XAFS studies on the local structures of Ti-HMS mesoporous molecular sieves and their photocatalytic properties

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Various Ti-containing HMS mesoporous molecular sieves having high surface areas and pore volumes have been prepared at ambient temperature. The Ti-HMS samples exhibited a well-defined XRD pattern of typical hexagonal lattice. UV-vis and XAFS spectra for the calcined forms of Ti-HMS indicated that the Ti ions are tetrahedrally coordinated in the framework of HMS for the samples of Ti-HMS(1) and Ti-HMS(2), while at least a fraction of Ti-oxides in Ti-HMS(10) is in octahedral coordination. UV irradiation of the Ti-HMS catalysts in the presence of NO was found to lead to the decomposition of NO to form N_2, O_2, and N_2O at 273 K with different yields and product distributions. The photocatalytic performance of Ti-oxides appears to be completely modified by their incorporation structure and reaction environment. High efficiency and selectivity for the formation of N_2 and O_2 in the photocatalytic decomposition of NO was achieved with the Ti-HMS(1) having highly dispersed isolated tetrahedral titanium oxide species, while the reactivity decreased with an increase in the Ti content.

Keywords: Mesoporous molecular sieves, Titanium oxide species, Photocatalytic decomposition of NO, Local structure, XAFS

1. Introduction

Ordered mesoporous materials (OMMs) have recently attracted a lot of attention because of the presence of an array of uniform size pore channels (hexagonal pores), (Corma, 1997; Kruk *et al*., 1999; Ying *et al*., 1999) ease of modification of the surface properties by incorporating heteroatoms such as Al, B, Ti, V, and Mo, which make them suitable for a wide variety of applications in catalysis, environmental cleanup, solid-phase extraction, and advanced materials design (Sayari, 1996). However, relatively little is known concerning the catalytic activities of titanium-substituted mesoporous molecular sieves, especially for the Ti-HMS. The present investigation focuses on the in-situ molecular structural characterization of the highly dispersed Ti-HMS under various conditions with several different molecular spectrocopies: XRD, UV-Vis, photoluminescence and XAFS. The structural information derived from these in-situ spectroscopic studies provide fundamental understanding about the properties of titanium oxide within mesoporous materials and demonstrate that the molecular structure of the highly dispersed titanium species within the mesoporous materials is sensitive to the preparation conditions titanium loading in particular. Furthermore, photocatalytic decomposition of NO as a probe reaction was employed to study the relationship between the reactivity and selectivity of Ti containing mesoporous photocatalyst and their local structures.

2. Experimental

A typical procedure for the synthesis of Ti-HMS is as follows (Zhang *et al*., 1996): Tetraethyl orthosilicate (TEOS), tetraisopropyl orthotitanate (TIPOT), and long-chain alkylamine surfactant(DDA) were used as sources of silica, titanium, and template, respectively. The final catalysts were denoted as Ti-HMS(x) (x is content of Ti). The actual composition of the Ti-HMS photocatalysts was determined by atomic absorption. The surface area, pore volume, and pore size distribution of samples heated at 873 – 1073 K were measured by a Quantachrome Corporation NOVA-1000 nitrogen gas sorption analyzer.

TiO_2 powered catalysts (P-25: anatase 92%, rutile 8%) were supplied as a standard reference catalyst by the Catalysis Society of Japan. The photocatalytic reactions of NO molecules were carried out with the catalysts in a quartz cell with a flat bottom connected to a conventional vacuum system. Prior to the photoreactions and spectroscopic measurements, the catalysts were pretreated in determined condition. UV irradiation of the catalysts in the presence of NO was carried out using a 75 W high-pressure Hg lamp ($\lambda > 280$ nm) at 275 K. The reaction products were analyzed by gas chromatography. The photoluminescence spectra of the catalysts were measured at 77 K using a Spex 1934D3 Phosphorimeter. The UV-vis absorption spectra were recorded with a Shimadzu UV-2200A spectrometer at 295 K. The X-ray absorption spectra were measured at the BL-7C facility of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba, Japan. The Ti K-edge absorption spectra were recorded in the transmission or fluorescence mode at 295 K. XRD patterns were recorded with a Shimadzu XD-D1 using Cu Ka radiation.

