

**MCM-41의 수열 안정성과 이온 교환 특성에 대한 연구:
 ^{129}Xe , ^{29}Si 핵자기 공명 분광학, X-선 회절 분석**

전 신애, 김 지만, 유 룡
한국과학기술원 화학과

**Hydrothermal Stability and Ion Exchange of Ultrastable MCM-41:
 ^{129}Xe NMR, ^{29}Si MAS NMR and Powder X-ray Diffraction**

Shinae Jun, Ji Man Kim and Ryong Ryoo
Department of Chemistry, KAIST

Introduction

The discovery of a new family of mesoporous molecular sieves designated as MCM-41 was reported by researchers at the Mobil Corporation in 1992.¹ The MCM-41 material consists of a uniform hexagonal array of linear channels constructed with a silica matrix like a honeycomb. The channel diameter can be tailored within the range of 1.6 - 10 nm by choosing the surfactant as a template. Due to the much larger pore diameters than those of conventional zeolites (≤ 1.3 nm), the MCM-41 material attracts much attention as a new host for large molecules as well as a new catalytic material.^{2,3} However, the practical application of the MCM-41 seems to be limited by the synthesis difficulty, weak stability and lack of ion exchange capacity of the material.

Recently, Ryoo and Kim have reported that the textural uniformity and thermal stability of MCM-41 was markedly improved by repeating NaOH neutralization with acetic acid during hydrothermal reaction of sodium silicate and hexadecyltrimethylammonium (HTA) chloride.⁴ Furthermore, when calcium and yttrium were ion exchanged onto an aluminosilicate MCM-41 (AlMCM-41) sample synthesized likewise with repeating NaOH neutralization, the AlMCM-41 could be heated to 1170 K in O_2 flow with water vapor before structure collapsed seriously.⁵

In the present work, hydrothermal stability of MCM-41 materials in aqueous solutions of acid, base and salt has been investigated by powder X-ray diffraction (XRD) method, BET specific surface area measurement and ^{29}Si MAS NMR spectroscopy. The ion exchanged AlMCM-41 has been studied using ^{129}Xe NMR spectroscopy and ΔH_{ads} of xenon, in order to probe the presence of the ions inside the AlMCM-41 channel.

Experimental

MCM-41 materials were obtained by hydrothermal synthesis using the procedure of Kim et al.⁵ The gel composition for the synthesis of a pure-silica MCM-41 was 6 SiO_2 : 1 HTA : 0.15 $(\text{NH}_4)_2\text{O}$: 1.5 Na_2O : 250 H_2O , and for the synthesis of AlMCM-41, 6 SiO_2 : 0.1 Al_2O_3 : 1 HTA : 0.25 dodecyltrimethylammonium bromide : 0.25 tetrapropylammonium bromide : 0.15 $(\text{NH}_4)_2\text{O}$: 1.5 Na_2O : 300 H_2O .

4. Ryoo, R. and Kim, J. M.: *J. Chem. Soc., Chem. Commun.*, 711 (1995).
5. Kim, J. M., Kwak, J. H., Jun, S. and Ryoo, R.: *J. Phys. Chem.*, in press.
6. Pak, C., Ryoo, R., *J. Kor. Chem. Soc.*, 36, 351 (1992).

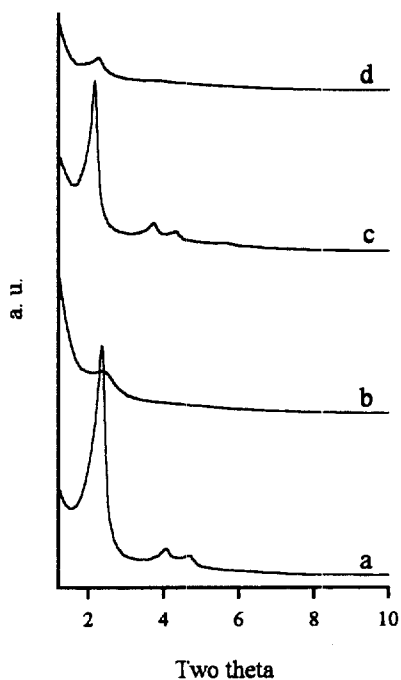


Figure 1. XRD patterns of MCM-41 materials after slurring in doubly distilled water for 12 h at 373 K: (a) AIMCM-41 synthesized with NaOH neutralization, (b) AIMCM-41 synthesized without NaOH neutralization, (c) pure-silica MCM-41 synthesized with NaOH neutralization and (d) pure-silica MCM-41 without NaOH neutralization.

