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Investigations on the photoluminescence properties of Mo-MCM-41 and the photocatalytic decomposition of NO in the presence of CO

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The photocatalytic decomposition of NO into N_2 and CO_2 on Mo-MCM-41 was found to proceed efficiently in the presence of CO. *In situ* photoluminescence measurements demonstrated that this reaction proceeds in a redox cycle between alternating Mo^{6+} and Mo^{4+} ions. The yields of N_2 formation in the photocatalytic reaction correspond with the yields of the photoluminescence of the tetrahedrally coordinated Mo oxide species, indicating that the charge transfer excited triplet state of the tetrahedral Mo oxide species plays a significant role in this reaction, leading to the formation of N_2 and CO_2 with a good stoichiometry.

Keywords: photocatalysis, photoluminescence, decomposition of NO, Mo-MCM-41

1. Introduction

Our previous report showed that Mo-MCM-41 involving the tetrahedrally coordinated Mo oxide species exhibited photocatalytic reactivity for the decomposition of NO in the presence of propane, leading to the formation of N_2 and oxygen-containing products such as acetone [1]. The importance and urgency of the reduction of global air pollution makes the need to address the elimination of CO as well as NO_x of great concern. Moreover, since CO poisons the catalysts and causes a decline in reactivity, it is vital that the reaction can proceed in the presence of CO.

Photoluminescence techniques are known to be very sensitive and useful in detecting the presence of tetrahedral Mo oxide species as well as in the clarification of the interaction of the reaction substrates with the Mo oxide species [2,3]. The present study investigates the photoluminescence properties of Mo-MCM-41 as well as the photocatalytic reactivity for the decomposition of NO into N_2 in the presence of CO on this catalyst. Moreover, a meticulous investigation of the *in situ* photoluminescence properties was carried out in the presence of NO and CO in order to elucidate the reaction mechanisms.

2. Experimental

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

Prior to photocatalytic reactions and photoluminescence measurements, the catalysts were 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 photocatalytic reactions of NO in the presence and absence of CO were carried out at 298 K with a high-pressure mercury lamp through an UV cut filter ($\lambda > 270$ nm) and were analyzed by on-line gas chromatography. The photoluminescence was measured at 77 K with a Shimadzu RF-501 spectrofluoro-photometer.

3. Results and discussion

The results of XRD analysis indicated that Mo-MCM-41 molecular sieves have the same structure as MCM-41 molecular sieves but with mesopores larger than 20 Å while no other phases of the Mo oxide species were formed.

The photocatalytic decomposition reactions of NO in the presence and absence of CO were performed on Mo-MCM-41 (1.0 wt% Mo). 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. As shown in figure 1, UV-irradiation of Mo-MCM-41 in the presence of a mixture of NO and CO leads to the formation of N_2 and CO_2 with a good linearity against the UV-irradiation time, while the turnover frequency exceeded unity after irradiation for 2 h. These results clearly indicate that the reaction proceeds photocatalytically. Also, after UV-irradiation for 3 h, NO conversion and selectivity for the formation of N_2 reached close to 100%, leading to the formation of small amounts of N_2O during this reaction [5].

In order to elucidate the active sites for the photocatalytic reaction, photoluminescence measurements were

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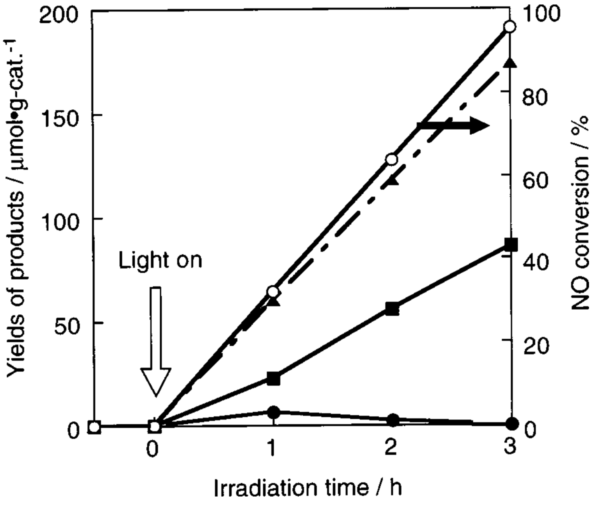

Figure 1. Reaction time profiles of the photocatalytic decomposition reaction of NO in the presence of CO on Mo-MCM-41 (1.0 wt% Mo): yields of CO_2 (▲), N_2 (■), N_2O (●) and conversion of NO (○). Amount of added NO or CO 180 μmol g-cat^{-1}.

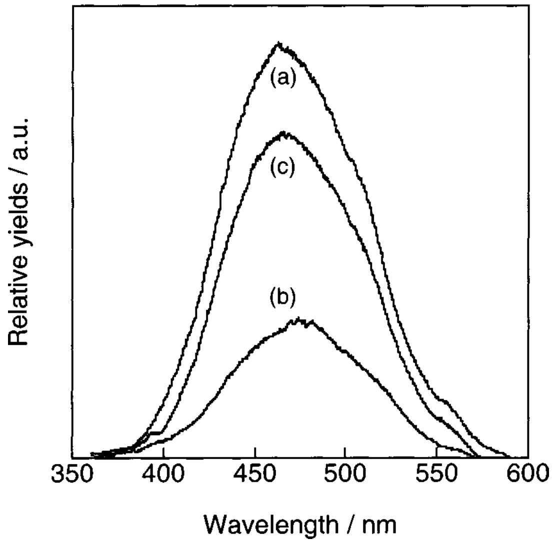

Figure 2. Photoluminescence yields of Mo-MCM-41 (2.0 wt% Mo): (a) original spectra; (b) after UV-irradiation in the presence of CO for 1 h and its subsequent evacuation at RT for 0.5 h, after exposure to NO under dark conditions for 0.5 h and its subsequent evacuation at RT for 0.5 h; (c) excited at 300 nm. Pressure of added CO or NO 10 Torr.

