Photoluminescence Property of Titanium Silicalite-2 Catalyst and Its Photocatalytic Reactivity for the Direct Decomposition of NO at 295 K

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(Received June 24, 1996)

The titanium silicalite-2 (TS-2) catalyst exhibits a photoluminescence spectrum at around 450-550 nm as well as the distinct and characteristic photocatalytic activity towards the direct decomposition of NO into N_2, O_2 and N_2O at 295 K under UV irradiation. XAFS and photoluminescence investigations indicated that the charge transfer excited state of the titanium oxide moieties having a tetrahetral coordination plays a significant role in the photoluminescence and photocatalytic reactivities of the TS-2 catalyst.

Zeolites having transition metals in their zeolite frameworks have attracted considerable attention for their interesting and distinctive catalytic properties. Titanium silicalites exhibit an unique catalytic reactivity in the oxidation reactions of alkanes and aromatics with H_2O_2 as an oxidizing agent while the titanium oxide species in the zeolite frameworks play a vital role as the active sites.[1,2] However, the true chemical nature and reactivities of these TS-2 catalysts are yet little known, especially their photochemical properties. The present study deals with the photoluminescence properties of the TS-2 zeolite catalyst and its photocatalytic reactivity leading to the direct decomposition of NO into N_2, O_2 and N_2O at 295 K.

Titanium silicalite was hydrothermally synthesized in accordance with previous literature using tetrabutyl ammonium hydroxide (TBAOH) as a template.[2] After crystallization, the solid samples were washed several times with distilled water, then dried at 375 K for 24 h, and finally calcined in air at 725 K for 5 h in order to remove the remaining template. The TS-2 catalyst has a Si/Ti ratio of 85.0, corresponding to a TiO_2 content of 1.39 wt %. The XRD pattern of the synthesized titanium silicalite zeolite was found to be the same as for silicalite-2. Prior to in situ photoluminescence measurements and photocatalytic reactions, the catalyst was heated with O_2 at 725 K for 3 h and then degassed at 475 K for 2 h up to 10^{-6} Torr. The photoluminescence spectrum of the catalyst was measured with a Shimadzu RF-501 spectrofluorophotometer at 77 or 295 K. Photocatalytic reactions were carried out in a quartz cell connected to a vacuum line (about 10^{-6} Torr). The products were analyzed by an on-line GC. A high pressure mercury lamp (Toshiba SHL-100UV) was used through a water filter. Further experimental details were the same as had been described previously.[3]

As shown in Figure 1, upon excitation of the TS-2 catalyst at around 250-280 nm, the TS-2 catalyst exhibits a strong and characteristic photoluminescence spectrum at around 450-550 nm having a peak at around 480 nm. With respect to the good similarity of the excitation and photoluminescence spectra of the tetrahedrally coordinated titanium oxide species highly dispersed on silica or Vycor glass,[4] the excitation and photoluminescence could be attributed to the following charge transfer processes on the titanium oxide moieties located in the zeolite framework of the TS-2 catalyst:

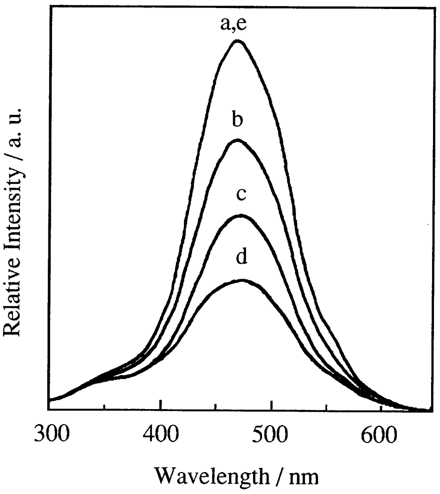

Figure 1. The photoluminescence spectrum of the TS-2 catalyst at 77 K (a) and the effect of the addition of NO on it (b-e). a) 0 Torr, b) 0.05 Torr, c) 0.1 Torr, d) 0.3 Torr NO added and e) after evacuation.

$$(Ti^{4+}\text{-}O^{2-}) \underset{h\upsilon'}{\overset{h\upsilon}{\rightleftharpoons}} (Ti^{3+}\text{-}O^{-})^*$$

As shown in Figure 1, the addition of NO onto the TS-2 catalyst leads to an efficient quenching of the photoluminescence in intensity while the lifetime of the photoluminescence was also found to shorten by the addition of NO, its extent depending on the pressure of NO added. These results indicate that the added NO is accessible to the emitting sites in the TS-2 catalyst and also interacts with the emitting sites. Figure 1 also shows that, after evacuation of the system, the photoluminescence of the catalyst recovers to its original intensity level. These findings clearly indicate that the TS-2 catalyst has remarkable capabilities for reactions with NO under UV irradiation, showing that it works as a photocatalyst.

