Characterization of Fe-Oxide Species Prepared onto ZSM-5 Zeolites and Their Role in the Photocatalytic Decomposition of N_2O into N_2 and O_2

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Investigations on the effect of the local structures on Fe-ZSM-5 zeolites by means of ESR, UV–Vis absorption and XRD measurements have shown that Fe-ZSM-5 with low Si/Al ratios includes highly dispersed Fe-oxides with tetrahedral and distorted tetrahedral coordinations, while the latter species could not be observed in Fe-ZSM-5 with high Si/Al ratios. Moreover, the photocatalytic decomposition of N_2O into N_2 and O_2 was found to proceed on Fe-ZSM-5 having low Si/Al ratios with a good linearity against the UV-irradiation time and a good stoichiometry. It was also observed that the photocatalytic efficiency decreased when the Si/Al ratio was increased. These results clearly suggest that a highly dispersed distorted tetrahedrally coordinated Fe-oxide species plays a significant role in the photocatalytic decomposition of N_2O into N_2 and O_2.

Fe-ZSM-5 catalysts have been widely investigated for such significant reactions as the SCR reaction of NO,[1] partial oxidation of benzene to phenol[2] and N_2O decomposition.[3] It is, therefore, very important to clarify the local structure of the Fe-oxide species on Fe-ZSM-5 and their role in these catalytic reactions. Recently, the photocatalytic decomposition of N_2O on various transition metal ions such as Cu,[4] Pr[5] and Ag[6] exchanged on pentasil-zeolites has been observed and the active sites were identified. Thus, a clarification of the relationship between the local structure of the Fe-oxide species in these zeolites and the catalytic and/or photocatalytic reactivity is vital yet little known.

In the present study, we have prepared Fe-ZSM-5 with different Si/Al ratios by a solid-state ion exchange method. This method enables polycharged ions such as Fe^{3+} or V^{5+} ions to be easily introduced into high silica pentasil-zeolites, and the effect of the Si/Al ratios on the local structure of the Fe-ZSM-5 was also investigated by means of UV–Vis and ESR spectroscopic methods. Special attention was focused on the relationship between the local structure of the Fe-ZSM-5 catalysts having different Si/Al ratios and the photocatalytic reactivity for the decomposition of N_2O into N_2 and O_2.

H-ZSM-5 zeolites having different Si/Al ratios (20, 34, 950) were supplied by Tosoh Co. Fe-ZSM-5 samples (1.0 Fe wt%) were prepared by the solid-state reaction of H-ZSM-5 with $FeCl_3$. The samples were calcined at 823 K for 9 h under ambient conditions. $FeCl_3$ was sublimed into H-ZSM-5 from the solid phase, where it reacted with the zeolite protons.[7] Prior to spectroscopic measurements and the photocatalytic decomposition reactions, the samples (100 mg) were calcined in dry air at 673 K for 1 h and then degassed at 473 K for 2 h. The XRD and UV–Vis spectra were measured at room temperature and the ESR spectra were recorded in the X-band at 77 K. The photocatalytic decomposition reaction of N_2O on Fe-ZSM-5 was carried out under UV-irradiation with a high pressure mercury lamp at 298 K. The products were analyzed by gaschromatography.

XRD measurements showed that, after calcination at 823 K, all Fe-ZSM-5 zeolites exhibited the same XRD pattern as that of the H-ZSM-5 zeolite, indicating that Fe-ZSM-5 maintains the MFI structure.

