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On the location of different titanium sites in Ti–OMS-2 and their catalytic role in oxidation of styrene

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Abstract

Octahedral manganese oxide molecular sieves (OMS-2) modified by impregnation of TiO₂ exhibit a higher catalytic activity for oxidation of styrene with *tert*-butylhydroperoxide in comparison to titanium-incorporated OMS-2, where the styrene conversions were *ca.* 70% and 45–50%, respectively. The framework of titanium species has no effect on the enhancement of catalytic activity, while the non-framework of titanium species induces a synergetic effect that enhances the oxidation of styrene with *tert*-butylhydroperoxide. © 2007 Elsevier B.V. All rights reserved.

Keywords: Titanium-incorporated octahedral manganese oxide molecular sieves; Non-framework titanium; Oxidation of styrene

1. Introduction

Octahedral manganese oxide molecular sieves (OMS-2) are currently considered as one of the potential catalysts in oxidation of alcohols and olefins [1–3]. OMS-2 materials are manganese oxide (MnO_x; $x = 1.85\text{--}2.00$) with a framework structure consisting of 2×2 type tunnels, built up of MnO₆ octahedra with a pore diameter of 4.6 Å [4]. Although, recently, the oxidation of styrene has been reported by using Me–OMS-2 (Me = Fe, Cu, Ni and Co) [5], it is desirable to study the catalytic performance of OMS-2 material with the addition or incorporation of titanium. An understanding of the synthetic methods of catalyst preparation is needed for the precise control of the structure and location of catalytically active sites on OMS-2. Here, we report on the study of the effect of the location of titanium sites, either in the framework or non-framework of OMS-2, and their catalytic role in the oxidation of styrene with *tert*-butyl hydroperoxide (TBHP) as the oxidant. X-ray powder diffraction (XRD), photolu-

minescence, surface area and pyridine adsorption measurements were used to characterize these samples. The catalytic activity of Ti containing OMS-2 was also compared with TS-1 as a reference catalyst.

2. Experimental

2.1. Synthesis

OMS-2 was prepared by a precipitation method according to [6]. A 0.4 M solution of KMnO₄ (13.3 g in 225 ml of deionized water) was added to a mixture of a 1.75 M solution of MnSO₄ · H₂O (19.8 g in 67.5 ml deionized water) and 6.8 ml of concentrated HNO₃. The resulting black precipitate was stirred vigorously and refluxed at 373 K for 24 h. The precipitate was filtered and washed with deionized water until neutral pH and dried at 393 K. This gave OMS-2. Titanium incorporated OMS-2 (Ti–OMS-2) was prepared by the stepwise addition of a KMnO₄ solution (13.3 g in 225 ml of deionized water) to different amounts of Ti₂SO₄ (25–75 ml) (15% v/v in H₂SO₄) in order to produce Ti–OMS-2 in the Ti/Mn ratio of 0.18, 0.43 and 0.67 (as analyzed by using an atomic absorption spectrometer). Upon completion, the mixture was stirred, refluxed,

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filtered, washed, and dried following the above procedure and it was labeled as Ti–OMS-2 (0.18), Ti–OMS-2 (0.43) and Ti–OMS-2 (0.67), where the number in parentheses is the molar ratio of Ti/Mn. Titanium(IV) tetra-2-propoxide ($\text{Ti}(\text{OPr}_4^i)$) was impregnated from its toluene solution into OMS-2 powder and calcined at 773 K for 3 h. Here, this modified OMS-2 is called Ti–OMS-2 (imp). The molar amount of Ti calculated to give the molar ratio of Ti/Mn was 0.18. For comparison, a mechanical mixture of TiO_2 and OMS-2 was prepared by the addition of a calculated amount of TiO_2 (rutile) powder to OMS-2 with a Ti/Mn molar ratio of 0.67. This catalyst was labeled as TiO_2 –OMS-2 (mix). Table 1 summarizes the preparation method, the chemical composition and labeling of titanium containing OMS-2. In this study, TS-1 was also used as a reference catalyst. TS-1 (2 mol% of titanium) was prepared according to a procedure described earlier [7,8].