XAFS (XANES and FT-EXAFS) spectra of the Ti K-edge of the TS-2 catalyst and bulk titania (p-25) as a reference are shown in Figure 2. In contrast to the bulk titania, a strong pre-edge peak of the TS-2 catalyst permits to conclude that the titanium oxide species in the TS-2 catalyst exists in a lower coordination state.[6] In the EXAFS spectrum of the TS-2 catalyst, only a single peak at around 1.5 Å (without phase correction) due to the neighboring oxygen is seen. The curve fitting of the EXAFS spectrum shows that the titanium oxide moieties are present in the tetrahedral coordination having a Ti-O bond distance of 1.81 Å. These findings indicate that the photoluminescence of the catalyst is originated from the tetrahedrally coordinated titanium oxide

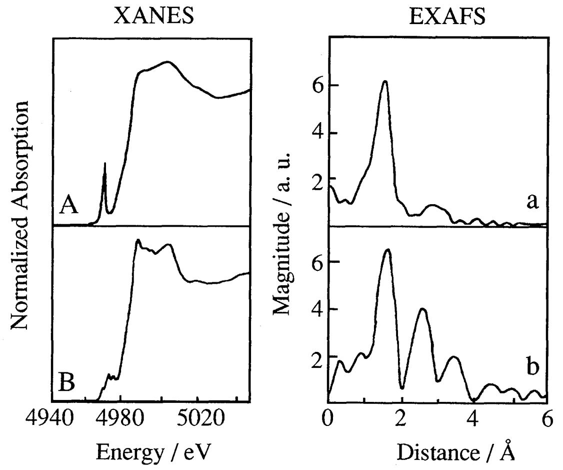

Figure 2. The XANES and EXAFS spectra of the TS-2 catalyst (A, a) and of the bulk TiO_2 as a reference (B, b) at 295 K.

species, being in a good agreement with the results reported in the previous papers.[7]

UV-irradiation of the catalyst in the presence of NO was found to result in the formation of N_2, O_2 and N_2O. The time profile of the photoformed N_2 in the photo-induced reaction is shown in Figure 3. Upon UV irradiation of the catalyst in the presence of NO at 295 K, the evolution of N_2, N_2O and O_2 (molar ratio 1:0.3:>0.1) takes place immediately, and their yields increasing with irradiation time. As soon as the UV irradiation was discontinued, the formation of N_2, N_2O and O_2 immediately ceased. While under dark conditions, no products were detected. After prolonged UV irradiation (120 hrs), the amount of the evolved N_2 exceeded the amounts of the Ti ions incorporated in the TS-2 zeolite. Thus, the turnover frequency of the catalyst exceeded unity after prolonged UV irradiation at 295 K. These results provide further evidence that this reaction proceeds photocatalytically.

The dynamic quenching of the photoluminescence of the TS-2 catalyst by the added NO clearly indicates that the charge transfer excited state of the titanium oxide moieties of the catalyst plays a vital role in the decomposition of NO into N_2, N_2O and O_2. Taking into account the photoreactivity of the tetrahedrally coordinated titanium oxide species,[3-5,7] it is likely that within the lifetime of the species the electron transfer from the electron trapped center of the excited state, i. e., Ti^{3+}, into the anti π^*-bonding orbital of NO takes place while a simultaneous electron transfer from the π-bonding orbital of another NO into the hole trapped center of the excited state, i. e., O^-, occurs. These electron transfer processes lead to the direct decomposition of the two NO species into N_2 and O_2 under UV irradiation at 295 K. Further detailed mechanisms behind this reaction are presently being investigated in our laboratory.

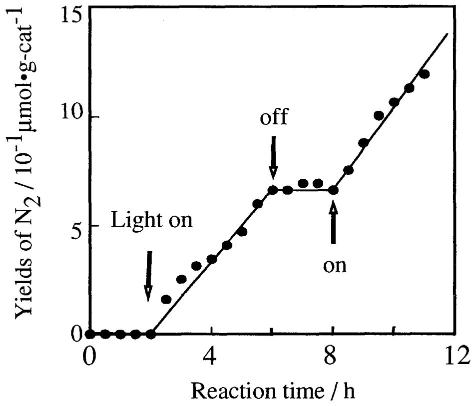

Figure 3. The time profiles of the photocatalytic decomposition reaction of NO into N_2 on the TS-2 catalyst at 295 K.

Investigations into the photoluminescence and photocatalytic reactivity of the TS-2 catalyst for the decomposition of NO is an unprecedented study which provides an insight not only into the local structure of the active site of the catalyst but also into the distinctive photochemical properties of the catalyst. These results demonstrate that titanium ions included within a zeolite framework are excellent candidates for new and effective photocatalysts.

The present work has been supported in part by the Grant-in-Aid on Priority-Area-Research on "Photoreaction Dynamics" (06239110), "Catalytic Chemistry of Unique Reaction Fields" (07242264) and International Joint Project Research (07044162) of the Ministry of Education, Science, Sports, and Culture of Japan. M. Anpo is much indebted to Osaka Prefecture for the Special Project Research and Tokyo Ohka Foundation for their financial support.

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