

RKCL3871

**PHYSICO-CHEMICAL STATE OF TITANIA IMPREGNATED ON  
MCM-41 MESOPOROUS MATERIAL UPON LIQUID-PHASE  
REACTION OF TITANIUM ALKOXIDE**

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*Received February 19, 2001*

*Accepted May 15, 2001*

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**Abstract**

Titania was impregnated on MCM-41 mesoporous material by the liquid-phase reaction of titanium butoxide followed by washing and calcination. The impregnated titania was highly dispersed on the pore wall with tetrahedral coordination. The impregnating amount of titania was considerably larger than 23%, and produced the peroxy radical upon the addition of hydrogen peroxide.

*Keywords:* Titania impregnation, mesoporous material, peroxy radical

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**INTRODUCTION**

Attempts at introducing titanium atoms into the zeolite structure have been made to prepare active catalysts for the partial oxidation of various hydrocarbons by hydrogen peroxide [1,2]. However, the applications of titanium-containing zeolites are limited due to their small pore entrance and low content of titanium [2]. Mesoporous materials synthesized using surfactants as templates are attractive materials with uniform mesopores, which are considerably large compared to zeolite [3]. The titanium-containing MCM-41 mesoporous material has catalytic activity for the partial oxidation of large molecules but its activity is small.

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This paper deals with the impregnation of titania on the pore wall of MCM-41 mesoporous material by a liquid-phase reaction of titanium butoxide. The physico-chemical states of impregnated titania on mesoporous material, especially dispersion and coordination of titania, are discussed based on XRD, XPS and ESR results.

## EXPERIMENTAL

MCM-41 mesoporous material and the titania-impregnated MCM-41 mesoporous material were prepared following the procedure described in the literature [3,4]. The composition was  $4\text{SiO}_2 : 1\text{HTABr} : 1\text{Na}_2\text{O} : 0.15(\text{NH}_4)_2\text{O} : 350\text{H}_2\text{O}$ . The average diameter of MCM-41 mesopores was estimated at  $35 \text{ \AA}$ . The impregnating amount of titania was controlled by varying the concentration of titanium butoxide in ethanol. The titania-impregnated MCM-41 mesoporous material was obtained by calcination at  $550^\circ\text{C}$  for 4 h, through removing the butoxide and converting the impregnated titanium butoxide into titania. Titania-impregnated mesoporous materials were denoted as  $\text{Ti}(x)\text{MCM-41}$ , and the “x” in the parentheses was the impregnating amount of titania on a weight basis. The sample prepared without washing was denoted by adding “\*” to its name.

The XRD pattern of mesoporous material was recorded in an X-ray diffractometer (Korean Basic Science Institute/Gwangju Branch, Rigaku, D/Max-2400) with  $\text{CuK}\alpha$  X-ray at 40 eV and 20 mA. A SEM (JEOL, JSM-5400) with an EDX attachment (Noran, Series II) was used to examine in order to determine the impregnating amount of titania. The dispersion of titania was investigated by XPS (Surface Science 2701 MX-Probe) with  $\text{AlK}\alpha$  X-ray at 10 kV and 8 mA. Beam size was  $300 \mu\text{m}$ . The surface of the sample was sputtered by an  $\text{Ar}^+$  ion beam with a sputtering speed of  $0.5 \text{ \AA s}^{-1}$  (as  $\text{SiO}_2$ ). Nitrogen adsorption isotherm was obtained using a home-built volumetric adsorption apparatus at liquid nitrogen temperature. The reaction between titanium butoxide and mesoporous material was examined using an FT-IR spectrometer (BIORAD, FTS 175C). A sample wafer was placed in a gas cell, which had a heating system and a vacuum manifold.

Radical formation on  $\text{TiMCM-41}$  mesoporous materials by the addition of hydrogen peroxide (35%, Junsei) was investigated using an ESR spectrometer (Bruker, ER-200D), which was operated at 9.45 GHz (X-band) microwave frequency. The modulation frequency was 100 kHz, and the detector (Anritsu, MF 76A) with an accuracy of  $\pm 0.1 \text{ kHz}$  was used. The g-factor of radicals was calibrated relative to the signal of DPPH ( $g = 2.0036$ ).

