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RESEARCH NOTE

Catalytic Oxidation of Ammonia over the SiO_2-Pillared Oxycompounds Containing Titanium and Manganese with Layered Structure

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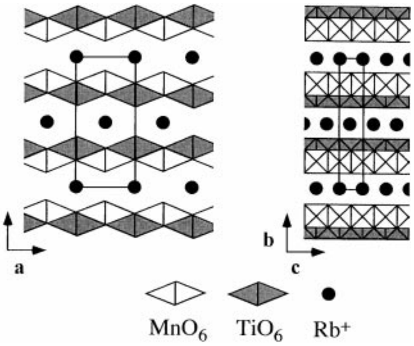
A SiO_2-pillared manganese titanate (SiO_2–MTO) with layered structure, which has a surface area as large as more than 700 m^2/g, effectively catalyzed the NH_3 oxidation with high selectivity to N_2. The H_2 temperature-programmed reduction results suggested that the manganese ions in SiO_2–MTO were in an oxidation state of +3 even in the absence of either Rb^+ or $C_{10}H_{21}NH_3^+$ ions as a charge-balancing cation. The observed high selectivity to N_2 is attributable to oxygen vacancies associated with Mn^{3+} ions in the layer. © 1999 Academic Press

Pillared clays have attracted much attention as a new type of microporous material with shape-selective catalytic activity and high-selective adsorption property since the pore size can be widely controlled from micro to mesopore by changing the size of the pillar. The most prominent clays in catalysis are montmorillonite and hectorite with silicate layers. The former was pillared with various metal oxides such as Al_2O_3 (1) and ZrO_2 (2) so as to have large surface area of 200–500 $m^2\,g^{-1}$. The other cation-exchangeable layered materials, which include zirconium phosphate (3), transition metal oxysalts such as titanates (4) and molybdates (5), and perovskite-type oxides (6), are potential targets for the synthesis of pillared materials. Yamanaka *et al.* (7) have recently found that a layer structured manganese titanate, $Rb_{0.75}Mn_{0.75}Ti_{1.25}O_4$ (denoted by Rb–MTO hereinafter), can be pillared with silica; Rb–MTO consists of the octahedral MnO_6 and TiO_6 layers, as illustrated below, and the charge-balancing cations, Rb^+ ions, are located in interlayers.



This material is expected to be a new-type mixed oxide catalyst with high surface area.

Ammonia (NH_3), mostly eluted from the combustion of coal and the stock farming, causes air pollution; therefore, the selective catalytic oxidation of NH_3 to dinitrogen (SCO reaction) is one of the important reactions for environmental protection (8). Among the metal oxides, manganese oxide is known as the most active catalyst in the oxidation of NH_3, but it showed the high selectivity to N_2O, not to N_2 (8). In the present report, the SiO_2-pillared oxycompound (denoted by SiO_2–MTO), which contains manganese ions in the layer and shows the high surface area, has been applied for SCO reaction, and its catalytic activity and selectivity were compared with the previously reported ones for the manganese oxide supported on silica. In addition, H_2-temperature-programmed reduction (H_2-TPR) measurements were carried out to get information on the oxidation state of manganese ion in the catalysts.

Details of the preparation method of SiO_2–MTO have been reported elsewhere (7). A mixture of Rb_2CO_3, MnO_2, and TiO_2 (anatase) was heated at 800°C for 15 h and then at 1000°C for 7 h to yield Rb–MTO. The resulting Rb–MTO was dispersed in $C_{10}H_{21}NH_3^+Cl^-$ solution with pH 2 at 80°C for 6 days to achieve the complete ion exchange between Rb^+ and $C_{10}H_{21}NH_3^+$ ions. Then, the ion-exchanged cake

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was kept in a tetraethyl orthosilicate (99.8%) solution at 80°C for 2 days, washed with ethanol and distilled water several times, dried at 50°C, and finally calcined at 400°C for 4 h to yield SiO_2–MTO. A reference catalyst, MnO_2/SiO_2, was prepared by the impregnation method with aqueous manganese nitrate. The manganese ion content and surface area were determined by inductively coupled plasma (ICP) analysis and BET method, respectively. X-ray powder diffraction (XRD) analysis was performed using Cu $K\alpha_1$ radiation ($\lambda = 1.54050$ Å).

