# The Effect of the Si/Al Ratio on the Photoluminescence Properties of Cu(I)SAPO-5 Catalysts

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Cu(I)SAPO-5 catalysts prepared by a combination of ion-exchange and an evacuation treatment at high temperatures were found to exhibit a fairly high photocatalytic activity for the decomposition of $N_2O$ into $N_2$ and $O_2$ under UV-light irradiation at 298 K. In contrast to other Cu(I) catalysts, such as Cu(I)ZSM-5, the coexistence of $H_2O$ in the reaction system of the Cu(I)SAPO-5 scarcely affected the photocatalytic activity. The relationship between the photoluminescence behavior due to the presence of Cu(I) species and the photocatalytic activity of Cu(I)SAPO-5 have been investigated as a function of the Si/Al ratio, showing that the excited state of the Cu(I) species plays a significant role in the photocatalytic reaction as an active site for the reaction.

Cu(I)-zeolite catalysts have attracted much attention due to their high catalytic performance in the direct decomposition of $NO_x$ into $N_2$ and $O_2$.[1–4] However, their lack of stability under hydrothermal conditions has been an unavoidable limitation. Meanwhile, silicoaluminophosphates (SAPO) have been widely used as acidic catalysts since their first synthesis in 1982.[5] In fact, B. I. Palella et al.[6] have found that Cu(I)SAPO-34 with the same Chabasite structures as ZSM-5 shows a higher structural stability under hydrothermal conditions than Cu(I)ZSM-5. Ishihara et al.[7,8] have also reported the high stability of CuSAPO-34 as compared with CuZSM-5 for NO conversion. However, thus far, there have been few reports on the photoluminescence properties and the photocatalytic activity of Cu(I)SAPO-5 catalysts.

In the present study, we have prepared various Cu(I)SAPO-5 catalysts with different Si/Al ratios and studied their photoluminescence properties as well as photocatalytic activities for the decomposition of $N_2O$ as a function of the Si/Al ratio. APO($n = 0$)/SAPO-5 was prepared from a reaction gel ($SiO_2$:$Al_2O_3$:$P_2O_5$:Triethylamine $= n$:1:1:1; $n = 0.0$–$1.2$) according to the literature.[9] It was found that all of the synthesized APO/SAPO-5 samples show XRD patterns attributed to characteristic AFI structure topology. These APO/SAPO-5 samples were ion exchanged with $Cu(NO_3)_2$ aqueous solution to produce Cu(II)SAPO-5 having different Si/Al ratios. The Cu(I)SAPO-5 catalysts were prepared by thermo-vacuum treatment of these samples at 1173 K for 1 h to completely reduce the Cu(II) to Cu(I). The Cu(I)ZSM-5 (Si/Al = 11.9) was prepared in the way described elsewhere.[1,2] The photocatalytic decomposition reactions of $N_2O$ were carried out under UV-light irradiation of Cu(I) catalysts (50 mg) in the presence of $N_2O$ (10 Torr) with a high pressure Hg mercury lamp ($\lambda > 200$ nm) through a UV-cut filter ($\lambda > 250$ nm) at 298 K. The reaction products were analyzed by gas chromatography (Shimadzu GC-7A). The photoluminescence spectra of Cu(I)SAPO-5 were recorded at 298 K with a spectrofluorimeter (Spex Fluorolog II) at an excitation wavelength of 285 nm. The Cu content of the catalysts was determined to be around 1 wt % as Cu metal by atomic absorption flame emission spectrophotometer (Shimadzu AA-6400F) and the ESR spectra were recorded at 77 K using a JES-RE2X spectrometer operating in the X-band mode.

The ESR spectrum (not shown here for clarity) of the dehydrated Cu(II)APO-5 samples show the Cu(II) species signals ($g_{\parallel} = 2.308$(162G), $g_{\perp} = 2.073$), while the dehydrated Cu(II)-SAPO-5 samples show the signals of two Cu(II) species with parameter sets of $g_{\parallel 1} = 2.315$(150G), $g_{\perp 1} = 2.065$ and $g_{\parallel 2} = 2.330$(145G), $g_{\perp 2} = 2.080$, respectively. The former, which is similar to the ESR parameters for Cu(II)APO-5, can be assigned to the square pyramidal Cu(II) ions[10] exchanged with the H proton of the Al(P)–OH groups while the later can be assigned to strongly distorted square pyramidal Cu(II) ions exchanged with the Brönsted acid sites of the bridging hydroxy groups (Si–OH–Al) generated after the addition of Si.