2.2. Characterization

All samples were characterized by powder XRD for the crystallinity and phase content of the solid materials using a Shimadzu XRD 6000 diffractometer with the $\text{CuK}\alpha$ ($\lambda = 1.5405 \text{ \AA}$) radiation as the diffracted monochromatic beam at 30 kV and 30 mA. Atomic absorption analysis (AAS) was employed for elemental composition analyses of manganese and titanium in the sample. A Perkin–Elmer model Analyst 400 spectrophotometer was used to carry out the analyses. The acidity of the solids was characterized by an absorbed base probe molecule. A wafer of the sample (10–12 mg) was locked in the cell equipped with CaF_2 windows, and evacuated at 400 °C under vacuum condition for 4 h. Pyridine as a probe molecule was introduced into the evacuated sample at room temperature. The IR spectra of the sample were monitored at room temperature after desorption of pyridine at 150 °C for 1 h. Photoluminescence

spectra were recorded in air at room temperature on a Perkin–Elmer LS 55 spectrometer. The emission spectra observed at an excitation wavelength was 430 nm.

2.3. Catalytic testing

Oxidation of styrene was carried out using the above catalysts. Styrene (5 mmol), 70% aqueous *ter*-butyl hydroperoxide (TBHP) (10 mmol), catalyst (50 mg) and acetonitrile (15 ml) as solvent were placed in a round-bottomed flask with a reflux condenser and the reaction was performed with stirring at 70 °C in an oil bath. The products were collected in a period of time and analyzed by GC and GC–MS.

3. Results and discussion

XRD patterns of OMS-2, Ti–OMS-2 (0.18) and Ti–OMS-2 (0.43) show that the samples are pure and highly crystalline and matched those of cryptomelane Q [9]; the natural counterpart of OMS-2 material (see Fig. 1). The results confirmed that OMS-2, Ti–OMS-2 (0.18) and Ti–OMS-2 (0.43) materials consist of the cryptomelane structure: 2×2 tunnels with a pore size of 4.6 Å, composed of double chains of edge sharing and corner sharing MnO_6 octahedra [4]. The absence of other peaks in the XRD patterns except the cryptomelane peaks suggested that Ti was successfully incorporated in the framework of Ti–OMS-2. In order to confirm the successful incorporation of titanium, the XRD patterns of Ti–OMS-2 were compared with the mechanical mixture of TiO_2 (rutile) and OMS-2 where the mixture (TiO_2 –OMS-2 (mix)) showed the presence of the rutile phase (see Fig. 1 and Table 1). If Ti is successfully incorporated in the framework of OMS-2, one expects that the bigger the substituted atom is, the bigger is the unit cell volume. Calculation of the unit cell volume of OMS-2

Table 1
Chemical composition and physicochemical properties of OMS-2, Ti–OMS-2 and TiO_2 –OMS-2

Samples	Molar ratio of Ti/Mn ^a	Molar amount of Mn ^b	Molar amount of Ti ^b	Methods of introduction of Ti species	Location of Ti species	Structure of non-framework Ti species	Surface area ($\text{m}^2 \text{ g}^{-1}$)
OMS-2	0.00	552.2	0.0	–	–	–	155
Ti–OMS-2 (0.18)	0.18	412.5	74.4	Direct synthesis	Framework	–	152
Ti–OMS-2 (0.43)	0.43	420.4	181.4	Direct synthesis	Framework	–	149
Ti–OMS-2 (0.67)	0.67	342.0	228.2	Direct synthesis	Framework and non-framework	Rutile	152
TiO_2 –OMS-2 (imp) ^c	0.18	552.0	99.4	Impregnation	Non-framework	Amorphous	N.d. ^e
TiO_2 –OMS-2 (mix) ^d	0.67	552.2	369.9	Mechanical mixing	Non-framework	Rutile	N.d. ^e

^a Analysis was carried out by atomic absorption spectrometer.

^b The amount of OMS-2, Ti–OMS-2 and TiO_2 –OMS-2 were 50 mg.

^c Titanium(IV) tetra-2-propoxide ($\text{Ti}(\text{OPr}_4^i)$) was impregnated from its toluene solution into OMS-2 powder and calcined at 773 K for 3 h.

^d Catalyst was prepared by addition of calculated amount of Ti from TiO_2 powder to OMS-2.

^e Not determined.