The catalytic oxidation of NH_3 was carried out in a fixed-bed flow reactor at 200–600°C. The reactant gases contained 6% of NH_3, 40% of O_2, and 54% of He as a balance gas. The total flow rate was 50 cm^3 min^{-1} and the catalyst weight was 0.05 g. The products were analyzed by a gas chromatography using Molecular Sieves 5A (for N_2, O_2, and NO) and Chromosorb 103 (for NH_3, N_2O, and H_2O). H_2-TPR profiles were measured from 25 to 600°C by flowing 2 vol% H_2/N_2 gas with 50 cm^3 min^{-1} of flow rate for the catalyst (0.2 g), which was preoxidized at 450°C for 2 h. The sample temperature increased with a rate of 5°C min^{-1} and the amount of H_2 consumed was measured by a TCD detector. The water formed during the H_2-TPR was removed by a liquid nitrogen trap (−196°C) placed just before the TCD detector.

XRD patterns of Rb–MTO and SiO_2–MTO are illustrated in Fig. 1. The diffractogram of Rb–MTO (Fig. 1a) was in good agreement with that of Rb–MTO reported by Reid *et al.* (9) and the peaks due to the other phase were negligibly weak. The XRD pattern of SiO_2–MTO, as shown in Fig. 1b, demonstrated the enlargement of the basal spacing in layers. The spacing estimated from the peak corresponding to the (020) plane was 23.6 Å. Consistent with this observation, the surface area of SiO_2–MTO was more than two orders larger than that of Rb–MTO (see Table 1); the surface area of SiO_2–MTO extends to those of various zeolites and montmorillonite clay pillared with oxide or even larger. In Fig. 1b, a very broad peak centered at ca. 25° was observed; it can probably be assigned to the amorphous silica as an oxide pillar.

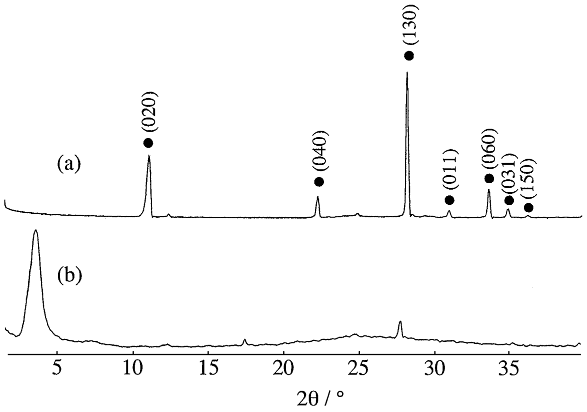


FIG. 1. X-ray powder diffraction patterns of (a) Rb–MTO and (b) SiO_2–MTO. The closed circles indicate the peaks of Rb–MTO (originally assigned by Reid *et al.* (8)).

TABLE 1

Catalytic Activities[a] for NH_3 Oxidation over Various Manganese Ion-Containing Catalysts

Catalyst	Mn content[b] (wt%)	Surface area[c] (m^2 g^{-1})	Temp. (°C)	Conversion of NH_3 (%)	S_{N_2} (%)
Rb–MTO[d]	16	<5	400	Trace	—
SiO_2–MTO	15	790	300	27	96
			400	73	92
			500	89	83
			600	100	86
MnO_2/SiO_2	4.7	314	400	71	24
			500	85	25
			600	100	53

[a] Reaction condition: NH_3, 6%; O_2, 40%; and W/F = 0.06 g s cm^{-3}.
[b] Determined by ICP analysis.
[c] Determined by BET method.
[d] Rb–MTO: $Rb_xMn_xTi_{2-x}O_4$ ($x = 0.75$).

Table 1 shows the conversion of NH_3 over SiO_2–MTO and Rb–MTO, together with the results of MnO_2/SiO_2 as a reference catalyst. The catalytic activity of SiO_2-MTO increased with the increment of temperature and reached unity at 600°C. In contrast, Rb–MTO showed a very poor catalytic activity even at 400°C. The higher catalytic activity of SiO_2–MTO is attributable to the increment of surface area and/or of active sites as a result of the enlargement of the basal spacing. In the temperature range 300–600°C, SiO_2 and TiO_2 without manganese exhibited essentially no catalytic activity, suggesting that Mn ion and/or Mn oxides are responsible for the NH_3 oxidation. The conversions of NH_3 over SiO_2–MTO catalyst were comparable to that over MnO_2/SiO_2 catalyst (Table 1).