Figure 1 shows the UV–Vis absorption spectra of Fe-ZSM-5 with Si/Al ratios of 950 and 20. Fe-ZSM-5 with a Si/Al ratio of 950 exhibits an intense absorption at around 250 nm due to the charge transfer (CT) transition from the ligand, O^{2-}, to Fe^{3+} of the isolated Fe-oxide species having tetrahedral or octahedral coordination (X) in Figure 1 (a). On the other hand, as can be seen in Figure 1 (b), the absorption spectrum of Fe-ZSM-5 with a Si/Al ratio of 20 can be deconvoluted into three components which show the absorption maximum at around 250 nm (X), 360 nm (Y), and 550 nm (Z), respectively. Fe-ZSM-5 having a Si/Al ratio of 20 exhibits a broad shoulder peak at around 360 nm (Y) due to the presence of small cluster Fe-oxide particles interacting with the Al ions on the catalyst. The broad peak at around 550 nm (Z) can be attributed to the bulk Fe_2O_3, in addition to the absorption at around 250 nm (X).[8] Thus, Fe-oxides were stabilized in different local structures from the isolated Fe-oxide species to large clusters within Fe-ZSM-5, depending on the Si/Al ratios.

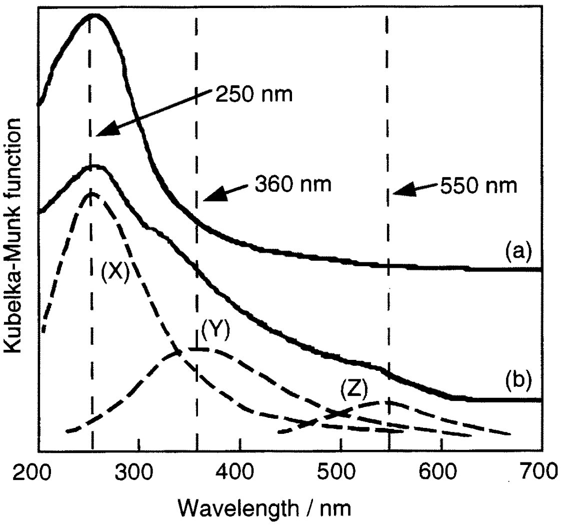

Figure 1. UV-Vis diffuse reflectance spectra of the Fe-ZSM-5: (a) Si/Al=950, (b) Si/Al=20. Spectrum (b) is deconvoluted into X, Y and Z components.

Figure 2 shows the ESR spectra observed with the Fe-ZSM-5 catalysts having various Si/Al ratios, which can be attributed to the presence of Fe^{3+}-oxide species with different structures. The ESR signal of Fe-ZSM-5 with a Si/Al ratio of 950 which exhibits a weak broad line at a *g* value of around 2.0 due to the Fe-oxide species in tetrahedral coordination could be observed for $FePO_4$, as shown in Figure 2 (a).[7,8] The intensive narrow line at the *g* value of 4.1 is attributed to the highly dispersed tetrahedrally coordinated Fe^{3+}-oxide species.[7] On the other hand, as shown in Figure 2 (c), Fe-ZSM-5 with a Si/Al ratio of 20 was found to involve the highly dispersed tetrahedrally coordinated Fe^{3+}-oxide species (g = 4.1) as well as the highly dispersed distorted tetrahedrally coordinated Fe^{3+}-oxide species (g = 6.0).[7] The intensity of the ESR signal at a *g*-value of 6.0 increases when the value of the Si/Al ratios of the zeolite decreases from 950 to 20, as can be seen in Figure 2 (a–c), suggesting that the species are formed by the interaction of Fe-oxide species with the Al ions on HZSM-5. Furthermore, the addition of a small amount of H_2O onto the sample led to a decrease in the peak intensity at a *g*-value of around 6.0, in proportion to the amount of H_2O added, as can be seen in Figure 2 (d). After evacuation of the hydrated sample at around 473 K, the ESR peak intensity at 6.0 recovered to its original intensity.[8]

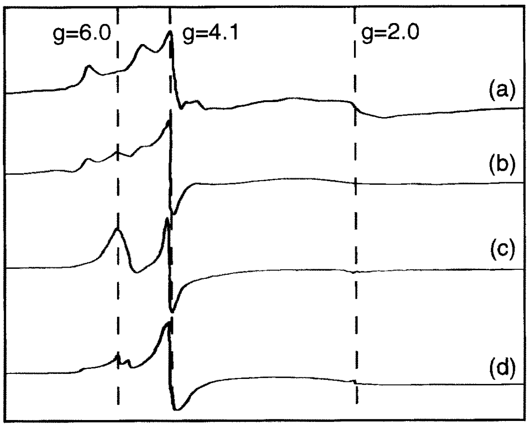

Figure 2. ESR spectra of the Fe-ZSM-5 with Si/Al ratios of (a) 950, (b) 34, (c) 20 and (d) the hydrated Fe-ZSM-5 where a small amount of water was added onto sample (c).

