

Adsorbate effect on $\text{AlO}_4(\text{OH})_2$ centers in the metal-organic framework MIL-53(Al) investigated by solid-state NMR spectroscopy



Christian Lieder, Sabine Opelt, Michael Dyballa, Harald Henning, Michael Hunger, Elias Klemm
Institute of Chemical Technology, University of Stuttgart, Stuttgart, Germany

Introduction

^1H and ^{27}Al MAS NMR spectroscopy have been applied for studying the effect of *o*-xylene and nitrogen bases on the hydroxyl protons of bridging AlOH groups and framework aluminum atoms in MIL-53. Adsorption of *o*-xylene led to three step-wise changes of the quadrupole coupling constant C_Q of framework aluminum atoms in MIL-53*ht*. While the first two changes occur for *o*-xylene loadings of lower than 4 molecules per unit cell (u.c.), and for all $\text{AlO}_4(\text{OH})_2$ centers, the third change was observed for *o*-xylene loadings higher than 4 *o*-xylene molecules per unit cell and for maximum 50% of the framework aluminum atoms. This third adsorbate-induced change of the C_Q value of framework aluminum atoms in MIL-53 is accompanied by a significant decrease of the adsorbate mobility.

Experimental

Synthesis of materials:

- Synthesis of MIL-53 to literature [2] at 453 K.
- XRD patterns agree with standard patterns [3].
- N_2 adsorption (dehydration at 573 K, 16 h), gave the specific surface area of $1320 \text{ m}^2 \text{ g}^{-1}$, $0.008 \leq \frac{p}{p_0} \leq 0.030$.
- The size of the cuboid-shaped crystals was 5 to 10 μm , determined by SEM.

Dehydration and loading:

- The material was filled into a 5 mm glass tube, heated from 393 to 673 K, evacuated for 2 h.
- Samples were loaded with adsorbate molecules and filled into 2.5 mm MAS NMR rotors in a glove box purged with dry N_2 .
- Loading by condensation of *o*-xylene as a function of the vapor pressure.
- Additional procedure of saturation with *o*-xylene and step-wise desorption in vacuum at room temperature up to 423 K.

Characterization techniques:

- X-ray diffraction: Bruker D8 ADVANCE, $\text{CuK}\alpha$ radiation.
- N_2 sorption at a Quantachrome Autosorb 3B.
- SEM pictures on a Cambridge CamScan 44.
- MAS NMR investigations performed on a Bruker MSL-400.
- Resonance frequencies of 400.13 (^1H) and 104.26 MHz (^{27}Al).
- $\frac{\pi}{2}$ and $\frac{\pi}{6}$ single-pulse excitation, repetition times of 30 and 0.5 s, 80 and 14.400 scans per spectrum, spinning rate of 20 kHz.

Adsorption of *o*-xylene on MIL-53*ht*

- Adsorption of alkylaromatics leads to double-sigmoidal adsorption isotherms, very pronounced for the adsorption of *o*-xylene, as shown in Fig. 1 [4].

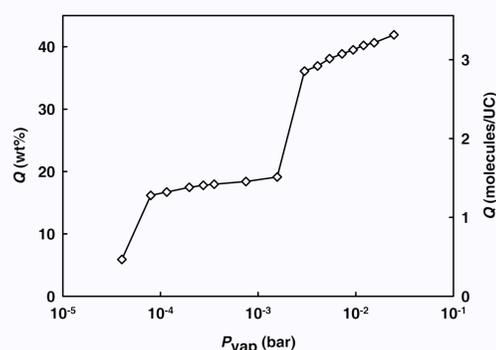


Fig. 1: Double-sigmoidal adsorption isotherm for *o*-xylene on MIL-53*ht* [4].

