Photoluminescence properties of tetrahedral titanium oxide species in zeolitic materials

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Received 28 April 1998; accepted 21 May 1998

The photoluminescence spectra of the Y-type zeolite modified with titanium ions and Ti-silicalite-1 have been investigated by varying the excitation energy. A three-dimensional image of the photoluminescence shows that the peak attributed to tetrahedral titanium oxide species is present at the excitation energy around 200–210 nm, which is consistent with the UV absorption of the samples. The technique enables the distinction of the photoluminescence of the titanium species from that of silicate species.

Keywords: photoluminescence, zeolite, Ti-silicalite, tetrahedral titanium oxide species

1. Introduction

Since 1983, when Taramasso reported the catalytic activity of zeolite containing titanium (Ti-zeolite) to the partial oxidation of organic compounds with an aqueous solution of H_2O_2 [1], many investigations on the Ti-zeolite and Ti-silicalite have been carried out [2–13]. Presence of tetrahedral titanium oxide species in these materials was confirmed by means of EXAFS and ESR, and the species are believed to play an important role in the reactions [8–13]. The tetrahedral species are also believed to be active sites for various photocatalytic reactions, e.g., decomposition of NO and reduction of CO_2 with H_2O over a Y-type zeolite ion-exchanged with titanium ions and Ti-silicalite [11–13]. Phosphorescence is often observed with photocatalysts, because it usually originates from the triplet-state of the photo-excited substance, and species with long lifetimes are effective in photocatalytic reactions [14]. Hence, an accurate detection of the phosphorescence is important for identification of the active species, especially in photocatalysts. The photoluminescence spectra of Ti-zeolites were observed at around 480 nm when they were excited at around 270 nm [11–13]. The photoluminescence may be attributed to the tetrahedral titanium species, however, the UV absorption band of the tetrahedrally coordinated titanium oxide species in the Ti-silicalite is present at ca. 210 nm [15,16], which is significantly different from the excitation band of the photoluminescence. Measurements of the photoluminescence spectra were carried out with a single excitation band, however, the emission spectrum was affected by the wavelength of the excitation. In this study, we have demonstrated that a clear distinction between the peak of the titanium species and silicate species is possible by observation of the photoluminescence spectra with various excitation bands, and the three-dimensional image of the photoluminescence spectra shows how the photoluminescence of the tetrahedral titanium oxide species relates to UV absorption.

2. Experimental

Ti-silicalite (TS-1, Ti/Si $= 0.02$) was hydrothermally synthesized from an aqueous mixture of tetraethoxysilane (99%, Kishida Co., Ltd.), titanium isopropoxide (99%, Kishida), tetrapropyl ammonium hydroxide (Tokyo Kasei Kogyo Co., Ltd.), and 2-propanol (99.5%, Kishida). The resulting solid was filtrated, washed, then dried in air at 375 K for 15 h, and finally calcined at 725 K for 5 h. The titanium-modified Y-type zeolite (Ti-Y, Ti/Si $= 0.02$) was prepared by ion exchange of NH_4-Y (Si/Al $= 5.6$, Tosoh Co., Ltd.) with an aqueous solution of titanium ammonium oxalate (99%, Kishida) [17]. The zeolite was treated by the same method for TS-1. Silica was supplied by Fuji Silicia Chemical, Ltd. (Cariact G-10).

The photoluminescence spectra were recorded at 77 K with a Hitachi F-4500 spectrophotometer under the phosphorescence mode. Prior to the measurements, a sample was evacuated at 725 K for 1 h and heated in O_2 at the same temperature for 1 h, then finally outgassed to 10^{-6} Torr at 475 K for 1 h.

3. Results and discussion

Figure 1 shows a three-dimensional image of the photoluminescence spectra of SiO_2. The emission spectra were recorded by varying the wavelength of the excitation light from 200 to 350 nm. The maximum intensity can be seen at the crosspoint of the excitation around 250 nm and emission around 450 nm. These values are found to be in good agreement with those reported for SiO_2 [18]. In the case of Ti-Y, the maximum intensity of the photoluminescence was

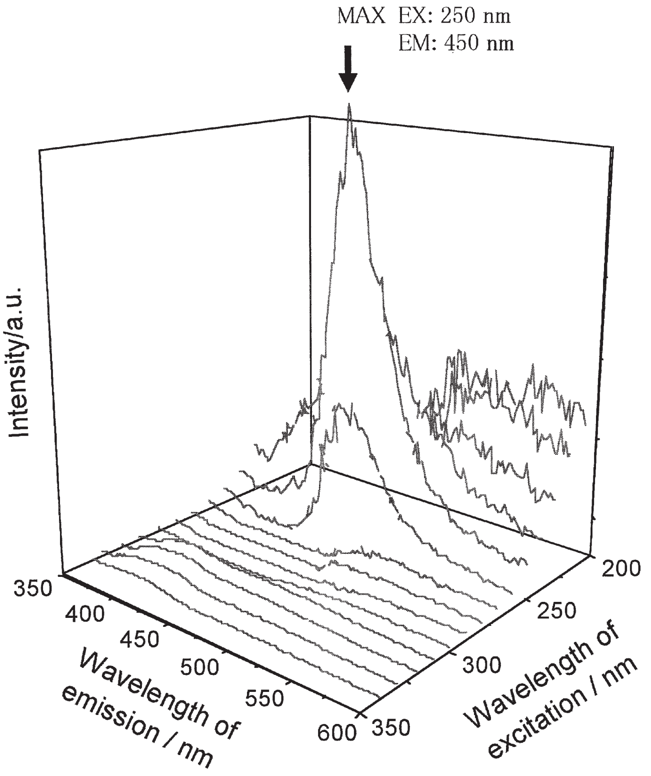

Figure 1. Three-dimensional image of photoluminescence spectra of SiO_2.