Under the present experimental conditions, N_2, N_2O, and H_2O were detected as products from the NH_3 oxidation for all the catalysts. The formation of expected NO and NO_2 was below detectable level. The selectivity to N_2 formation (S_{N_2}) was summarized in Table 1, where S_{N_2} is defined by

$$\begin{aligned} S_{N_2} &= 100 \times 2 \cdot [\text{Amount of } N_2 \text{ formed}]/ \\ &\quad [\text{Amount of } NH_3 \text{ consumed}] \\ &\approx 100 \times [\text{Amount of } N_2 \text{ formed}]/ \\ &\quad ([\text{Amount of } N_2 \text{ formed}] \\ &\quad + [\text{Amount of } N_2O \text{ formed}]) \end{aligned}$$

Interestingly, the S_{N_2} values of SiO_2-MTO were extremely higher than those of MnO_2/SiO_2; the values are as high as those of supported transition metal oxides such as MoO_3, V_2O_5, Bi_2O_3, and PbO (8, 10) and Cu-zeolite (11) reported previously and have never been reported for Mn-containing catalysts. Thus, SiO_2–MTO was concluded to exhibit high selectivity to N_2 in the catalytic oxidation of NH_3. The S_{N_2} values of MnO_2/SiO_2 were quite low, but with the high selectivity to N_2O.

The reduction–oxidation behavior of catalysts strongly affects the catalytic performance in the catalytic oxidation of NH_3 (10). Hence, H_2-TPR measurements were carried out to elucidate the oxidation state of the catalysts with different reaction performance with regard to selectivity. The H_2-TPR profiles for SiO_2–MTO, Rb–MTO, and MnO_2/SiO_2 are shown in Fig. 2. For MnO_2/SiO_2 (Fig. 1c), the H_2-TPR profile consists of a large reduction peak centered at ca. 320°C with an additional shoulder at ca. 420°C. A similar H_2-TPR profile has been previously reported for MnO_2/Al_2O_3 (12). The amounts of oxygen taken up from catalysts during the H_2-TPR measurement were evaluated from the total H_2 consumption measured at 25–600°C. For the MnO_2/SiO_2 catalyst, the O/Mn atomic ratio is close to 1.0, indicating the reduction sequence of MnO_2 to MnO ($Mn^{4+} \rightarrow Mn^{2+}$) by a two electron reduction (12, 13). The amount of H_2 consumed for the peak centered at ca. 320°C was two times larger than that for the 420°C peak, suggesting that the former peak can be attributable to $MnO_2 \rightarrow Mn_3O_4$ and the latter peak to $Mn_3O_4 \rightarrow MnO$.

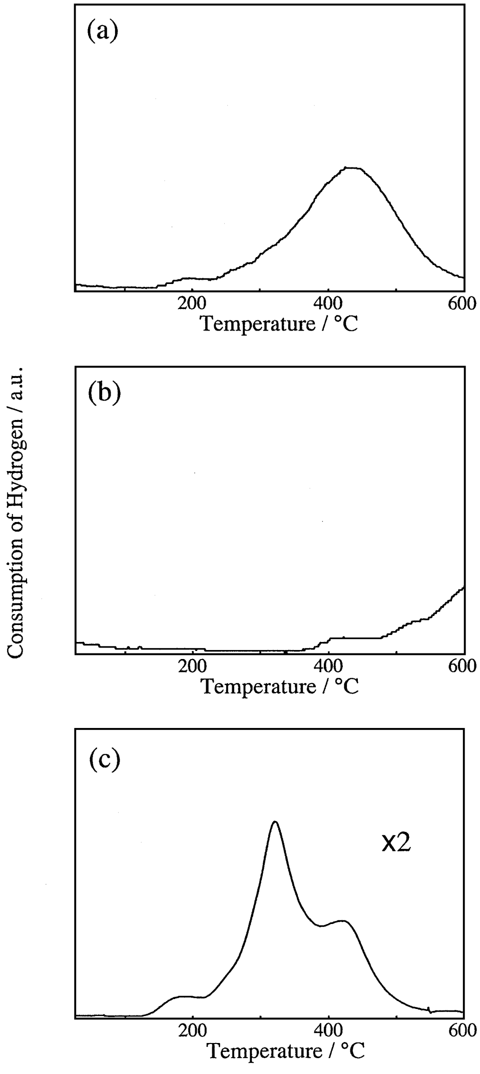
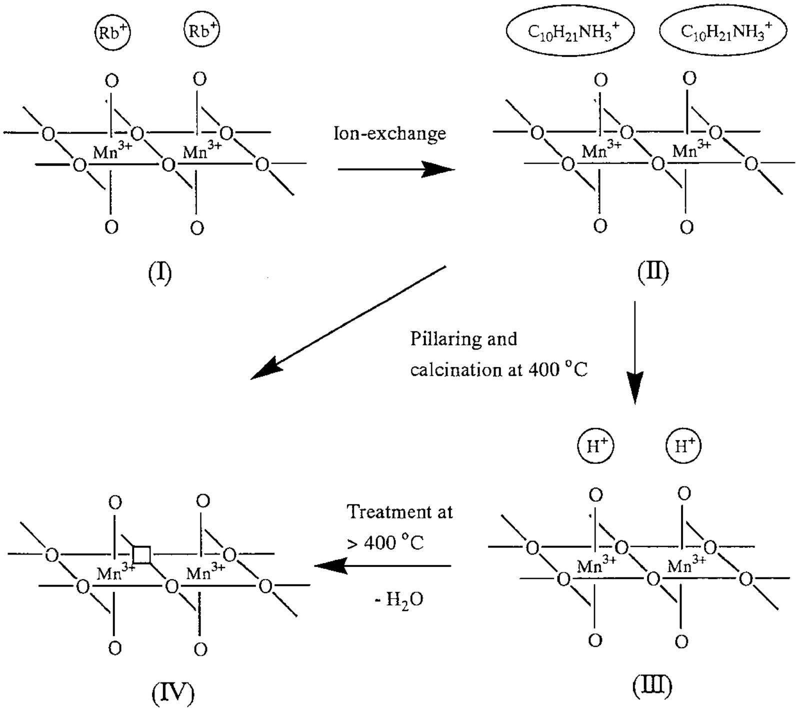