carried out in the presence of NO and CO. Under UV-irradiation at around 300 nm, the photoluminescence spectrum at around 400–600 nm attributed to the radiative decay from the charge transfer excited triplet state of the tetrahedrally coordinated Mo oxide species can be seen in figure 2(a) (equation (1)),

$$\left[Mo^{6+}{=}O^{2-}\right] \xrightarrow{h\nu} \left[Mo^{5+}{=}O^{-}\right] \xrightarrow{h\nu'} \left[Mo^{6+}{=}O^{2-}\right] \qquad (1)$$

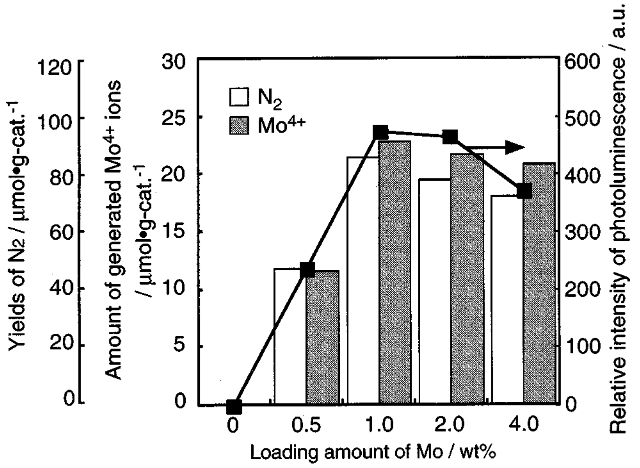

Figure 3. N_2 yields in the photocatalytic decomposition reaction of NO in the presence of CO for 3 h (empty bar), the amount of generated Mo^{4+} ions in the photoreduction of Mo^{6+} with CO under UV-irradiation for 0.5 h (dark) and the photoluminescence yields (solid line) on Mo-MCM-41 (0.5, 1.0, 2.0 and 4.0 wt% Mo).

Figure 3 shows the effect of Mo content on the yields of N_2 in the photocatalytic decomposition reaction of NO in the presence of CO. As shown in figure 3, the photocatalytic reactivity is the highest in the case of Mo-MCM-41 (1.0 wt% Mo), however, an increase in Mo content (from 1.0 to 4.0 wt% Mo) did not lead to any improvement in the reactivity. The yields of N_2 formation in the photocatalytic reaction show a good correspondence with the yields of the photoluminescence due to the tetrahedral Mo oxide species as well as the amount of the generated Mo^{4+} ions through the photoreduction of Mo^{6+} with CO (the number of Mo^{4+} ions are estimated by the number of photo-formed CO_2 molecules). These results indicate that the charge transfer excited triplet state of the tetrahedral Mo oxide species plays a vital role in the photocatalytic decomposition reaction of NO in the presence of CO to form N_2 and CO_2.

UV-irradiation of Mo-MCM-41 in the presence of CO alone and its subsequent evacuation at 293 K led to an efficient quenching of the photoluminescence, as can be seen in figure 2(b), which suggests that the charge transfer excited triplet state of the $[Mo^{5+}–O^{-}]^*$ complex reacts with CO, leading to the formation of Mo^{4+} ions as well as CO_2 (equation (2)) [2,3]. Exposure of the photo-reduced Mo^{4+} ions into NO molecules led to the formation of N_2O under dark conditions (equations (3) and (4)) [5]. In fact, after subsequent evacuation, the photoluminescence intensity recovered, but not to its original photoluminescence intensity (figure 2(c)) due to the formation of carbonyl species such as $[Mo^{4+}–CO]$ which decompose only upon heating at temperatures above 373 K [6–8]. Furthermore, exposure of N_2O onto Mo^{4+} ions under dark conditions led to the formation of N_2 (equation (5)). After the subsequent evacuation of the catalyst, the photoluminescence intensity recovered accompanied by the oxidation of Mo^{4+} to Mo^{6+} ions, as in the case of the addition of NO [5],

$$\left[Mo^{5+}–O^{-}\right]^* + CO \rightarrow Mo^{4+} + CO_2 \qquad (2)$$

$$Mo^{4+} + NO \rightarrow Mo^{6+} \cdots NO^{2-} \qquad (3)$$

$$Mo^{6+} \cdots NO^{2-} + NO \rightarrow Mo^{6+}{=}O^{2-} + N_2O \qquad (4)$$

$$Mo^{4+} + N_2O \rightarrow Mo^{6+}{=}O^{2-} + N_2 \qquad (5)$$

It was thus demonstrated that the photocatalytic decomposition reaction of NO in the presence of CO did, in fact, proceed by means of *in situ* photoluminescence measurements.

4. Conclusions

The photocatalytic decomposition reaction of NO into N_2 on Mo-MCM-41 was found to proceed much more efficiently in the presence of CO. The yields of N_2 in this reaction correspond with the yields of the photoluminescence of the tetrahedrally coordinated Mo oxide species, indicating that the charge transfer excited triplet state of the tetrahedral Mo oxide species plays a significant role in this reaction. *In situ* photoluminescence measurements demonstrated that this reaction proceeds in a redox cycle between alternating Mo^{6+} and Mo^{4+} ions, i.e., it was found that the photo-formed Mo^{4+} ions through the reaction of the charge transfer excited triplet state with CO are oxidized to the original Mo^{6+} ions in the presence of NO or N_2O, leading to the formation of N_2.

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