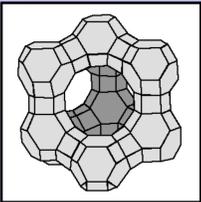


# Preparation and Characterization of Mesoporous Silicoaluminophosphates

A. Buchholz, W. Wang, J. Jiao and M. Hunger

Institute of Chemical Technology, University of Stuttgart, D-70550 Stuttgart



## Introduction

Microporous silicoaluminophosphates (SAPOs) consisting of aluminum, phosphorus, and silicon atoms on tetrahedral sites are interesting materials for heterogeneous catalysis. The incorporation of silicon atoms into the framework of microporous aluminophosphate molecular sieves generates bridging OH groups responsible for the Brønsted acidity of these materials. Since the discovery of a new family of aluminosilicate-based mesoporous molecular sieves, recently this concept was used to prepare novel silicoaluminophosphates with acidic properties. For catalytic applications, the stability of calcined and rehydrated mesoporous silicoaluminophosphates is important concerning the structure of the molecular sieves and the behavior of the Brønsted acid sites.

In the present work, the mesoporous silicoaluminophosphates UHM-3 and Hex-1 have been synthesized and studied. The calcined and hydrated materials were characterized within a period of 8 weeks by  $N_2$  adsorption, NMR, and XRD to investigate the stability. *In situ* solid-state CF (CF: continuous-flow) MAS NMR spectroscopy was applied to observe changes and damages of the UHM-3 and Hex-1 framework towards ammoniation/hydration followed by a deammoniation/dehydration. The investigations were performed to determine the variation of the aluminum coordination upon water and ammonia adsorption, the formation of framework defects and defect SiOH groups, and the conditions of water and ammonia desorption.

## Experimental Part

### Synthesis of UHM-3 and Hex-1:

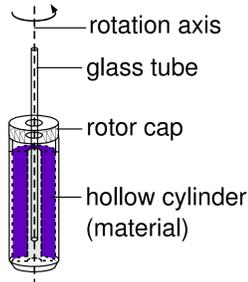
UHM-3 was synthesized according to Ref. [1]. Hex-1 was prepared according to a recipe for the synthesis of mesoporous AlPOs, with addition of silicon [2].

### Characterization

Powder XRD patterns were obtained on a Siemens D5000 diffractometer ( $CuK_{\alpha}$  radiation).  $^1H$ ,  $^{27}Al$ ,  $^{29}Si$ , and  $^{31}P$  MAS NMR measurements were performed on a Bruker MSL 400 spectrometer at resonance frequencies of 400.13, 104.26, 79.49 and 161.98 MHz, respectively, with samples spinning rates of 4 kHz for  $^{29}Si$  and 10 kHz for  $^1H$ ,  $^{27}Al$ , and  $^{31}P$  MAS NMR spectroscopy.  $N_2$  adsorption was performed on a Micromeritics ASAP 2010.

### *In situ* solid-state NMR studies

The *in situ* MAS NMR investigations were carried out by applying a Bruker 4 mm MAS NMR probe modified with a gas injection system. A glass tube with an outer diameter of 1 mm was inserted into a 4 mm MAS NMR rotor via a hole in the rotor cap. Using a special tool, ca. 50 mg of the powder material was pressed to a hollow cylinder inside the MAS NMR rotor. The *in situ* CF MAS NMR experiment were carried out with a sample spinning rate of 10 kHz, single pulse  $\pi/2$  and  $\pi/12$  excitation, repetition times of 10 s and 500 ms, and 64 and 1200 accumulations for  $^1H$  and  $^{27}Al$  nuclei, respectively. During the *in situ* CF MAS NMR experiments, a flow of nitrogen ( $\dot{V}(N_2) = 25$  or 50 ml/min) loaded with water ( $p_{H_2O} = 2.3$  kPa, hydration) or mixed with ammonia ( $\dot{V}(NH_3) = 0.2$  ml/min, ammoniation) or of dry nitrogen (deammoniation, dehydration) was injected into the spinning MAS NMR rotor.



## Results and Discussion: Hydration and Ammoniation Behavior

### Hydration of UHM-3

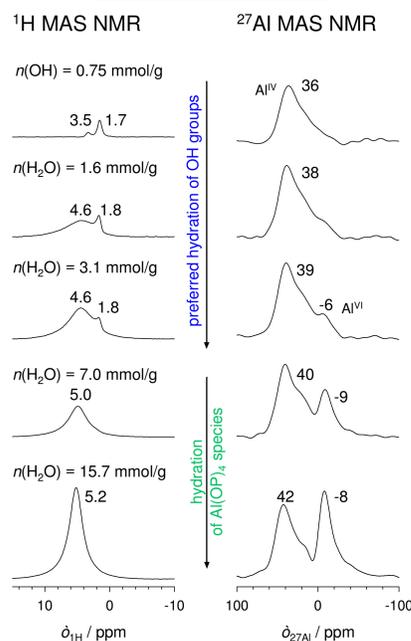


Fig. 3: *In-situ* MAS NMR spectra recorded during hydration of UHM-3.

### Ammoniation of Hex-1

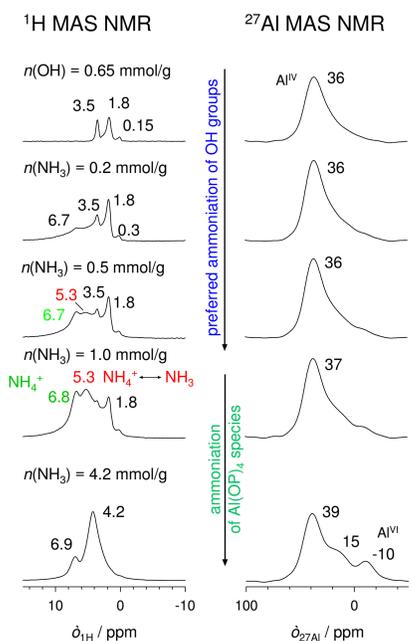


Fig. 4: *In-situ* MAS NMR spectra recorded during ammoniation of Hex-1.

