

## Ti가 치환된 MCM-41의 제조 및 특성 분석에 관한 연구

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### Preparation and Characterization of Ti-substituted MCM-41

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#### Introduction

Researchers at Mobil corporation reported the discovery of a new family of mesoporous molecular sieve, designated as MCM-41 in 1992[1,2]. MCM-41 extended the pore range of uniform hexagonal array from micropores of conventional zeolites ( $<1.3\text{nm}$ ) to mesopores up to  $10\text{nm}$ , by employing the templates of different molecular sizes in the synthesis[3,4]. These materials have potential to useful catalysts or adsorbents. It has been reported that the partial substitution of Si in the framework of MCM-41 by Ti (Ti-substituted MCM-41) produces active and selective catalysts in the oxidation of hydrocarbons with air or  $\text{H}_2\text{O}_2$  as oxidants. This represents a significant improvement over a conventional TS-1(Titanium silicalite with MFI structure) catalyst, whose applications are limited due to small pore opening ( $\sim 0.73\text{nm}$ ) of the catalyst. In this work, we studied the characteristics of Ti-substituted MCM-41 prepared under different conditions.

#### Experiments

Ti-substituted MCM-41 was synthesized by using amorphous fumed silica (zeosil), tetraethylorthosilicate (TEOS), tetrabutylorthotitanate (TBOT), and alkyltrimethylammoniumbromides(ATMABr) as templates. The different Ti-substituted MCM-41 were obtained from the hydrothermal synthesis at  $394\text{K}$  for 3 days, by changing the template/Si molar ratios, the Si/Ti molar ratios, templates, and titanium source. The prepared catalysts were washed, dried at ambient temperature, and then calcined at  $813\text{K}$  for 1 h in He flow, and the for 6 h in  $\text{O}_2$  flow. The catalysts were characterized by high resolution transmission electron microscope(HRTEM), X-ray diffraction(XRD), FT-IR,  $\text{N}_2$  adsorption and X-ray absorption fine structure(XAFS). The thermal stability of Ti-substituted MCM-41 was tested by heating calcined samples at a temperature of  $873 \sim 1273\text{K}$  for under helium flow[5,6,7]

#### Results and Discussion

For Ti-substituted MCM-41 synthesized with different templates of the fixed Si/Ti molar ratio of 69, the pore sizes analyzed by XRD, TEM, and  $\text{N}_2$  adsorption have shown the similar trends. For Figure 1 and 2, Ti-substituted MCM-41 synthesized by  $\text{C}_{12}\text{TMABr}$  and  $\text{C}_{14}\text{TMABr}$  showed the best defined X-ray structure. The real image of the local structure by the TEM shown by Figure 3 clearly showed the uniform array of hexagonal channels. The wall thickness was independent of the pore size of the catalysts and remained at ca.  $1\text{nm}$ . As the molar ratio of Si/Ti was decreased, (100) peak positions by XRD shifted at lower angle.

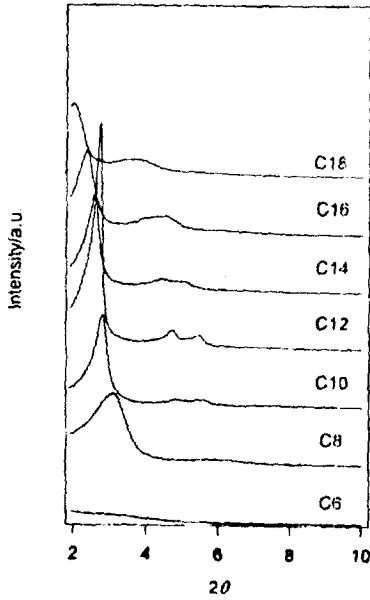


Figure 1. XRD pattern for varying the template sizes (calcined, titanium source: TBOT, Template/Si=0.5, Si/Ti=69)

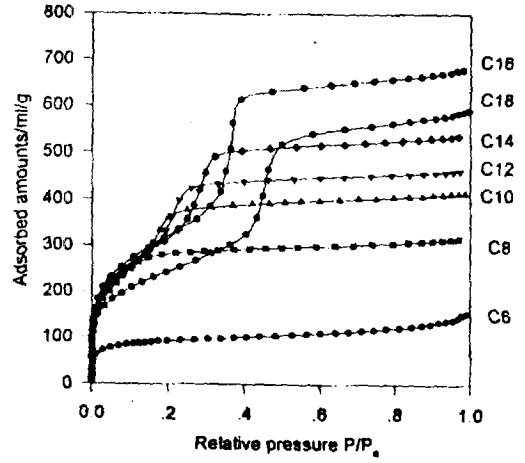


Figure 2. N2 adsorption isotherm for Ti-substituted MCM-41 (calcined, titanium source: TBOT, Template/Si=0.5, Si/Ti=69)

