by the following ion-exchange procedure: first, exchange of the surface OH groups on SiO_2 by treatment with ammonia, i. e., $\text{-Si-OH} + NH_3 \longrightarrow \text{-Si-O}^-NH_4^+$, secondly followed by competitive exchange with aqueous $(Cu(NH_3)_4)^{2+}$ solution (0.02-0.05 M), while the solution pH was held between 10.5 and 11.5. The exchanged sample was then centrifuged and washed with aqueous ammonia. After the exchange, the Cu^{2+}/SiO_2 sample (1.1 Cu wt%) was obtained, then dried in air at 353 K and calcined in oxygen at 693 K. Prior to the measurements, the samples were pretreated as follows: they were degassed at 673 K for 1 h, heated at the same temperature under 20 Torr O_2 for 1 h, and, finally degassed at the desired temperature. Photoluminescence spectra of the catalysts and the lifetimes were recorded at 77 K with a Shimadzu RF-501 spectrofluorophotometer and an apparatus for lifetime measurements, respectively.4) Photoreactions were carried out at 275 K using a Toshiba (SHL-100UV) mercury lamp ($\lambda > 270$ nm). Reaction products were analyzed by gas chromatography. ESR spectra were measured at 77 K with a Jeol (JES-RE2X) spectrometer (X-band).

As shown in Fig. 1, the increase in the degassing temperature of the Cu^{2+}/SiO_2 samples causes a decrease in the intensity of the ESR signal due to Cu^{2+} ions (curve: a). No ESR signal can be seen for the samples which were evacuated at temperatures higher than 673 K, and for only these catalysts (Cu^{+}/SiO_2), photoluminescence of the catalyst becomes observable when it is excited at around 300 nm beam. Figure 2 shows a typical photoluminescence spectrum at 77 K of the Cu^{+}/SiO_2 catalyst which was prepared by evacuation of the Cu^{2+}/SiO_2 sample at 873 K under vacuum. Absorption of the catalyst at around 300 nm and photoluminescence at around 520 nm are attributed to the electronic transition in the Cu^{+}–Cu^{+} dimers, i. e., ($3d^{10} \rightarrow 3d^9 4s$) transition and ($4s\sigma \rightarrow 4s\sigma^*$) radiative transition, respectively.5,6) The desorption of NO by progressive heating of the system in vacuum from 273 to 773 K (NO TPD) after a complete quenching of the photoluminescence by added NO exhibits that two NO molecules are adsorbed on the 520 nm emitting sites by a weak interaction, supporting the assignment mentioned above.8)

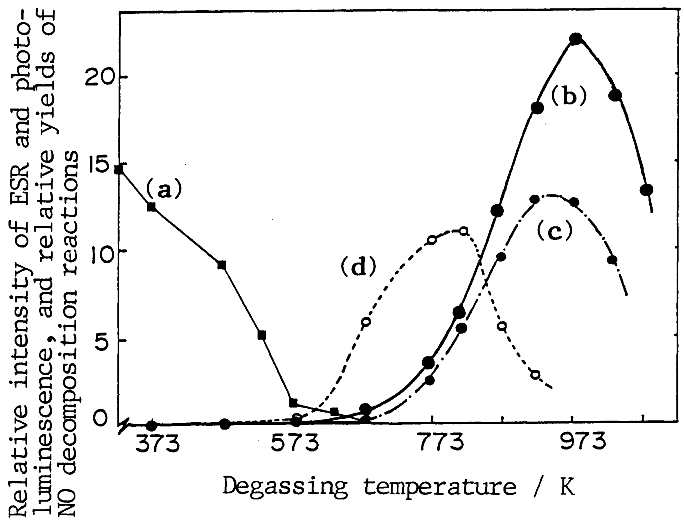

Fig. 1. Effects of the evacuation temperature of Cu^{2+}/SiO_2 samples upon the ESR signal due to Cu^{2+} ions (a), the intensity of photoluminescence of the Cu^{+}/SiO_2 catalyst (b), the yields of photocatalytic decomposition of NO at 275 K (c), and of catalytic decomposition of NO at 673 K (d) on the Cu^{+}/SiO_2 catalyst.

These results suggest that degassing of the Cu^{2+}/SiO_2 sample at high temperature causes a reduction of Cu^{2+} ions to Cu^{+} ions. A decrease in the intensity of the ESR signal due to Cu^{2+} ions upon the thermalevacuation treatment of the sample at high temperature has been widely attributed to the chemical reduction of Cu^{2+} to Cu^{+}.[9)] As seen in Fig. 1 (curve: b), the intensity of the photoluminescence due to Cu^{+} ions increases with the degassing temperature, passing through a maximum at around 973 K, and then decreases.