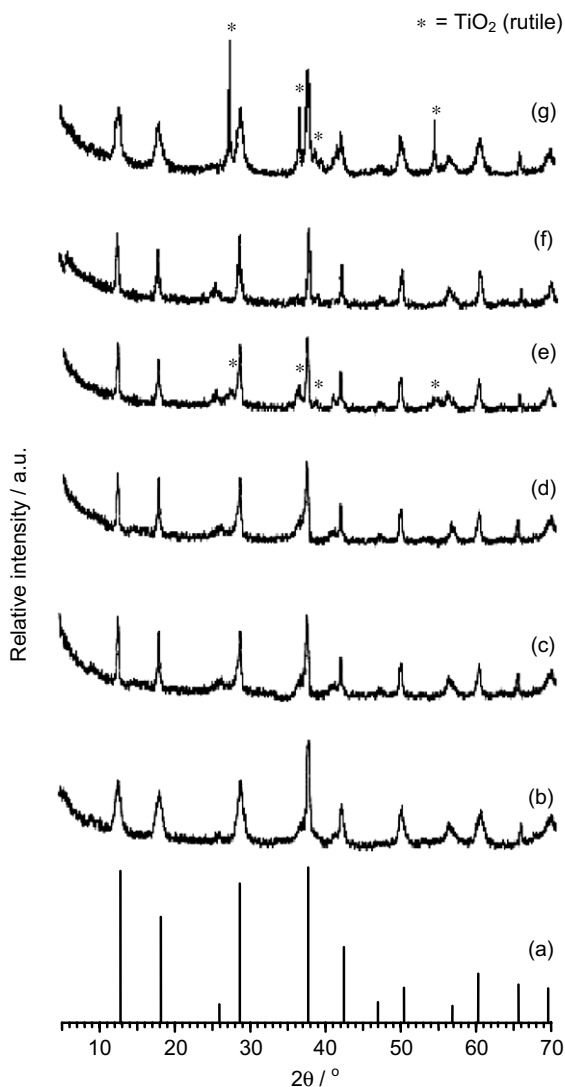


Fig. 1. X-ray diffractograms of (a) cryptomelane (JCPDS 29, 102), (b) OMS-2, (c) Ti-OMS-2 (0.18), (d) Ti-OMS-2 (0.43), (e) Ti-OMS-2 (0.67), (f) TiO₂-OMS-2 (imp) and (g) Ti-OMS-2 (mix).

(271 Å³) and Ti-OMS-2 (0.43) (277 Å³) shows that the unit cell volumes increase on incorporation of Ti in the framework of OMS-2. The lattice enlargement originates from the replacement of the smaller ionic Mn⁴⁺ (ionic radius is 0.53 Å) by the relatively larger ionic Ti⁴⁺ (ionic radius is 0.61 Å). This shows a strong evidence of isomorphous substitution of Mn atoms by Ti into the framework of Ti-OMS-2. Moreover, it can be found that with the incorporation of Ti, the full width at half maximum decreases indicating an increase in the grain size. It is observed that the peaks of the rutile phase of TiO₂ appear at a Ti/Mn ratio higher than *ca.* 0.5 and are not observed at a Ti/Mn ratio less than *ca.* 0.5 (see Fig. 1). By considering the upper limit of the titanium that can be incorporated into the framework, one would expect non-framework titanium species to be formed when the Ti/Mn ratio reached *ca.* 0.5. The amount of Ti located in the non-framework is *ca.* 25% in Ti-OMS (0.67). This argument is supported by

the presence of the rutile phase of TiO₂ in Ti-OMS-2 (0.67) (see Fig. 1). However, no reflection for the rutile phase of TiO₂ is observed in TiO₂-OMS-2 (imp) where the catalyst is prepared by the impregnation method. This result implies that the structure of TiO₂ in TiO₂-OMS-2 (imp) is in the amorphous form.

The photoluminescence (PL) was also used to confirm the absence of non-framework TiO₂, because non-framework TiO_x with a very small crystallite size cannot be detected by XRD. The PL spectra are useful to disclose the efficiency of charge carrier trapping, migration and transfer, and to understand the nature of electron-hole pairs in TiO₂ semiconductor particles since PL emission results from the recombination of photo-excited free carriers [10]. In this study, the 430 nm excited PL spectra of all pressed-powder samples at room temperature were examined in the range of 560–680 nm. The PL spectra of OMS-2, Ti-OMS-2 (0.43) and TiO₂-OMS-2 (mix) are shown in Fig. 2. The results indicated that the photoluminescence intensity of TiO₂-OMS-2 (mix) ($\lambda_{em(max)} \sim 600 \pm 10$ nm; FWHM ~ 40 nm) was substantially higher than that of OMS-2 and Ti-OMS-2 (0.43) (see Fig. 2). The relative intensity of Ti-OMS-2 (0.43) and TiO₂-OMS-2 (mix) is similar suggesting that there are no TiO_x particles exist in Ti-OMS-2 (0.43) sample. This result reinforces our suggestion that Ti is incorporated in the framework of Ti-OMS-2. The incorporation of Ti in the framework of OMS-2 was also further supported by the surface area analysis (see Table 1). It is revealed that the surface area of OMS-2 and Ti-OMS-2 is almost the same.

