Local structures of active sites on Ti-MCM-41 and their photocatalytic reactivity for the decomposition of NO

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The characterization of mesoporous Ti-MCM-41 prepared at ambient temperature, with Ti contents in the 0.15–2.00 wt% range, was carried out using XAFS, FT-IR and photoluminescence methods. For Ti contents up to 0.60 wt%, isolated tetrahedrally coordinated Ti-oxide species was found to be formed in the MCM-41 network structures, while at higher titanium contents, dimeric or oligomeric Ti-oxide species, with Ti (IV) in tetrahedral coordination, became overwhelming. It was found that only the highly dispersed isolated tetrahedrally coordinated Ti-oxide species act as active sites in the photocatalytic decomposition of NO into N_2 and O_2.

KEY WORDS: photocatalyst; local structure of Ti-oxide; decomposition of NO; Ti-MCM-41.

1. Introduction

NO_x is an especially harmful atmospheric pollutant and the main cause of acid rain and photochemical smog. The removal of nitrogen oxides (NO_x: NO, N_2O, and NO_2), i.e., the direct decomposition of NO_x into N_2 and O_2, has been a great challenge for many researchers [1,2]. As a promising way to address such concerns, mesoporous materials incorporating transition metal ions (TMI) such as Ti^{4+} and V^{5+} have attracted much attention not only as active catalysts for the partial oxidation of alkenes but also as effective photocatalysts for the decomposition of NO_x into N_2 and O_2 [3–6]. Such systems exhibit the advantage of having a high dispersion of TMI because of their high internal surface area and nanoscaled pore reaction fields. In fact, these mesoporous materials incorporated with TMI are found to exhibit unique and high photocatalytic activity for various reactions; however, the relationship between the local structure of TMI and their photocatalytic reactivity has not yet been clarified. In this work, we investigate the relationship between the local structure of the Ti^{4+} centers in MCM-41-type materials and their photophysical and photocatalytic features by applying various spectroscopic techniques.

2. Experimental

In this study, MCM-41 and Ti-MCM-41(x), (content of Ti as wt%, $x = 0.15$, 0.60, 0.85, and 2.00), were synthesized in accordance with previous literature [7], using tetraethyl orthosilicate and tetraisopropyl orthotitanate as the starting materials and cetyltrimethylammonium bromide as the template. After the as-synthesized products were recovered by filtration, washed thoroughly with deionized water and dried at 373 K for 12 h, calcination of the samples was performed in air at 823 K for 6 h. The titanium content in these materials was determined by atomic absorption analysis.

Prior to photocatalytic reactions and spectroscopic measurements, the catalysts were degassed at 723 K for 2 h, heated in O_2 at the same temperature for 2 h and finally degassed at 473 K for 2 h. The samples were then characterized by XAFS (XANES and FT-EXAFS, Photon Factory, Tsukuba, Japan; Ti K-edge absorption spectra recorded in the transmission or fluorescence mode), photoluminescence (Spex 1943D3) and IR (adsorbed NH_3; Jasco FT/IR 660) spectroscopic investigations. UV irradiation of the catalysts under NO was carried out using a 100-W Hg lamp ($\lambda > 240$ nm) at 295 K. The reaction products were analyzed by gas chromatography.

3. Results and discussion

The XRD patterns showed that the Ti-MCM-41 catalysts have an MCM-41 mesoporous structure. The

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XAFS experiments indicated that in all of the Ti-MCM-41 catalysts, the overwhelming part of the titanium centers are in tetrahedral coordination. Especially, in Ti-MCM-41 having a Ti content of less than 2.00 wt%, the Ti^{4+} centers are highly dispersed and located in tetrahedral coordination with the four oxygen atoms having a Ti–O bond length of 1.81 Å.