3. Results and discussion

The results of XRD analysis, N_2 adsorption isotherm and UV-vis absorption indicate that Ti-HMS is typical of HMS as described by the group of Pinnavaia (Zhang *et al*., 1996) and their XRD reflections which were located at 2.1 ~ 2.2 degree can be indexed on a hexagonal lattice. The pore sizes of Ti-HMS are larger than 2 nm and the inflection point for Ti-HMS (10) is less unambiguous as compared with that of Ti-HMS(1) and Ti-HMS(2). The results of UV-vis absorption suggest that most of the Ti atoms in our Ti-HMS samples occupy site-isolated positions in the silica framework. In the high Ti content samples Ti-HMS(10), the shift and the increase in the width of the 210 nm band may be indicative of Ti in a distorted tetrahedral environment or of the presence of Ti species in a octahedral coordination sphere.

Figure 1 shows the XANES spectra of three different samples Ti-HMS(1), Ti-HMS(2) and Ti-HMS(10) used in present work. The lack of inversion symmetry in the tetrahedral environment results in a single intense prepeak. The intensity of preedge peak decreased in the order of Ti-HMS(1), Ti-HMS(2) and Ti-HMS(10). The pre-edge features of samples show differences with increasing Ti content from Ti-HMS(1) to Ti-HMS(10), with the peak intensity in Ti-HMS(1) being significantly higher, suggesting that the average coordination number of Ti atoms is lower in lower Ti-content samples. As can be seen in Fig. 1(c) for the Ti-HMS(10), the single preedge peak is rather weak, indicating that the catalyst consists of a mixture of tetrahedrally and octahedrally coordinated oxide species. The samples of Ti-HMS(1) and Ti-HMS(2) consist of one sharp and strong preedge peak with small differences in intensity. The peak intensity and energy position clearly indicate there is mainly the tetrahedral coordination of Ti in the samples Ti-HMS(1) and Ti-HMS(2) (Blasco *et al*., 1998). Previous publications (Yamashita *et al*., 1996) have reported that the pre edge peak becomes less intense and wider, and is shifted to higher energy when octahedral Ti is present in the form of extraframework anatase or in systems with significant disorder in Ti-O distances and Ti-O-Si angles.

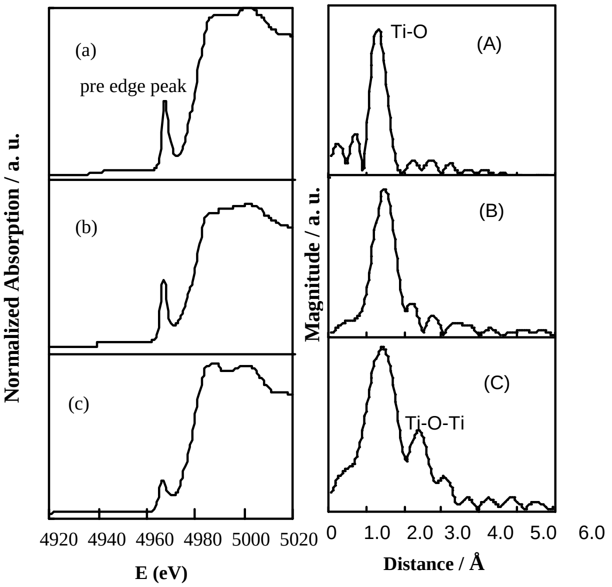

Figure 1
XANES (a, b, c) and FT-EXAFS (A, B, C) spectra of the Ti-HMS(1), Ti-HMS (2) and Ti-HMS (10), respectively.

Figure 1 also shows the FT-EXAFS spectra of the catalysts. All of the catalysts exhibit a strong peak at around 1.6 Å (without phase shift correction) which can be assigned to the neighboring oxygen atoms (Ti-O). The Ti-HMS(1) and Ti-HMS(2) exhibit only a Ti-O peak indicating the presence of an isolated titanium oxide species, while the Ti-HMS(10) exhibits an intense peak at around 2.7 Å. This peak can be assigned to the aggregation of the titanium oxide species in the catalyst.

Ti-HMS samples exhibited a photoluminescence spectrum at around 450-600 nm by an excitation at around 260-290 nm at 77 K. Figure 2 shows the typical photoluminescence observed on Ti-HMS(1) by the excitation with UV light. The observed photoluminescence and absorption bands are in good agreement with those previously observed with the highly dispersed tetrahedrally coordinated titanium oxides prepared in silica matrices (Yamashita *et al*., 1996), where the absorption of UV light at around 280 nm brings about an electron transfer from the lattice oxygen (O_1^{2-}) to the titanium ion (Ti^{4+}) to form a charge transfer excited state. We can therefore conclude that the observed photoluminescence spectrum is attributed to the radiative decay process from the charge transfer excited state formed in this way to the ground state of the highly dispersed titanium oxide species having a tetrahedral coordination.

