Photoluminescence Properties of Mo-MCM-41 Mesoporous Molecular Sieves and Their Photocatalytic Reactivity for the Decomposition of NOx

Shinya Higashimoto, Rie Tsumura, Shu Guo Zhang, Masaya Matsuoka, Hiromi Yamashita, Catherine Louis,†
Michel Che,† and Masakazu Anpo*
Department of Applied Chemistry, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531
†Laboratoire de Réactivité de Surface, Université P. et M. Curie, UNR 7609-CNRS, 4 place Jussieu,
Tour 54, 75252 Paris Cedex 05, France

(Received December 27, 1999; CL-991094)

Investigations of the mesoporous Mo-MCM-41 molecular sieves have shown that they include the tetrahedrally coordinated Mo-oxide species, which exhibits a photoluminescence spectrum attributed to the radiative decay from the charge transfer excited state. Also, the photocatalytic reaction of NO into N_2 was found to proceed much more efficiently in the presence of propane than in the absence of propane. The dynamic quenching of the photoluminescence spectrum by the addition of NO or propane indicates that the excited state of the highly dispersed Mo-oxide species having a tetrahedral coordination plays a significant role in this reaction.

Zeolites involving transition metal ions within their frameworks are known to exhibit unique and fascinating properties for applications not only in catalysis but also for various photochemical processes.[1] The transition metal ions were incorporated within the zeolite framework in a highly dispersed state and exhibited high photocatalytic reactivity for such reactions as hydrogenation, oxidation and the metathesis reaction of hydrocarbon. The capacity of the Mo-oxide species in the framework is limited due to the great strain which occurs by the insertion of large transition metal ions in the rigid zeolite framework. However, the Mo-oxide species can be easily incorporated into the framework of MCM-41 due to its greater flexibility in structure.[2] It was found to enable the design of tetrahedrally coordinated Mo-oxide species with high loading amounts of at least up to 1 wt% of Mo with this MCM-41, while only 0.1 wt% of Mo for the anchoring method using a facile reaction of $MoCl_5$ with the surface OH groups on SiO_2 was possible, showing one of the advantages of using this MCM-41 system.[3] Recently, we have shown that photoluminescence measurements can provide unique information on zeolites containing V, Ti or Cr ions in their frameworks and thus implications for high photocatalytic reactivity.[4, 5] The present study investigates the photoluminescence properties and the photocatalytic reaction of NO in the presence and absence of propane on Mo-MCM-41.

The Mo-MCM-41 mesoporous molecular sieves (0.5, 1.0, 2.0, 4.0 Mo wt%) were synthesized using tetraethyl orthosilicate (TEOS) and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ as starting materials and cetyltrimethylammonium bromide (CTMABr) as a template in accordance with previous literature.[2] After the products were recovered by filtration, washed with distilled water several times and dried at 373 K for 12 h, the calcination of the samples were performed under a dry flow of air at 773 K for 8 h.

Prior to spectroscopic measurements and photocatalytic reactions, the catalyst was degassed at 773 K for 2 h and calcined in O_2 (>20 Torr) at 773 K for 2 h, then degassed at 473 K for 2 h. The photoluminescence and lifetimes were measured at 77 K with a Shimadzu RF-501 spectrofluorophotometer and an apparatus for lifetime measurements, respectively. The photocatalytic reactions of NO in the presence and absence of propane were carried out at 298 K with a high pressure mercury lamp through a UV cut filter ($\lambda > 270$ nm). After each run, the catalyst bed was heated to 573 K for the collection of products that tightly adsorbed on the catalyst at room temperature. The desorbed products were frozen out in a trap cooled by liquid nitrogen, and were analyzed by online gaschromatography.

The results of XRD analysis indicated that Mo-MCM-41 mesoporous molecular sieves have the same structure of MCM-41 molecular sieves but having mesopores larger than 20 Å and no other phases of the Mo-oxide species are formed.[6]

As shown in Figure 1, Mo-MCM-41 (1.0 Mo wt%) exhibits a photoluminescence spectrum at around 400-600 nm upon excitation at around 295 nm (defined as X), which coincides with the photoluminescence spectrum of the tetrahedrally coordinated Mo-oxide species highly dispersed on SiO_2.[4, 7] The excitation and emission spectra are attributed to the following charge transfer processes on the Mo-O moieties of the tetrahedral molybdate ions (MoO_4^{2-}), involving an electron transfer from the O^{2-} to Mo^{6+} ions and a reverse radiative decay from the charge transfer excited triplet state (eq. 1).[4, 7] The width and the wavelength at the maximum intensity of the emission band do not change upon varying the excitation wavelength, indicating that there is only one luminescent species (photoluminescence lifetime: 2.25 ms). These results indicate that the Mo-oxide species showing absorption in the region of 295 nm, form a tetrahedral coordination in a highly dispersed state.