We have found that UV-irradiation of Fe-ZSM-5 catalysts in the presence of N_2O led to the decomposition of N_2O into N_2 and O_2 at 298 K. In blank experiments, no products were observed during UV-irradiation of N_2O on parent H-ZSM-5 zeolites. Figure 3 shows the yields of N_2 and O_2 in the photocatalytic decomposition of N_2O at 298 K on Fe-ZSM-5 with different Si/Al ratios. Under UV-irradiation, the photocatalytic decomposition of N_2O proceeds on Fe-ZSM-5 with a Si/Al ratio of 20, leading to the formation of N_2 and O_2 with a good linearity against the UV-irradiation time and a good stoichiometry, while under dark conditions, no products could be observed. After prolonged irradiation, the turnover frequency of the catalyst, defined by the number of N_2 produced and divided by the total number of Fe atoms included within the catalyst, exceeded 1.0, indicating that the reaction proceeds photocatalytically at 298 K. It was also found that the photocatalytic efficiency increased when the Si/Al ratio was decreased. Almost no products could be detected when UV-irradiation (λ > 270 nm) of Fe-ZSM-5 with a Si/Al ratio of 20 in the presence of N_2O was carried out, suggesting that only the Fe-oxide species having UV-absorption in the region of 250 nm exhibits photocatalytic activity. Furthermore, the addition of a small amount of H_2O into this catalyst caused a decrease in the photocatalytic efficiency in proportion to the amount of H_2O added, and after evacuation of the hydrated sample at around 473 K, the photocatalytic reactivity was recovered almost to its original level. Taking the results of these ESR and UV–Vis data into consideration, the photocatalytic reactivity shows a good relationship with the concentration of the highly dispersed Fe-oxide species with a distorted tetrahedral coordination.

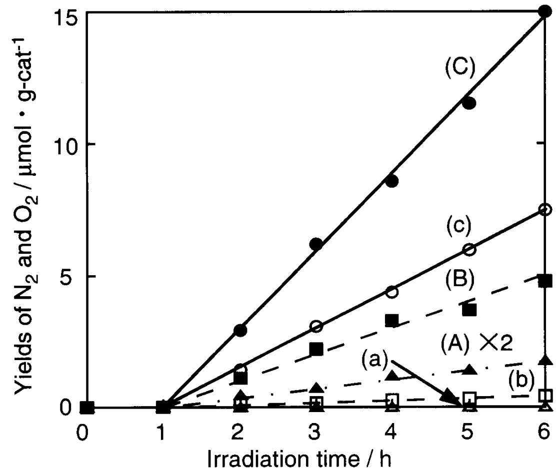

Figure 3. Reaction time profiles of the photocatalytic decomposition of N_2O on the Fe-ZSM-5 catalysts with Si/Al ratios: (A, a) 950, (B, b) 34, (C, c) 20. Yields of N_2 (A, B, C) and O_2 (a, b, c).
Added N_2O: 300 μmol·g-cat^{-1}

In conclusion, it was found that Fe-ZSM-5 with a low Si/Al ratio exhibits photocatalytic activity for the decomposition of N_2O into N_2 and O_2, with a good stoichiometry. The highly dispersed distorted tetrahedral Fe-oxide species interacting with the Al ions of ZSM-5 was found to play a significant role in the photocatalytic decomposition of N_2O into N_2 and O_2.

References

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