Reaction products of oxidation of styrene using TBHP as the oxidant catalyzed by TiO₂ (rutile phase), OMS-2, TiO₂-OMS-2 and Ti-OMS-2 were analyzed by GC. The major products in this reaction proved to be benzaldehyde, styrene oxide and phenylacetaldehyde. The selectivities towards benzaldehyde, styrene oxide and phenylacetaldehyde as the reaction products are shown in Fig. 3. As

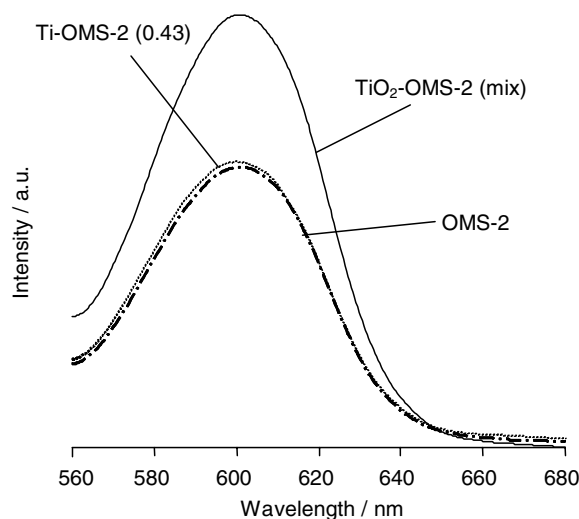


Fig. 2. Photoluminescence spectra of OMS-2, Ti-OMS-2 (0.43) and TiO₂-OMS-2 (mix). The excitation wavelength is 430 nm.

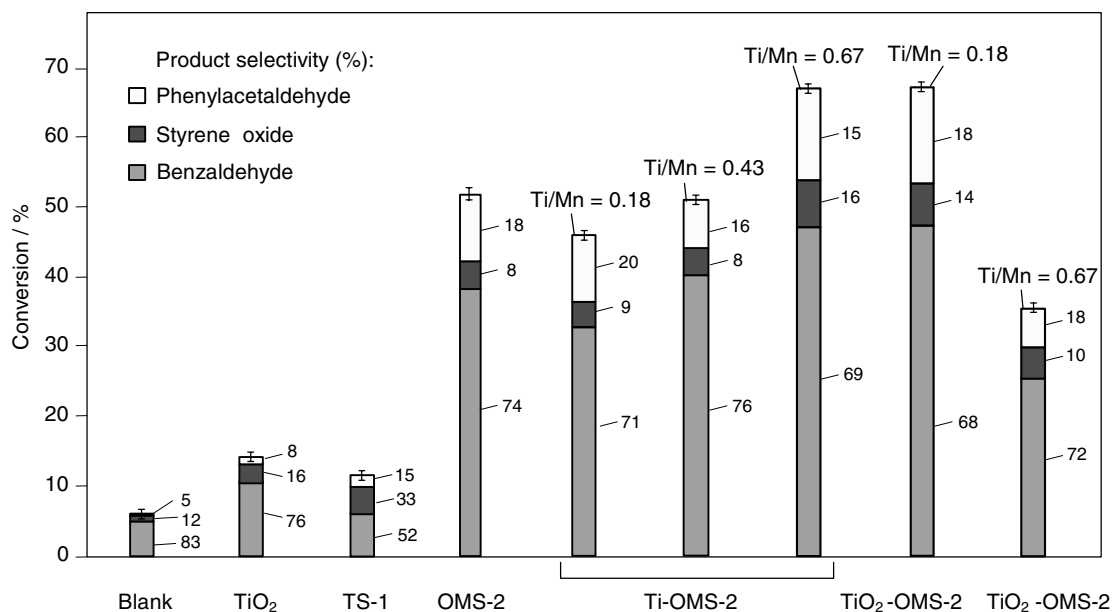


Fig. 3. The conversion and product selectivity of oxidation styrene with *tert*-butyl hydroperoxide (TBHP) using TiO₂, TiO₂-OMS-2, Ti-OMS-2, OMS-2 and TS-1. All reactions were carried out at 70 °C with styrene (5 mmol), 70% aqueous TBHP (10 mmol), acetonitrile (15 ml) and catalyst (50 mg) with vigorous stirring.