FIG. 2. H_2-TPR profiles of (a) SiO_2–MTO, (b) Rb–MTO, and (c) MnO_2/SiO_2.

The H_2-TPR profile for SiO_2–MTO catalyst gave a very broad peak with a maximum value at ca. 420°C (Fig. 2a). Since neither TiO_2 nor SiO_2 showed clear reduction peaks at 25–600°C, the observed broad peak is attributable to the reduction of manganese ions in the layers. In contrast to the result of MnO_2/SiO_2 catalyst, the O/Mn atomic ratio of SiO_2–MTO is close to 0.5, indicating that one electron reduction of manganese ion takes place, either $Mn^{4+} \rightarrow Mn^{3+}$ or $Mn^{3+} \rightarrow Mn^{2+}$. The latter reduction may be appropriate for the broad peak because no more reduction peak was observed at higher temperatures up to 750°C. Consistent with this argument, the reduction peaks of both samples containing Mn, SiO_2–MTO, and MnO_2/SiO_2 were completed at almost the same temperature, ca. 500–600°C (Figs. 2a and 2c). It was concluded in the present study that one electron reduction of manganese ion took place by H_2 in the temperature range 25–600°C for SiO_2–MTO while two electron reduction for MnO_2/SiO_2. The H_2-TPR results suggest that the manganese ions in SiO_2–MTO were in a oxidation state of +3 even in the absence of either Rb^+ or $C_{10}H_{21}NH_3^+$ ion as a charge- balancing cation. In the case of structurally determined Rb–MTO which involves Mn^{3+} and Rb^+ cations, the reduction peak attributable to $Mn^{3+} \rightarrow Mn^{2+}$ should be observed in H_2-TPR profile in the temperature range 25–600°C. The reduction peak of Rb–MTO, however, started to develop above a high temperature of 400°C with less intensity (Fig. 2b). This indicates that Rb–MTO was difficult to be reduced by H_2. The low reducibility of Rb–MTO may originate from slow diffusion rate of H_2 into the interlayer; on the other hand, for SiO_2–MTO, H_2 easily diffuse into the interlayer with oxide pillar.

We presume that the valence state of manganese ions could be a dominant factor to the selectivity for the oxidation reaction, although further studies are required to clarify it. A proposed sequence of manganese oxide layers in the course of SiO_2–MTO preparation is schematically shown in Scheme 1.

The manganese ion in Rb–MTO is located at the center surrounded by the six oxygens (9). The valence state of manganese ion is +3 and the charge neutrality is maintained by the balancing cation, Rb^+ in Rb–MTO (I) and $C_{10}H_{21}NH_3^+$ in the ion-exchanged MTO (II). The TPR results suggest that the oxidation state of +3 was kept even after pillaring and calcination at 400°C. There are two possibilities to maintain the neutrality; the presence of the other



SCHEME 1

balancing cation, probably H^+ (III in Scheme 1) and the formation of oxygen vacancies (IV in Scheme 1). The former could be transformed into the latter by an accompanying desorption of H_2O at elevated temperatures. Some catalytically active sites on metal oxides for the NH_3 oxidation reaction have been proposed so far. Holbrook and Wise (14) have reported for NH_3 oxidation that the selectivity to N_2 or N_2O formation is closely related to the surface density of charged oxygen species. Keenan *et al.* (15) and de Boer *et al.* (10) have proposed that the active site for N_2 formation is on oxygen vacancies. Our H_2-TPR results as well as the catalytic performance suggest that, to be consistent with the mechanisms proposed by Keenan *et al.* and de Boer *et al.*, the presence of oxygen vacancy together with Mn^{3+} might be responsible for the observed high selectivity of the SiO_2–MTO catalyst toward N_2 formation.

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