As shown in Fig. 2, the addition of NO to the Cu^{+}/SiO_2 catalyst leads to a drastic quenching of the photoluminescence in both the intensity and the lifetime. These results clearly indicate that the Cu^{+}/SiO_2 catalyst strongly interacts with NO molecules not only in the ground state but also in the excited state. In fact, UV irradiation of the Cu^{+}/SiO_2 catalyst in the presence of NO at 275 K was found to lead to photocatalytic decomposition of NO into N_2 and O_2 with a good stoichiometry. As shown in Fig. 3, decomposition of NO proceeds linearly with UV irradiation time. The yields of the photocatalytic decomposition of NO (Fig. 1, curve: c), like photoluminescence (curve: b), increases with the evacuation temperature of the original Cu^{2+}/SiO_2 samples, passing through a maximum at 973 K, and then decreases. A good parallel relationship between the intensity of the photoluminescence and the yields of photocatalytic reaction clearly indicates that the excited state ($4s\sigma$) of $Cu^{+}-Cu^{+}$ dimers on SiO_2 plays a significant role in the photocatalytic decomposition of NO on the Cu^{+}/SiO_2 catalyst. It is likely that an electron transfer from the excited state of copper ion into an anti-bonding π orbital of NO is involved in the photocatalytic decomposition of NO. This electron exchange would weaken

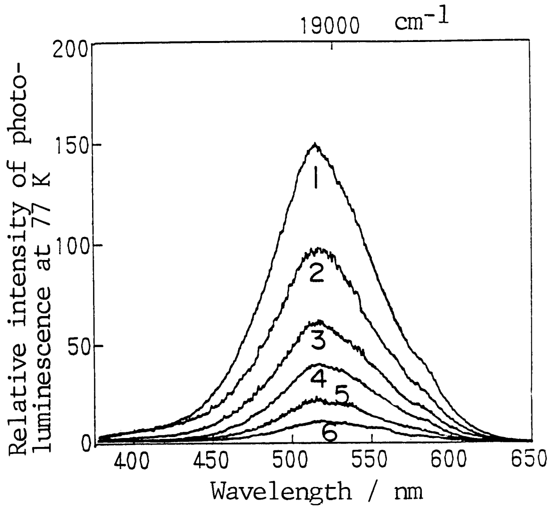

Fig. 2. Photoluminescence of the Cu^{+}/SiO_2 catalyst at 77 K (1), and the effect of NO added.
(NO in Torr, 2: 0.028, 3: 0.12, 4: 1.1, 5: 6.9, 6: 20)

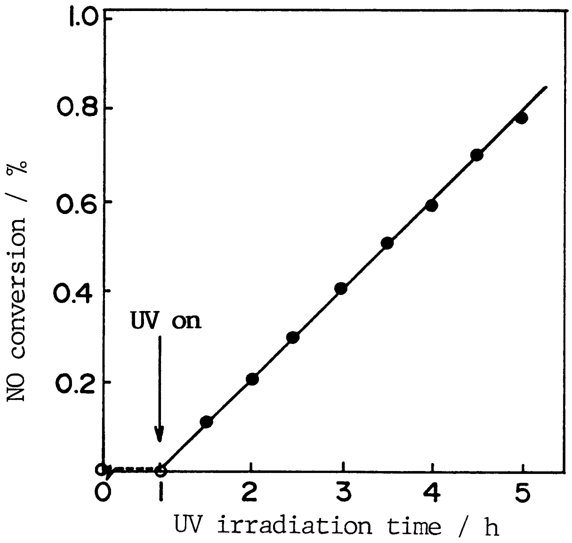

Fig. 3. Time profile of the photocatalytic decomposition of NO at 275 K on the Cu^{+}/SiO_2 catalyst.
(amount of NO, 6.7×10^{-5} mol/g-catal.)

the N - O bond and initiate decomposition of NO.

Being in agreement with the previous reports,$^{1,2)}$ catalytic decomposition of NO was found to proceed on the Cu^+/SiO_2 catalyst above 673 K to produce N_2 and O_2. As shown in Fig. 1 (curve: d), the efficiency of the catalytic decomposition of NO increases with the evacuation temperature of the original Cu^{2+}/SiO_2 sample, passing through a maximum at around 823 K, and then decreases. Thus, the optimal activity for the catalytic reaction has been achieved with the catalyst which had been obtained by the evacuation of the Cu^{2+}/SiO_2 sample at 823 K. This is lower than the temperature producing an optimal Cu^+ concentration of the catalyst by about 150 K. This suggests that, unlike photocatalytic activity, not only Cu^+ ions but also other unkown species such as Cu^{2+} ions which could not be observed by ESR might be associated with the catalytic activity.

Although a number of photocatalytic systems have been reported, most works have been done on semiconducting materials such as TiO_2 and ZnS. The present results obtained on the Cu^+/SiO_2 catalyst suggest the possibility of its utilization as a new promising type of photocatalytic material.

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