indicated in Fig. 3, the reaction catalyzed by all the catalysts produced the highest yield of benzaldehyde and their selectivities towards the formation of products are almost similar to each other. The high selectivity (52%) towards benzaldehyde over TS-1 was surprising since that phenylacetaldehyde and benzaldehyde were the major products from the oxidation of styrene catalyzed by the TS-1 zeolite [10], while a speculated product, styrene oxide, was not detected. Brønsted acid sites originating from framework titanium species catalyze the rearrangement of the intermediate, leading to the formation of phenylacetaldehyde [11]. This argument is in agreement with our oxidation of styrene over TS-1, since no Brønsted acid sites have been detected in our TS-1 which has been analyzed by the pyridine adsorption method [7]. IR spectrum of acidity study by pyridine adsorption after evacuation under a vacuum at 400 °C and 150 °C revealed in Fig. 4a shows that Lewis acid sites are formed in Ti-OMS-2 (0.43) as indicated by the appearance of peaks at 1447 cm⁻¹, 1489 cm⁻¹ and 1604 cm⁻¹. In contrast, no peaks are observed for the OMS-2 sample in Fig. 4b. The absence of peaks at 1540 cm⁻¹ confirms that there are no Brønsted acid sites in both samples. This is the possible reason why TiO₂-OMS-2, Ti-OMS-2, TiO₂ and OMS-2 catalysts are not selective towards phenylacetaldehyde. A high selectivity towards benzaldehyde may be due to OMS-2 and TiO₂ promoting the carbon-carbon bond cleavage, thus resulting in the formation of benzaldehyde.

As shown in Fig. 3, a considerable increase in the conversion of styrene over Ti-OMS-2, OMS-2, TiO₂-OMS-2, TiO₂ and TS-1 after 3 h of the reactions is clearly observed when Ti-OMS-2 (0.67) and TiO₂-OMS-2 (imp) are used as catalysts. The increase in oxidation activity of Ti-OMS-2

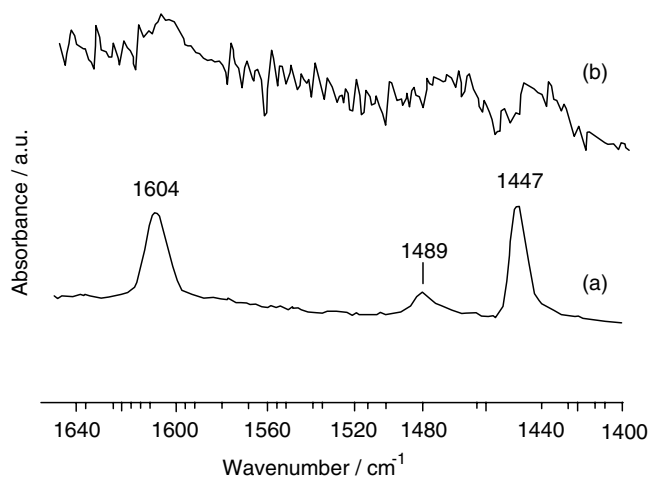


Fig. 4. FTIR spectra of (a) Ti-OMS-2 (0.43) and (b) OMS-2 after evacuation under vacuum at 400 °C for 4 h followed by pyridine adsorption at room temperature and evacuation at 150 °C for 1 h.

(0.67) and TiO₂-OMS-2 (imp) can be explained on the basis of the presence of non-framework titanium species. The superior performance of Ti-OMS-2 (imp) and Ti-OMS-2 (0.67) strongly suggests the occurrence of a synergistic effect of non-framework Ti with OMS-2, since Ti-OMS-2 (mix), a mechanical mixture of TiO₂ and OMS-2, gives a relatively lower conversion of styrene (see Fig. 3). Leaching is a particular problem of solid catalysts in liquid phase reactions. The catalysts were recycled three times. The activities of the recovered and dried Ti-OMS-2, OMS-2 and TiO₂-OMS-2 showed an insignificant change (*ca.* 3–5%) that corresponds to experimental observations within experimental error in their catalytic activity in the

recycling test. This suggests a good regenerability of the catalysts in the oxidation of styrene with *tert*-butylhydroperoxide.

The results of this investigation lead to the conclusion that the framework of titanium species in Ti–OMS-2 has no effect on the enhancement of catalytic activity, while the existence of Ti in the non-framework structure of OMS-2 induces a synergetic effect that enhances the catalytic activity in the oxidation of styrene with *tert*-butylhydroperoxide. Ti–OMS-2 containing non-framework Ti is highly active (*ca.* 70% conversion of styrene) and selective towards the oxidation of styrene to give benzaldehyde (68%) as the main product. Further detailed studies are, however, necessary to understand the interactions between TiO₂ and OMS-2 support and the reaction mechanism.

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