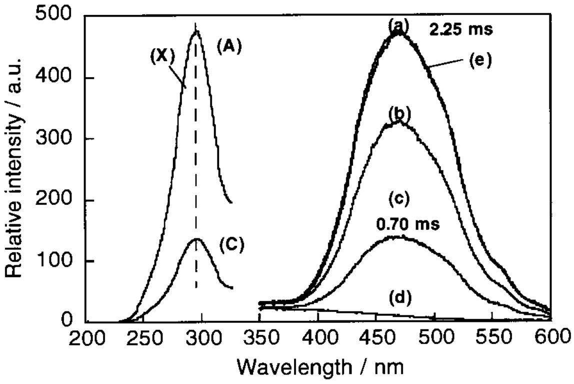

Figure 1. Effect of the addition of NO on the photoluminescence spectrum and its excitation spectrum (X) of the Mo-MCM-41 (1.0 Mo wt%). Pressure of added NO : (A, a) 0, (b) 0.07, (C, c) 0.4 Torr, (d) excess, (e) degassed after (d).

$$(\mathrm{Mo}^{6+}=\mathrm{O}^{2-}) \underset{h\nu'}{\overset{h\nu}{\rightleftharpoons}} (\mathrm{Mo}^{5+}-\mathrm{O}^{-})^{*} \quad \text{(eq. 1)}$$

(charge transfer excited state)

On the other hand, as shown in Figure 2, there are at least two luminescent species (the absorption spectrum can be deconvoluted into two components having the wavelength regions of X and Y in Figure 2: 295 and 310 nm, respectively) on the Mo-MCM-41 (4.0 Mo wt%). The increase of Mo content (from 1.0 to 4.0 Mo wt%) leads to the formation of the other emitted site (in the region of Y) probably induced by Mo-Mo interactions via oxygen ion (Mo-O-Mo), which causes a more efficient radiationless energy transfer leading to a decrease in the photoluminescence lifetime (0.91 ms).

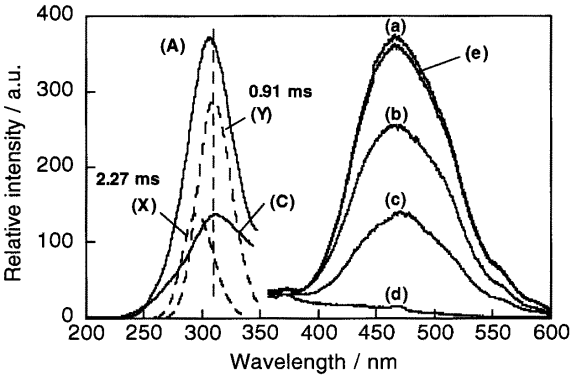

Figure 2. Effect of the addition of NO on the photoluminescence spectrum and its excitation spectrum of the Mo-MCM-41 (4.0 Mo wt%).
Pressure of added NO : (A, a) 0, (b) 0.6, (C, c) 4 Torr, (d) excess, (e) degassed after (d).
Spectrum (A) can be deconvoluted into (X) and (Y).

The addition of propane or NO onto Mo-MCM-41 (1.0 Mo wt%) leads to the efficient quenching of the photoluminescence as well as a shortening of the photoluminescence lifetime, whereas on Mo-MCM-41 (4.0 Mo wt%), NO or propane interacts with the Mo-oxide species showing absorption in the region of X more efficiently than Y. It can, therefore, be expected that Mo-oxide species which has the absorption in the region of X shows a high photocatalytic reactivity for the decomposition of NO in the presence of propane.