## RESULTS AND DISCUSSION

The XRD pattern of the MCM-41 mesoporous material prepared was in agreement with that reported previously [3]. The impregnating amounts of titania on MCM-41 mesoporous materials are listed in Table 1. The maximum of titania impregnation on MCM-41 mesoporous material was 23%. Without washing after the reaction, some titanium butoxide in the pore could be deposited as a separated titania phase during the calcination treatment, increasing the impregnating amount of titania to 28%.

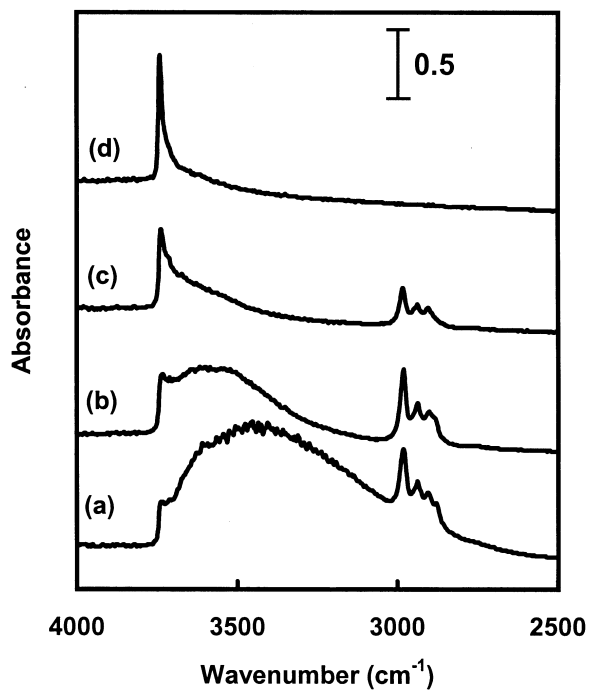
Capillary condensation in the mesopores was observed at 0.40 of  $P/P_0$  on the nitrogen adsorption isotherm of MCM-41 mesoporous material. Although nitrogen uptake at high  $P/P_0$  decreases with titania impregnation, the capillary condensations of mesopores were still observed. The XRD peaks observed at about  $2^\circ$  were reduced to half by titania impregnation, but peaks relating to the crystalline titania phase were not observed even on Ti(23)MCM-41 with the largest amount of titania impregnation. On the other hand, small diffraction peaks of anatase, crystalline titania with an octahedral coordination, were observed at  $25^\circ$ ,  $38^\circ$  and  $48^\circ$  on Ti(28)\*MCM-41 prepared without removing non-reacted titanium butoxide. Observation of the anatase phase indicated the conversion of non-reacted titanium butoxide to crystalline titania. However, the titanium butoxide reacted with hydroxyl groups of the mesoporous material was dispersed on the pore wall without formation of any crystalline structure. No large decrease in nitrogen uptake due to the pore blocking of titania was observed due to high dispersion of titania. The gradual decrease of average pore size indicated the narrowing of pore walls by titania impregnation.

**Table 1**

Impregnating amounts of titania and surface areas of the prepared TiMCM-41 mesoporous materials

Titania-impregnated MCM-41	Added amount (wt.% as TiO <sub>2</sub> )	Retained amount (wt.% as TiO <sub>2</sub> )	BET surface area (m <sup>2</sup> /g)
MCM-41	-	-	1150
Ti(1.8)MCM-41	3.7	1.8	1130
Ti(4.0)MCM-41	7.4	4.0	1120
Ti(11)MCM-41	13	11	1110
Ti(23)MCM-41	58	23	1030
Ti(28)*MCM-41	58	28*	990