## Results and Discussion: Stability of Mesoporous SAPOs

### XRD

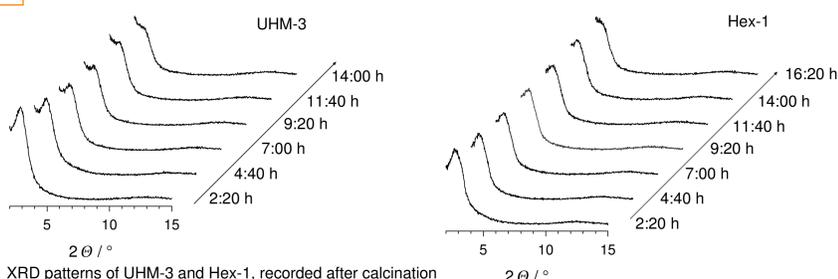


Fig. 1: XRD patterns of UHM-3 and Hex-1, recorded after calcination and  $N_2$  adsorption.

The XRD patterns of Hex-1 and UHM-3 show a strong decrease of the long-range order after an aging of 14 to 16 h.

### $^{31}P$ MAS NMR spectra

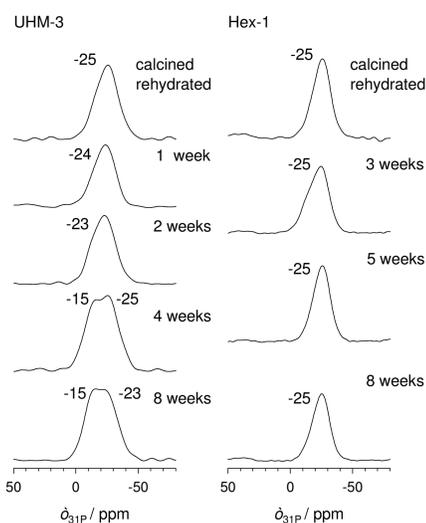


Fig. 2:  $^{31}P$  MAS NMR spectra of UHM-3 and Hex-1 recorded after different aging times.

The  $^{31}P$  MAS NMR spectra of Hex-1 remain while those of UHM-3 recorded after 4 weeks show a change of the phosphorus coordination.

### BET surface

Tab. 1: Change of surface as a function of time.

BET surface $m^2/g$	UHM-3	Hex-1
calcined	---	919
rehydrated	755	770
1 week	563	---
2 weeks	396	---
3 weeks	---	611
4 weeks	296	---
5 weeks	---	627
8 weeks	176	635

### Hydroxyl concentration

Tab. 2: Concentration of hydroxyl groups obtained by  $^1H$  MAS NMR.

$\alpha(OH)$ $mmol/g$	UHM-3	Hex-1
calc./dehydrated	1.12	1.24
calc./total rehydrated/dehydrated	0.7	0.65

## Discussion and Conclusions:

### $^{31}P$ MAS NMR (Fig. 2), different phosphorus coordinations

- 25 ppm, phosphorus tetrahedrally coordinated to 4 aluminum atoms,  $P(OAl)_4$
  - 15 ppm, phosphorus atoms coordinated to 1 OH group,  $P(OH)(OAl)_3$ .
- The presence of either acidic protons, ammonium cations or coordinated water may cause a down field chemical shift of the  $^{31}P$  MAS NMR signals [2]. This indicates an attack at phosphorus atoms leading to a destruction of the framework.

### $N_2$ adsorption (Tab. 1)

- UHM-3: specific surface area drops from 755 to 176  $m^2/g$  after 8 weeks.
  - Hex-1: specific surface area drops from 770 to ca 600  $m^2/g$  after 8 weeks.
- The framework degradation is higher for UHM-3 than for Hex-1.

### Hydroxyl concentration (Tab. 2)

- The hydroxyl concentration of the dehydrated samples of 1.1 to 1.2 mmol/g decreases to 0.65 to 0.7 mmol/g after complete rehydration and subsequent dehydration of UHM-3 and Hex-1.

### *In situ* MAS NMR

$^1H$  MAS NMR signals at 1.8 and 3.5 ppm are caused by SiOH and SiOHA1.

Hydration:  $^1H$  MAS NMR signal of water shifts from 4.6 to 5.2 ppm.

(Fig. 3)  $^{27}Al$  MAS NMR signal of Al(VI) appears immediately after starting the hydration, simultaneous coordination of water at OH groups and Al atoms in the framework.

Ammoniation:  $^1H$  MAS NMR signals at 6.7 to 6.9 ppm are due to  $NH_4^+$  and at 5.3 and 4.2 ppm are caused by an exchange of  $NH_4^+ / NH_3$ , the highest loading of  $NH_3$  is low in comparison with microporous SAPOs [3].

$^{27}Al$  MAS NMR signal of Al(VI) appears immediately after starting the ammoniation, simultaneous coordination of ammonia at OH groups and Al atoms in the framework.

## References

- Z. Luan, D. Zhao, H. He, J. Klinowski, L. Kevan, J. Phys. Chem. B 102 (1998) 1250.
- Y. Z. Khimyak, J. Klinowski, Phys. Chem. Chem. Phys. 2 (2000) 5275.
- A. Buchholz, W. Wang, M. Xu, A. Arnold, M. Hunger, J. Phys. Chem. B, in press,

Financial support of this work by Fonds der Chemischen Industrie, Max-Buchner-Forschungsförderung and Deutsche Forschungsgemeinschaft is gratefully acknowledged.