The photocatalytic reactions of NO in the presence and absence of propane were performed on Mo-MCM-41. No products could be detected under dark conditions. UV-irradiation of Mo-MCM-41 in the presence of NO led to the evolution of N_2 as well as N_2O and NO_2. Furthermore, the photocatalytic reaction of NO proceeded in the presence of propane much more efficiently than in the direct decomposition of NO on Mo-MCM-41, leading to the formation of propylene and oxygen-containing compounds such as CH_3COCH_3 and CO_2 etc. It was found that the total amount of oxygen involving the oxygen-containing products corresponds well to the amount of NO consumed in the photocatalytic reaction. Furthermore, the turnover frequency (defined as to the value of the number of photo-formed N_2 molecules divided by the total number of Mo species involved in the used catalyst) exceeded unity after prolonged UV irradiation in the presence of a mixture of NO and propane. These results clearly indicate that the reaction proceeds photocatalytically.

Figure 3 shows the relationship between the yields of N_2, or acetone formation and relative intensity of the absorption spectra observed in the region of 295 nm for Mo-MCM-41 (0.5, 1.0, 2.0 and 4.0 Mo wt%). As shown in Figure 3, the intensities of the absorption spectra in the region of 295 nm have a good relationship with the yields of N_2 or acetone formation, suggesting that the charge transfer excited triplet state of the tetrahedrally coordinated Mo-oxide species in a highly dispersed state, having absorption in the region of 295 nm, plays a significant role in the photocatalytic reaction of NO in the presence of propane, leading to the formation of N_2 and acetone.

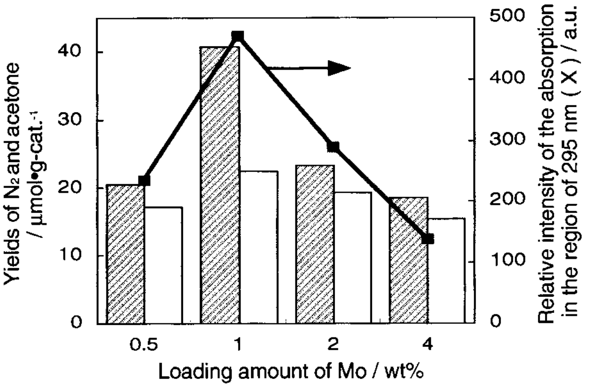

Figure 3. Relationship among the yields of N_2 (left), acetone (right) formation and the relative intensity of the absorption in the region of 295 nm (X) calculated by the deconvolution of the original excitation spectrum of the Mo-MCM-41 (0.5, 1.0, 2.0, and 4.0 Mo wt%).
Added propane or NO: 180 μmol•g-cat.$^{-1}$

After UV-irradiation of Mo-MCM-41 in the presence of propane, its subsequent evacuation at 295 K did not lead to the recovery of original photoluminescence intensity but exhibited the ESR signals of the Mo^{5+} ions, showing that the charge transfer excited triplet state of the Mo-oxide species abstracts the H atom from propane, leading to the formation of the hydrocarbon-radical.[8] Furthermore, only small amounts of NO or propane were photoadsorbed under UV-irradiation, however, a great enhancement of the photoadsorption occurred in the presence of a mixture of NO and propane. Taking these results into consideration, we are able to propose the importance of the intermediate species formed from NO and the hydrocarbon-radicals, which were subsequently followed by further reaction with NO to produce N_2 as well as oxygen-containing compounds.

References

1 M. Anpo, S. G. Zhang, S. Higashimoto, M. Matsuoka, H. Yamashita, Y. Ichihashi, Y. Matsumura, and Y. Souma, *J. Phys. Chem.*, **103**, 9295 (1999).
2 W. Zhang, J. Wang, P. T. Tanev, and T. J. Pinnavaia, *J. Chem. Soc., Chem. Commun.*, **1996**, 979.
3 C. Louis, M. Che, and M. Anpo, *J. Catal.*, **141**, 453 (1993).
4 M. Anpo and M. Che, *Adv. Catal.*, **44**, 119 (1999).
5 H. Yamashita, M. Ariyuki, S. Higashimoto, T. Ono, S. G. Zhang, J. -S. Chang, S. -E. Park, J. M. Lee, Y. Ichihashi, Y. Matsumura, and M. Anpo, *Proc. 12th Intern. Zeolite Conf.*, **1999**, 667.
6 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature*, **359**, 710 (1992).
7 M. Anpo, M. Kondo, S. Coluccia, C. Louis, and M. Che, *J. Am. Chem. Soc.*, **111**, 8791 (1989).
8 S. Higashimoto, S. G. Zhang, H. Yamashita, and M. Anpo, *Chem. Lett.*, **1997**, 1127.