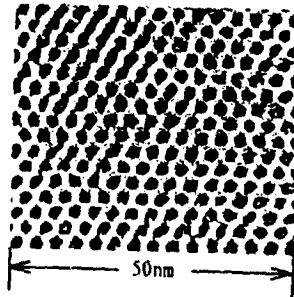


Figure 3. High resolution TEM image of Ti-substituted MCM-41

Additions of above 5.56 mol.% of Ti resulted in the formation of rutile or anatase-like TiO<sub>2</sub> aggregates. Structural regularity appeared to be reduced as Ti replaced by Si sites in the MCM-41 framework. When the molar ratios of template/Si were varied, synthesized catalysts had different structures. Only hydrothermal synthesis at the ratios among 0.5 and 1.0 gave MCM-41 structure. The X-ray absorption near-edge structures(XANES) spectra for Ti K-edge showed the difference between a highly symmetric octahedral environment and a tetrahedral environment in which inversion symmetry was broken. For comparing Figure 4 with Figure 5, the peak shapes of Ti-substituted MCM-41 at pre-edge energy (ca.4965 eV) were different from those of TiO<sub>2</sub> rutile or anatase, but similar to that of TS-1. They also shared the similar local structure as evidenced by EXAFS. The pre-edge peak showed at Figure 5 that the substitutional Si sites were fully filled with Ti at the Si/Ti molar ratio of 12. However, XRD peak for the Si/Ti molar ratio of 12 shown by Figure 6 showed that MCM-41 structures had been broken. Therefore, the maximum amount of Ti that could be introduced within MCM-41 structure was the Si/Ti molar ratio of 24. MCM-41 substituted by Si/Ti = 39 only could be conserved its hexagonal pore structure until 1173K, but did Ti(IV) state within tetrahedral site up to 1273K shown by Figure 7.

### **Conclusions**

Ti-substituted MCM-41 was produced with hydrothermal synthesis. For preservation of the MCM-41 structure(uniform hexagonal pore array), the ratio of template to Si was among 0.5 and 1.0. Ti-substituted MCM-41 with best structural regularity was obtained with templates of C12 and C14. The pore sizes among 1.5nm and 4.0nm. were obtained through changing the template sizes(carbon chain length). Structure regularity decreased as the ratio of Si/Ti decreased. Maximum Ti molar fraction within MCM-41 framework was 0.04(Si/Ti=24). Ti-substituted MCM-41 maintained the hexagonal pore structure until 1173K.

### **Reference**

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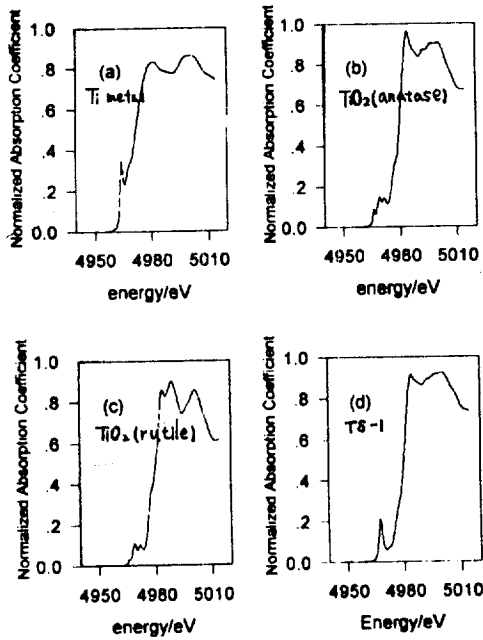


Figure 4. Reference XANES spectra for comparing with Ti-substituted MCM-41

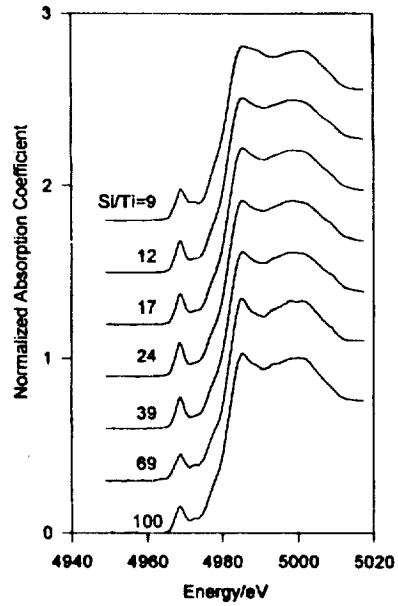


Figure 5. XANES spectra for varying the Si/Ti ratios (calcined, titanium source: TBOT, Template/Si=0.5, template: C12TMABr)

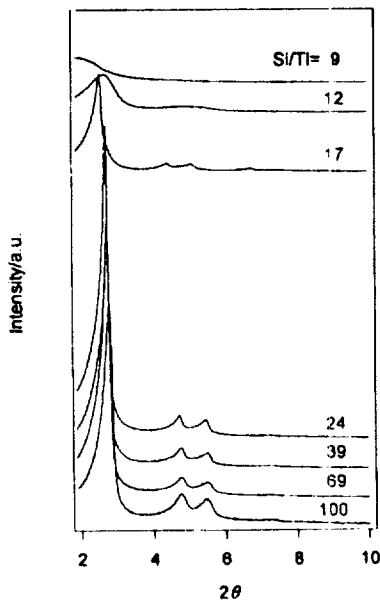


Figure 6. XRD pattern for varying the Si/Ti ratios (calcined, titanium source: TBOT, Template/Si=0.5, template: C12TMABr)

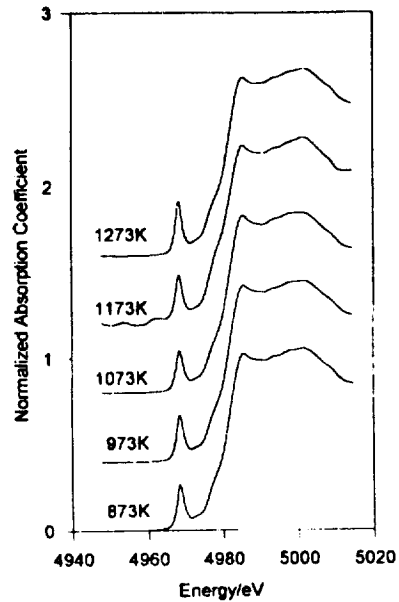


Figure 7. XANES spectra by temperature effect (calcined, titanium source: TBOT, Template/Si=0.5, Si/Ti=39, template: C12TMABr)