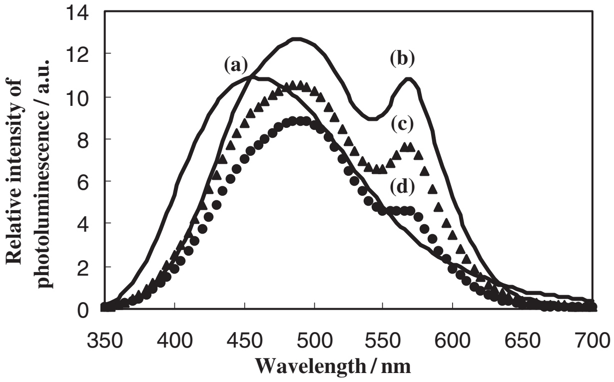

**Figure 1.** The observed photoluminescence spectra of (a) Cu(I)APO-5 and (b) Cu(I)SAPO-5 (Si/Al = 0.45), and the effect of the addition of (c) 0.3 Torr $N_2O$ and (d) 0.6 Torr $O_2$ on the photoluminescence of Cu(I)SAPO-5.

Cu(I)APO-5 (Si/Al = 0) exhibits only one photoluminescence band at around 460 nm, while Cu(I)SAPO-5 shows two main bands at around 490 and 570 nm with a shoulder at around 460 nm, as shown in Figure 1. Considering that there is only one Cu(II) species present in APO-5 zeolites, according to the ESR signals, the photoluminescence band at 460 nm can be assigned to the radiative deactivation process of the photoexcited Cu(I) ions ($3d^9 4s^1 \rightarrow 3d^{10}$) reduced from the Cu(II) ions exchanged with the H protons of the Al(P)–OH groups of the SAPO/APO-5 surface. It should be noted that Cu(I)APO-5 (Si/Al = 0) shows no activity for $N_2O$ decomposition in spite of a fairly strong photoluminescence observed at around 460 nm, indicating that Cu ions exchanged with the hydroxy of the surface of

SAPO/APO-5 show little contribution to the photocatalytic $N_2O$ decomposition, as shown in Figure 2. On the other hand, the photoluminescence bands at 490 nm and 570 nm can be assigned to the radiative deactivation process of two kinds of photoexcited Cu(I) species $\alpha$ and $\beta$, respectively, which were reduced from those Cu(II) ions exchanged with the bridging hydroxy groups (Si–OH–Al). According to the previous photoluminescence study on Cu(I)ZSM-5,[11] Cu(I) species $\beta$ were assumed to be coordinated by $-SiO(AlOPOAlO)_nSi-$ groups having relatively larger number of n as compared to Cu(I) species $\alpha$. Also, the addition of $N_2O$ onto the Cu(I)SAPO-5 catalysts led to the efficient quenching of the photoluminescence, as shown in Figure 1c. These results clearly suggest that $N_2O$ molecules interact with the photoexcited state of the Cu(I) ions. In fact, we found that UV-light irradiation of Cu(I)SAPO-5 in the presence of $N_2O$ led to the efficient decomposition of $N_2O$ into $N_2$ and $O_2$. As shown in Figure 3, the reaction proceeds linearly against UV-light irradiation after irradiation for 0.5 h and, after prolonged irradiation, the amount of the photogenerated $N_2$ (or $O_2$) from $N_2O$ exceeded the amount of Cu(I) ions of the catalysts (1.38 mol $N_2$/mol Cu, 8 h), showing the photoreaction proceeds catalytically under UV-light irradiation. Furthermore, the photocatalytic activitiy of Cu(I)SAPO-5 shows a good parallel relationship against the intensity of the photoluminescence band at around 490 nm due to Cu(I) species $\alpha$, as shown in Figure 2. Figure 1d shows that the addition of $O_2$ caused the species $\beta$ to be quenched more easily than the species $\alpha$ when comparing their relative photoluminescence intensity before and after quenching, indicating that photoexcited species $\beta$ interact more easily with the $O_2$ formed. This interaction, maybe induced the deactivation of both of species $\alpha$ and $\beta$, while species $\beta$ were deactivated more easily than species $\alpha$ and led to a decrease in the reaction rate caused by the output of $O_2$ in the first 0.5 h of the decomposition of $N_2O$, as shown in Figure 3a.