In order to monitor the relative amount of the Ti-oxide species exposed at the surface walls of the various Ti-MCM-41 materials, the IR spectra of ammonia irreversibly adsorbed at room temperature were recorded. No bands due to the adsorbed species were observed for pure MCM-41. Conversely, the spectra of the Ti-MCM-41 samples in contact with ammonia exhibit, in the 1800–1350 cm^{-1} range, a characteristic band at 1608 cm^{-1} ($\delta_{asym}NH_{3ads}$) due to the NH_3 molecules irreversibly adsorbed on the Ti(IV) centers of the tetrahedrally coordinated Ti-oxide species [8,9], as shown in figure 1. The increase in the Ti content leads to an increase in the intensity of this band, indicating that the amount of tetracoordinated Ti(IV) sites exposed at the surface walls of the channels of the Ti-MCM-41 materials increased with the Ti content. The bands at 1708, 1660, and 1453 cm^{-1} can be assigned to the vibrational bending modes of NH_4^+, formed by a protonation of the ammonia molecules by the acidic surface hydroxyl groups. The band at 1553 cm^{-1} is attributed to the Ti–NH_2 or Si–NH_2 bending mode formed by the irreversible reaction of NH_3 with the Si–O–Ti bridges or distorted surface Si–O–Si bridges formed because of the incorporation of Ti into the Si–O–Si networks [8].

Nevertheless, the photoluminescence spectra exhibited different degrees of dependence on the titanium content. As shown in figure 2, Ti-MCM-41 exhibits a typical photoluminescence spectrum at around 450–550 nm upon excitation of its charge-transfer band at around 220–260 nm at 295 K, which coincides well with those previously observed for isolated tetrahedrally coordinated Ti-oxides species highly dispersed in silica matrixes [10–12]. The photoluminescence spectra are attributed to the reverse radiative decay process from the charge transfer excited state to the ground state of the isolated Ti-oxides in tetrahedral coordination [11]. As can be seen in figure 2, the intensity of this photoluminescence increases with an increase in the Ti content up to 0.60 wt% and then sharply decreases with a higher titanium content. Furthermore, it was found that an increase in the Ti content from 0.60 to 0.85 wt% leads to a decrease in the phosphorescence lifetime from 0.1 to 0.025 ms. On the basis of these data, it can be proposed that, when the Ti-MCM-41 materials are photoexcited by UV light, only the isolated tetrahedrally coordinated Ti-oxide species, which are more abundant for a Ti content up to 0.60 wt%, can produce the excited state long enough to allow the appearance of photoluminescence as a radiative decay to the ground state. Moreover, the dimeric and/or oligomeric tetrahedrally coordinated Ti-oxide species, which are likely the overwhelming species present at higher Ti contents, decay quickly to the ground state through non-radiative, vibrational processes, which are apparently favored by their clustered structure.

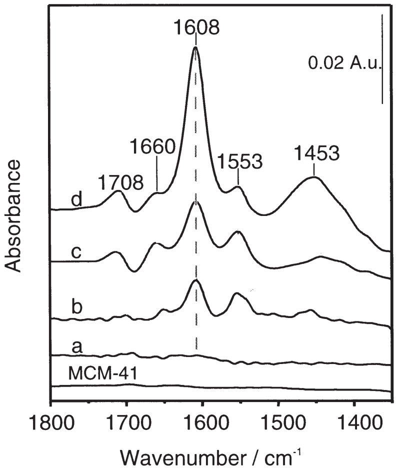

Figure 1. FT-IR spectra of NH_3 molecules adsorbed on MCM-41 and Ti-MCM-41 ((a) 0.15, (b) 0.60, (c) 0.85, and (d) 2.00 Ti wt%) observed after admission of 10 torr NH_3 and subsequent outgassing at 295 K for 1 min.