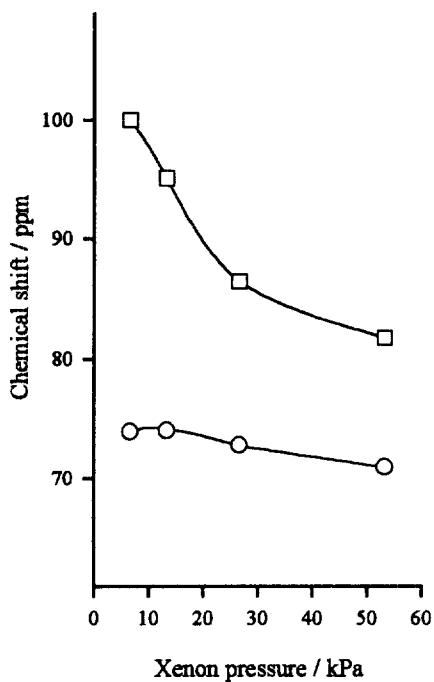


Figure 2. The chemical shift in ^{129}Xe NMR spectra of adsorbed xenon on ion exchanged AIMCM-41 (Si/Al = 39) plotted against xenon pressure at 296 K: (○) Na^+ -exchanged AIMCM-41 and (□) Ca^{2+} -exchanged AIMCM-41.

distilled water for 12 h at 373 K. The XRD patterns in Figure 1(a) and (c) consist of one very intense line and three weak lines, which are indexed to (100), (110), (200) and (210) diffraction lines characteristic of a hexagonal structure of MCM-41, respectively. The XRD lines for the MCM-41 materials synthesized without NaOH neutralization in Figure 1(b) and (d) are severely broadened due to a loss in the textural uniformity upon the hydrolysis of Si-O-Si bond in water. This is confirmed by ^{29}Si MAS NMR spectra. The spectra indicate that the ratio between Si(-OSi) $_3$ OH and Si(-OSi) $_4$ tetrahedral silicon atoms (Q_3/Q_4) increases after slurring in water at 373 K for the MCM-41 synthesized without NaOH neutralization considerably compared with as-calcined sample, while the Q_3/Q_4 silicon ratio for the sample synthesized with NaOH neutralization is not affected by the hydrothermal treatment. The NMR spectra indicate that the Si-O-Si bond in MCM-41 synthesized without NaOH neutralization is easily hydrolyzed by water. The XRD patterns show that the structure of AlMCM-41 is not affected by the concentration of Na^+ ion in water and stable in the range of pH 1 - 10.

The ion exchange of AlMCM-41 can be confirmed by reversible uptakes of sodium and potassium when the AlMCM-41 sample is subjected to "slurry-filtration-wash" cycles using NaNO_3 and KNO_3 solutions in turn. Assuming that the ion exchange occurs with a monovalent metal ion per tetrahedral aluminum site, the results with Na/Al and K/Al in Table 1 suggest that approximately 40% of the total aluminum atoms in the calcined AlMCM-41 are tetrahedrally coordinated within framework.

The chemical shift of the xenon is plotted against the xenon pressure in Figure 2. The ^{129}Xe NMR chemical shift for the Na^+ -exchanged AlMCM-41 is almost independent of xenon pressure changes. However, the chemical shift for the Ca^{2+} -exchanged AlMCM-41 is much larger than the chemical shift for the Na^+ -exchanged AlMCM-41. The chemical shift difference at the same pressure increases as xenon pressure decreases. The chemical shift increase for the Ca^{2+} -exchanged AlMCM-41 against the pressure decrease is very similar to that for Ca^{2+} -exchanged Y zeolite which has been attributed to strong adsorption of xenon on Ca^{2+} ions located inside the supercage.⁶ The heat of adsorption of xenon on the Ca^{2+} -exchanged AlMCM-41 at 296 K confirms strong adsorption of xenon on Ca^{2+} inside the AlMCM-41 channel.

In conclusion, the MCM-41 materials synthesized with NaOH neutralization during the hydrothermal reaction have much better hydrothermal stability in water than the sample synthesized without NaOH neutralization. The high quality AlMCM-41 has a significant ion exchange capacity. Good hydrothermal stability and high ion exchange capacity of MCM-41 suggest that the material can be very useful for supporting catalytic active sites.

Reference

1. Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli J. C. and Beck, J. S.: *Nature*, **359**, 710 (1992).
2. Wu, C.-G. and Bein, T.: *Science*, **264**, 1757 (1994).
3. Tanev, P. T., Chibwe, M. and Pinnavaia, T. J.: *Nature*, **368**, 321 (1994).