\* without washing



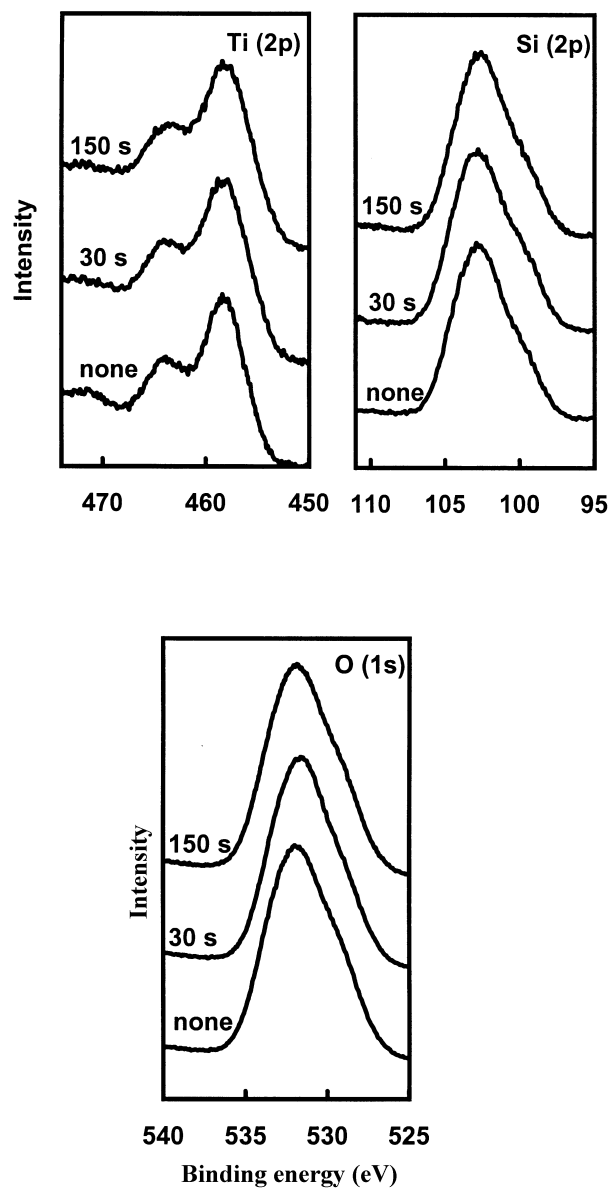
**Fig. 1.** IR spectra of MCM-41 mesoporous material reacted with titanium butoxide. a) evacuated at 25°C, b) at 300°C, c) at 500°C and d) at 550°C for 10 min

**Table 2**

Integrated area of the absorption band of hydroxyl group on TiMCM-41 mesoporous materials after evacuation at 550°C for 1 h

Mesoporous material	Integrated area (arbitrary unit) <sup>a)</sup>
MCM-41	55
Ti(1.8)MCM-41	50
Ti(11)MCM-41	42
Ti(23)MCM-41	35

<sup>a)</sup> Integrated area of absorption band at 4000–3400  $\text{cm}^{-1}$



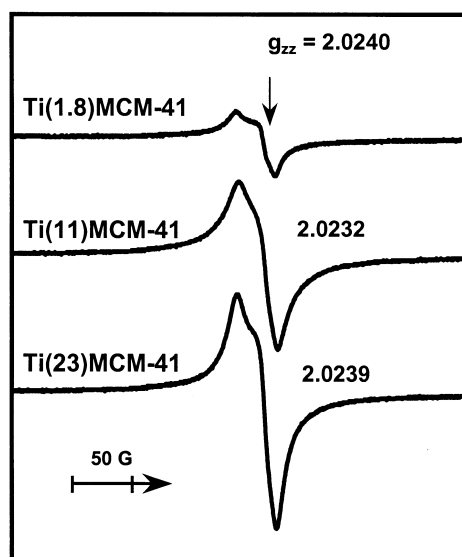
**Fig. 2.** XPS spectra of Ti(23)MCM-41 sample. a) as received, b) after sputtering for 30 s and c) 150 s