observed at the crosspoint of the excitation around 210 nm and emission around 490 nm (figure 2). The excitation band is significantly different from that for SiO_2, and it is in harmony with the UV absorption band previously reported [15,16]. It was confirmed that the titanium ions in Ti-Y are present as an isolated tetrahedral species [11,12], hence, the photoluminescence can be attributed to the tetrahedral titanium oxide species. The photoluminescence of TS-1 is somewhat different from that of Ti-Y, although the EXAFS studies of the sample evidenced that titanium is present as a well-isolated tetrahedral titanium oxide species [13]. The maximum photoluminescence was recorded at an emission around 455 nm and an excitation around 200 nm, while measurement at shorter wavelengths than 200 nm was not possible because of limitations in the light source (figure 3). A shoulder peak also appeared at an emission of 450 nm and excitation of 250 nm. Since the position is very similar to that of the photoluminescence of SiO_2 (see figure 1), the shoulder peak can be attributed to the silicate species in TS-1. The excitation band of the major peak is close to the UV absorption band at ca. 210 nm due to the presence of the tetrahedral titanium oxide species [15,16]. Hence, the peak can be attributed to the tetrahedral species, while the photocatalytic activity of TS-1 was found to be similar to that of Ti-Y. The difference in the emission band between TS-1 and Ti-Y may reflect the coordinative structure of the titanium ions in the solids. That is, in Ti-Y the titanium ions are supposed to interact with aluminum ions via oxygen atoms as well as silicon ions; in contrast, a very slight amount of aluminum ions are present in TS-1.

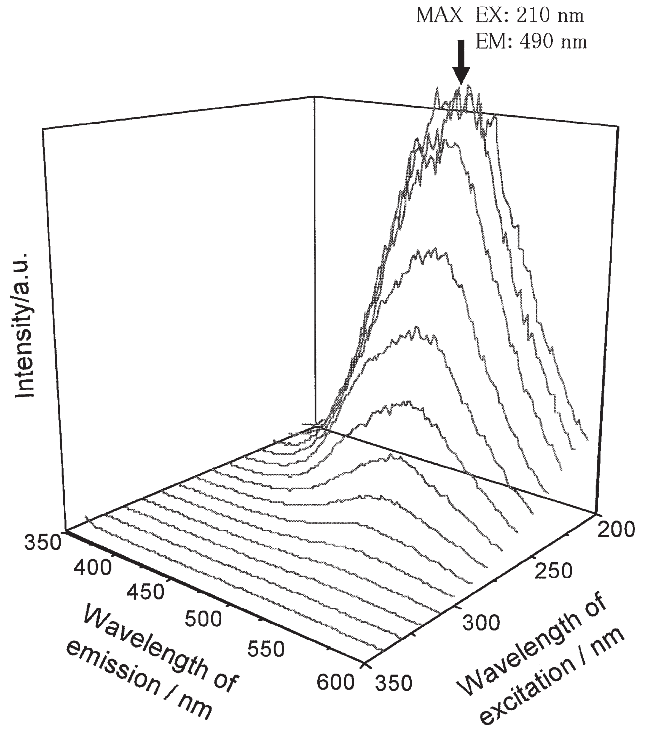

Figure 2. Three-dimensional image of photoluminescence spectra of Ti-Y.

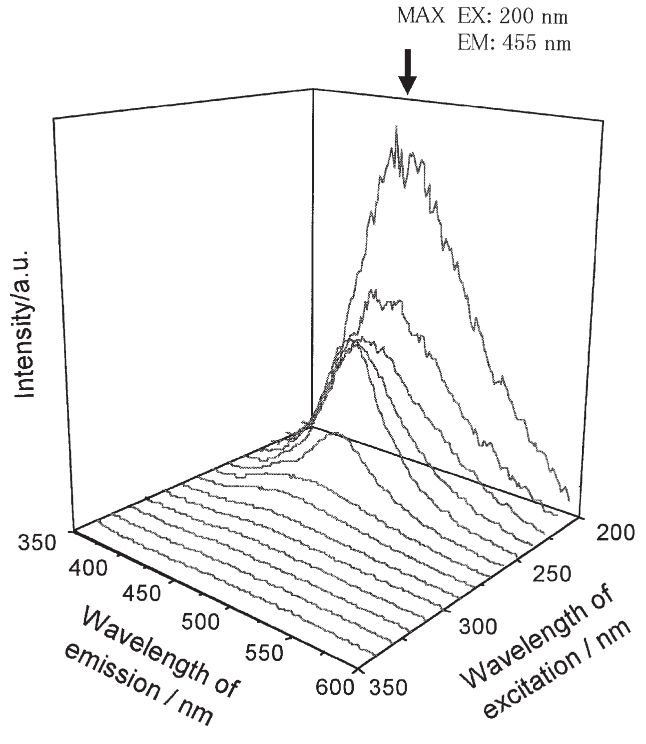

Figure 3. Three-dimensional image of photoluminescence spectra of TS-1.

Consequently, the three-dimensional images of the photoluminescence spectra can provide the information on the detailed structure of the tetrahedral titanium oxide species, and at the same time, the measurement enables clear distinction of the peaks arising from the titanium species and silicate species.

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