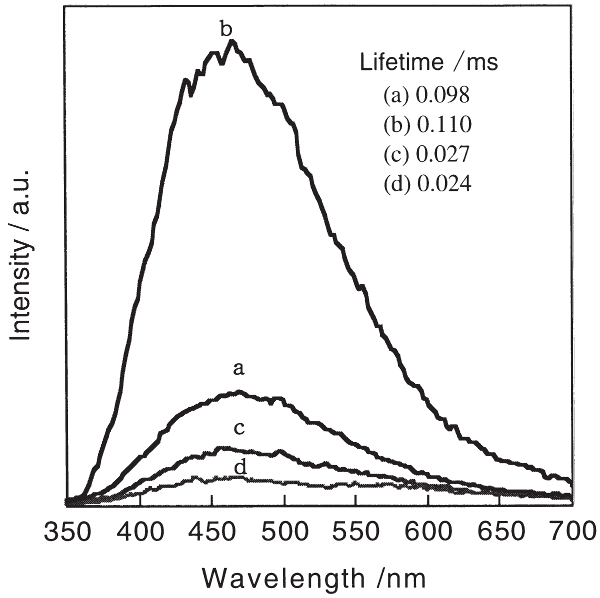

Figure 2. The photoluminescence spectra of Ti-MCM-41 with different Ti-contents (a) 0.15, (b) 0.60, (c) 0.85, and (d) 2.00 wt% measured at 295 K.

It was found that UV irradiation of Ti-MCM-41 in the presence of NO leads to the formation of N_2, O_2, and N_2O, their yields increasing in proportion to the irradiation time, while under dark conditions, no products could be detected. These results clearly indicate that the reaction proceeds photocatalytically on Ti-MCM-41 at 295 K. Figure 3 shows the effect of Ti content on the reactivity of photocatalytic decomposi-

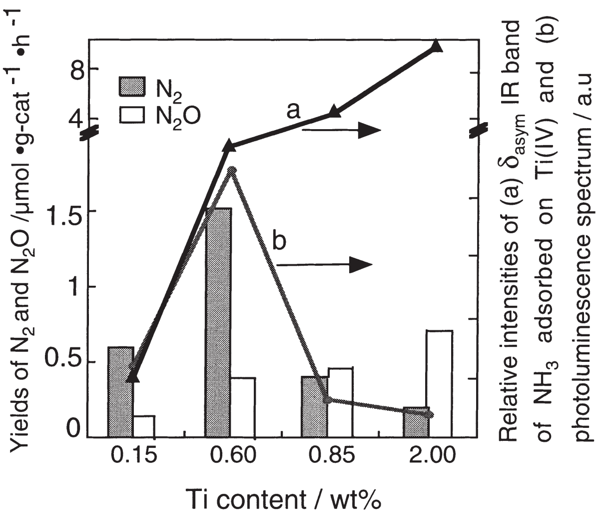

Figure 3. Relationship among the yields of N_2, N_2O, the intensities of the IR band of $\delta_{asym}NH_3$ adsorbed on Ti(IV) (a) and photoluminescence spectra (b) of Ti-MCM-41 with various Ti contents.

tion of NO. As shown in figure 3, the yield and selectivity of N_2 in the decomposition of NO is the highest in the case of Ti-MCM-41 (0.60 Ti wt%), and an increase in Ti content only leads to a decrease in the reactivity, showing a good correspondence with the intensities of photoluminescence spectra due to the isolated tetrahedrally coordinated Ti-oxide species. Thus, the amount of the isolated tetrahedrally coordinated Ti-oxide species, not the total amount of the Ti-oxide species exposed at the surface walls of the Ti-MCM-41 channels as monitored by the intensity of the $\delta_{asym}NH_3$ band, appeared to play an important role. These results indicate that only the highly dispersed isolated tetrahedrally coordinated Ti-oxide species act as active sites in the photocatalytic decomposition of NO into N_2 and O_2.

4. Conclusions

It was found that mesoporous Ti-MCM-41 catalysts prepared at ambient temperature with Ti contents up to 0.60 wt% involve isolated tetrahedrally coordinated Ti-oxide species as the major species, while dimeric or oligomeric Ti-oxide species with Ti(IV) in tetrahedral coordination becomes overwhelming within Ti-MCM-41 with higher Ti contents. The photocatalytic reactivity of these Ti-MCM-41 for the decomposition of NO was found to strongly depend on the local structure of the Ti-oxide species. The yield and selectivity of N_2 in the photocatalytic decomposition of NO corresponded with the yield of the photoluminescence of the isolated tetrahedrally coordinated Ti-oxides species, indicating that only these species are responsible for such photocatalytic reactivity.

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