The reaction between mesoporous hydroxyl groups and titanium butoxide was examined by FT-IR. Figure 1 shows the IR spectra of the MCM-41 mesoporous material, reacted with titanium butoxide. The sample was washed with anhydrous ethanol after the reaction and dried at 100°C. In the dried state, the reacted mesoporous materials showed butoxyl absorption bands at 2800~3000  $\text{cm}^{-1}$ . The disappearance of the absorption band at 3740  $\text{cm}^{-1}$  indicates that the reaction sites of the mesoporous material with titanium butoxide are the hydroxyl groups. With increasing evacuation temperature, the absorption band of the butoxyl group decreased, while that of the hydroxyl group was restored. The absorption band of the butoxyl group was diminished with evacuation at 550°C. These results showed that titanium butoxide molecules reacted with hydroxyl groups of the mesoporous material, and titanium atoms were bonded with oxygen atoms of the surface as titania after removing the butoxyl group by evacuation at an elevated temperature. Since titanium butoxide reacts with the hydroxyl group of MCM-41 mesoporous material, the surface concentration of the hydroxyl group must be decreased with titania impregnation. The integrated band areas of the hydroxyl group of TiMCM-41 mesoporous materials are listed in Table 2. The band area was determined by the integration from 4000 to 3400  $\text{cm}^{-1}$  and denoted as relative values with an arbitrary unit. The band area of the hydroxyl group was small on TiMCM-41 with a large amount of titania impregnation.

If titania is mainly deposited on the external surface, the titanium atom signal of the XPS spectra decreases with sputtering treatment. In comparison, a constant ratio of titanium atom signal to oxygen atom signal will be observed when titania is highly dispersed on the pore wall. Figure 2 shows XPS peaks of Ti, Si and O from Ti(23)MCM-41. The binding energies of the titanium atom of Ti(23)MCM-41 were 464.4 eV and 458.4 eV, while silicon and oxygen were 103.3 eV and 531.6 eV. These binding energies were in good agreement with titania an amorphous tetrahedral coordination [5,6]. The peak intensities were not changed with sputtering for 30 and 150 s. Sputtering of 30 s corresponds to about the depth of 15 Å and that of 150 s at a depth of 75 Å. Since the average pore diameter of prepared mesoporous material is 35 Å, these depths correspond to the internal surface of the mesopore not to the external surface. The fact that the intensities of the titanium signal relative to those of oxygen and silicon atoms do not vary with sputtering time means a high dispersion of titania on the pore wall as well as the external surface.

Titanium atoms incorporated in the zeolite skeleton show a catalytic activity in the partial oxidation of hydrocarbon with hydrogen peroxide [1,2,4]. The catalytic function is demonstrated by the appearance of a yellow peroxo titanium species with the addition of hydrogen peroxide [7]. The formation of peroxo radical on TiMCM-41 was confirmed by ESR as shown in Fig. 3. The

$g_{zz}$  values were observed at 2.0232~2.0240, and in good accord with the  $g_{zz}$  (= 2.0238) value of peroxy radicals formed on titanium silicate. The formation of peroxy radicals on TiMCM-41 mesoporous material suggests its effective application as an oxidation catalyst [7], because the content of titania is extraordinarily high (23%) and mesopores are large to accept large organic molecules.



**Fig. 3.** ESR spectra of peroxy radical formed on titania-impregnated mesoporous materials by reacting with hydrogen peroxide

## CONCLUSION

Titania can be impregnated on MCM-41 mesoporous material by the liquid-phase reaction of titanium butoxide. The nitrogen adsorption isotherm, XRD, XPS, and FT-IR results show a high dispersion of titania on the pore wall with tetrahedral coordination. The formation of the peroxy radical on TiMCM-41 mesoporous material suggests application as a partial oxidation catalyst of large hydrocarbons due to its large content of titania.

**Acknowledgement.** This work was supported by Korea Science and Engineering Foundation (97-0502-0601-3). We appreciate to Dr. S.J. Kim of KIST for ESR examination.

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