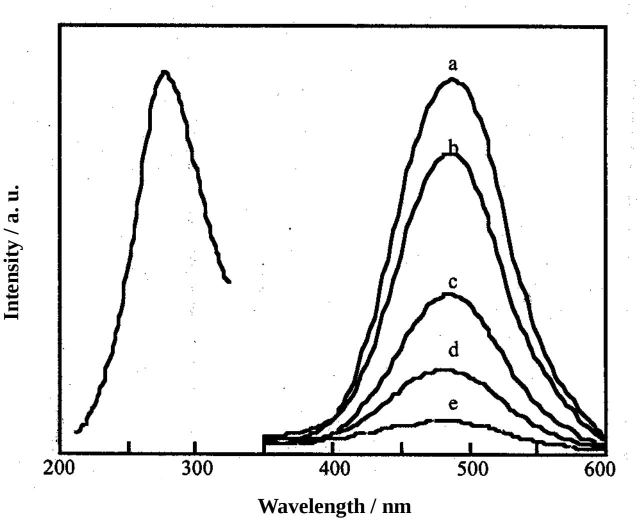

Figure 2
Photoluminescence spectrum of Ti-HMS (1) catalyst (a), and the effect of the addition of NO on the photoluminescence spectra (b-e).
Measured at 77 K, excitation beam: 270 nm, amounts of added NO: (a) 0.0, (b) 0.2 (c) 0.8, (d) 7.6, (e) 21.3 mmol g^{-1}.

UV irradiation of powdered TiO_2 and Ti-HMS photocatalysts in the presence of NO was found to produce N_2, O_2, and N_2O in the gas phase at 275 K with different yields and product selectivities. The photocatalytic reactivities of various titanium oxide catalysts for the direct decomposition of NO are shown in Fig. 3. Of special interest is the comparison of the photocatalytic reactivities of Ti-HMS catalysts with that of the widely used bulk TiO_2 powdered catalyst. From Fig. 3, we can deduce the yields of the photoformed N_2 and N_2O (efficiency) and their selectivity in the photocatalytic decomposition of NO on various types of titanium oxide catalysts. It is clear that the efficiency and selectivity for the formation of N_2 strongly depend on the type of catalysts. The Ti-HMS(1) and Ti-HMS (2) exhibit a high reactivity and a high selectivity for the formation of N_2 while the formation of N_2O is found to be the major reaction on the bulk TiO_2 catalyst. Therefore, the results obtained with Ti-HMS catalysts show the significant difference in selectivity as well as efficiency with the difference of Ti-content.

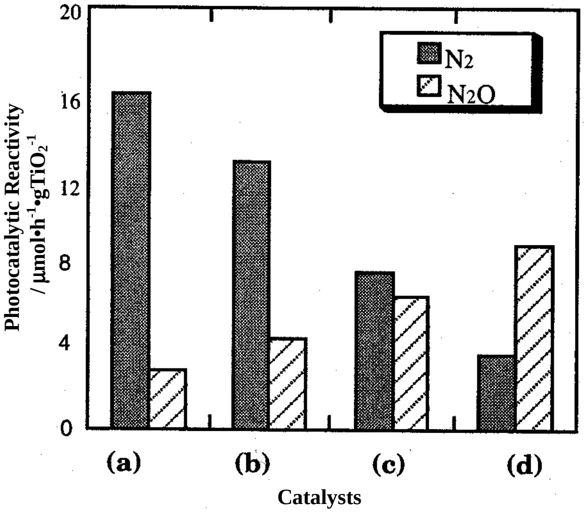

Figure 3
Products distribution of the photocatalytic decomposition of NO on the different photocatalysts: (a) Ti-HMS (1); (b) Ti-HMS (2); (c) Ti-HMS(10); (d) TiO_2 power (P-25).

4. Conclusions

A high photocatalytic efficiency and selectivity for the formation of N_2 in the photocatalytic decomposition of NO was achieved with the Ti-HMS(1) catalyst having highly dispersed isolated tetrahedral titanium oxide species. The performance was deteriorated with increasing Ti content. The formation of N_2O in the photocatalytic decomposition of NO was found to proceed on the bulk TiO_2 catalysts and on the Ti-HMS(10) involving aggregated octahedrally coordinated titanium oxide species.

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