결과 및 토론

촉매 제조 및 제조된 Cu-ZSM-5의 특성 분석

Table 1. Effect of Seed crystal and acetone to the synthesized ZSM-5 crystal

Sample	Seed	Acetone/ Silica	Product	Crystal size(μm)	SiO ₂ /Al ₂ O ₃	Surface Area(m ² /g)(BET)	Crystallization time(hr)
A	-	-	ZSM-5	6.0	70	189	40
B ^(a)	-	-	H-ZSM-5	0.3	50	420	-
C ^(b)	-	-	Na-ZSM-5	3.0	68	291	-
D	B	0.7	ZSM-5	1.9	52	345	3
E	C	0.7	ZSM-5	4.0	50	220	12
F	C	-	ZSM-5	5.0	50	195	12

(a) from PQ Co., (b) from DuPont Co.

Table 1의 결과에서 보듯이 Seed를 첨가할 경우 Seed를 첨가하지 않고 합성할 경우에 비교하여 빠른 시간에 ZSM-5 결정이 합성되었다. 또한 seed 크기가 증가할수록 ZSM-5의 크기는 증가하고 표면적은 감소하였다. 아세톤을 첨가할 경우 결정 크기 분포가 더 고르게 나타남을 SEM 사진으로 확인할 수 있었다. Narita 등⁽³⁾은 아세톤의 첨가에 따라 seed 이외의 핵생성이 억제되어 균일한 크기의 ZSM-5 결정이 얻어진다고 보고하였다.

Fig. 1의 (a)는 Cu-ZSM-5를 300°C에서 전처리 후 암모니아를 흡착시킨 것으로 500°C에서 전처리한 (b)에 비해 비교적 저온에서 많은 양의 암모니아를 탈착하였다. 이는 (b)의 경우 고온에서 배기시 수분과 산소가 탈착하여 Cu²⁺의 환원이 많이 일어나고 산점이 생성되기 때문으로 생각할 수 있다. 한편 유기주형물질이 첨가되어 제조된 (c)의 경우 산량이 다른 촉매에 비해 상당히 작으며 200-300°C, 300-450°C에서 두개의 탈착 봉우리가 나타났다. 이는 TPA-Cu-ZSM-5를 500°C에서 전처리할 경우 강산점과 약산점의 두가지 산점이 생성되기 때문에 나타나는 현상으로 사료된다.

IR 분석

Fig. 2의 (a)는 500°C에서 2시간 동안 산소 처리한 후 상온에서 CO를 흡착시킨 결과로 2157cm⁻¹에서 CO-Cu⁺에 할당된 밴드가 나타나지 않았는데 이는 제올라이트내에 구리이온이 대부분 Cu²⁺ 상태로 존재하기 때문이다. (a)의 시료를 500°C에서 H₂를 통과시키면서 2시간 동안 처리한 후 상온에서 CO를 흡착시킨 후의 결과를 (b)에 나타내었는데 (a)의 경우와 같은 결과가 나타났다. 한편 500°C의 H₂처리 후 EPR 스펙트럼 결과에서 Cu²⁺에 기인한 미세구조가 사라지는 결과를 얻을 수 있었다. 따라서 따라서 고온의 H₂처리시 ZSM-5에 이온교환된 구리이온은 대부분 Cu⁰의 형태로 존재하는 것으로 사료된다. CO의 처리온도를 높일수록

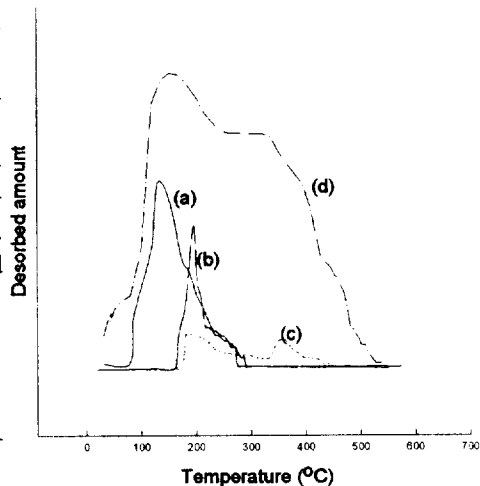


Fig. 1. Temperature programmed desorption of ammonia, (a) Cu-ZSM-5-145 pretreated at 300°C for 2hr, (b) Cu-ZSM-5-145 (c) TPA-Cu-ZSM-5 (d) CuNa-Y-69.8, pretreated at 500°C in He for 2hr for (b),(c),(d), respectively