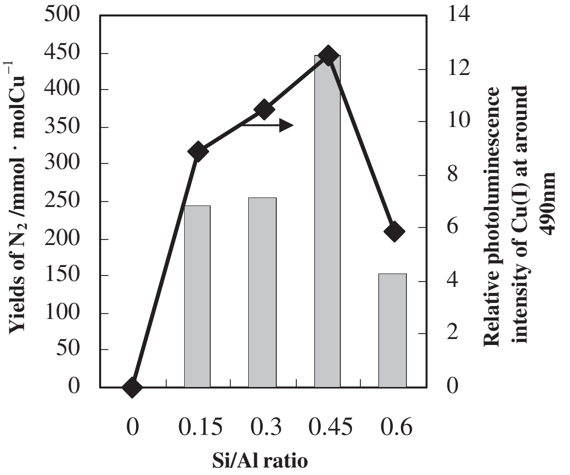

**Figure 2.** The effects of the Si/Al ratios of Cu(I)SAPO-5 catalysts on the yields of $N_2$ in the photocatalytic decomposition of $N_2O$ and the relative intensity of photoluminescence of these Cu(I)SAPO-5 due to the presence of the Cu(I) species $\alpha$.

The photoexcited Cu(I) species $\alpha$ was, thus, shown to play a significant role in the photocatalytic reaction as an stable active site for the decomposition of $N_2O$. Although the photoluminescence intensity of the Cu(I) species $\alpha$ increases with an increase in the Si/Al ratio until it reaches a maximum at a ratio of 0.45, further addition of Si to the SAPO-5 zeolite led to low photocatalytic activity and a decrease in the photoluminescence intensity, as observed for Cu(I)SAPO-5 (Si/Al = 0.6) in Figure 2. This phenomena may be associated with the fact that the increase in Si content produces a large amount of silicious islands or silanol bonds (Si–O–Si), which prevent the acid sites from being exchanged with the Cu(II) ions and, therefore, leading to low photocatalytic activity.

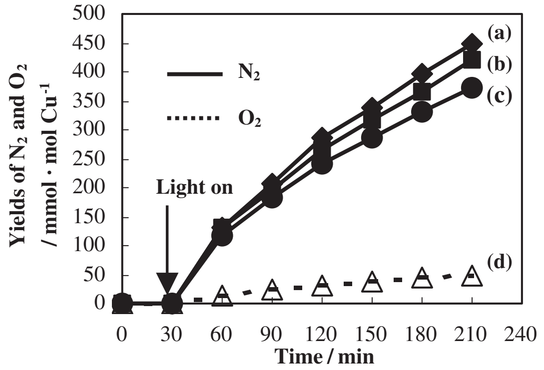

**Figure 3.** Reaction time profiles of the photocatalytic decomposition of $N_2O$ into (a) $N_2$ and (d) $O_2$ on Cu(I)SAPO-5(Si/Al = 0.45) and the effect of the coexistence of (b) 4% $H_2O$ vapor and (c) 10% $H_2O$ vapor on the photocatalytic reaction.

As shown in Figure 3, Cu(I)SAPO-5 photocatalysts have exhibited a fairly high photocatalytic activity for the decomposition of $N_2O$ into $N_2$ and $O_2$ at 298 K. $N_2$ yield after 3 h irradiation was found to be 447 mmol $N_2$/mol Cu for Cu(I)SAPO-5 and 385 mmol $N_2$/mol Cu for Cu(I)ZSM-5. Most importantly, the coexistence of 4% $H_2O$ vapor leads only 6% deactivation for Cu(I)SAPO-5 but 27% deactivation for Cu(I)ZSM-5 based on the yields of $N_2$. The Cu(I) species $\alpha$ reduced from the Cu(II) ions exchanged with the bridging hydroxy groups (Si–OH–Al), and characterized by the photoluminescence at around 490 nm, was found to play an important role as a stable active species in the photocatalytic decomposition of $N_2O$. However, when the Cu(I) species were reduced from Cu(II) ions exchanged with the hydroxyl groups on the APO/SAPO surface, it contributed little toward this reaction in spite of their fairly strong photoluminescence at around 460 nm.

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