- X-ray investigations indicated an intermediate phase MIL-53*iX* after adsorption of 0.4 to 0.8 *o*-xylene molecules per u.c.
- Increase of the *o*-xylene loading on MIL-53 of up to 3.3 molecules per u.c., a structure similar to MIL-53*ht* was determined [4].
- For investigating the sensitivity of ^{27}Al solid-state NMR spectroscopy on framework aluminum, a stepwise loading of with *o*-xylene vapor up to saturation was performed.
- The reversibility of the changes of the NMR spectroscopic parameters of $\text{AlO}_4(\text{OH})_2$ centers was investigated by stepwise desorption up to 423 K.
- ^1H and ^{27}Al MAS NMR spectra of MIL-53*ht* loaded with 1.3 to 5.3 *o*-xylene molecules per u.c in Figs. 2 & 3.
- Loadings of 4.2 and 5.3 molecules per u.c., higher than maximum adsorption capacity, assuming that all 4 symmetry-equivalent sites in the pore corners are occupied [2]. \rightarrow Xylene in the inter-particle space, allows view on structure transformations of MIL-53 from the gas- to the liquid-phase adsorption.

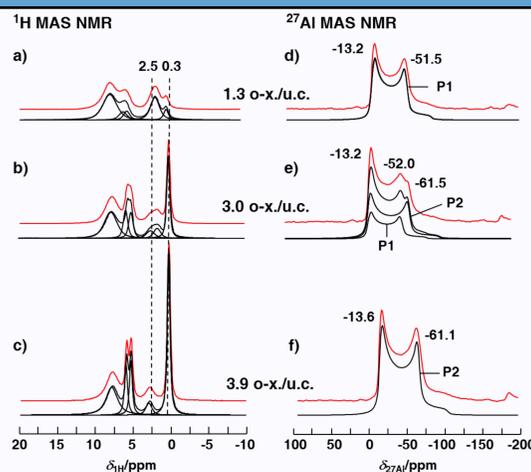


Fig. 2: ^1H MAS NMR (a-c) and ^{27}Al MAS NMR spectra (d-f) of MIL-53*ht*, *o*-xylene loadings of 1.3 (a, d) to 3.9 molecules per u.c. (c, f). Experimentally recorded spectra (red) compared with the simulated spectra (black).

- Nearly no effect on resonance position of AlOH groups: ^1H MAS NMR signals at 2.0 - 2.3 ppm for low loadings, for loadings >1.3 molecules per u.c. a signal at ca. 2.5 ppm. Small resonance shift \rightarrow no interaction of adsorbate with hydroxyl protons, c.f. structure models of interaction of CH_3 groups with carboxylate [2, 4].

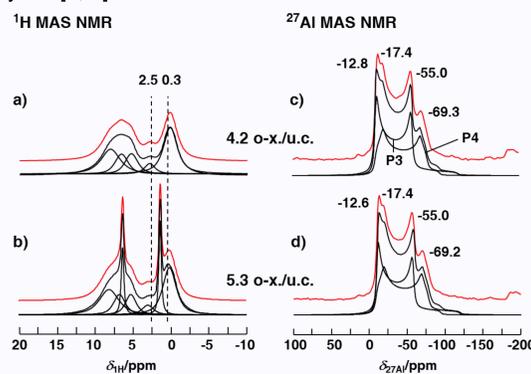


Fig. 3: ^1H MAS NMR (a-b) and ^{27}Al MAS NMR spectra (c-d) of MIL-53*ht*, *o*-xylene loadings of 4.2 (a, c) and 5.3 molecules per u.c. (b, d). Experimentally recorded spectra (red) compared with the simulated spectra (black).

- ^1H MAS NMR line-shapes of adsorbate signals: for loadings <4 molecules per u.c. occur narrow signals at 0.3 ppm (CH_3), 5.3 and 5.8 ppm (CH), an indication for high mobility, for >4 molecules per u.c. there is a broadening of signals, which means low mobility of adsorbate. For loadings >5 molecules per u.c. occur again narrow signals, a hint for adsorbate molecules in inter-particle space.
- ^{27}Al MAS NMR: Loadings of 0.8 and 1.3 molecules per u.c., quadrupolar pattern P1 with smaller C_Q of 8.0 MHz (c.f. Tab. 1), compared with P0 (unloaded, $C_Q = 8.5$ MHz). On 1.3 molecules per u.c., single pattern P1 \rightarrow MIL-53*iX*, responsible for first plateau (Q1) of adsorption isotherm [4].

Tab. 1: Assignment of quadrupolar patterns (P0 - P4), contents of these patterns, isotropic chemical shifts $\delta_{27\text{Al}}$, quadrupole coupling constants C_Q and asymmetry parameters η_Q , of aluminum in MIL-53*ht*, different loadings.

Loading	Pattern	Content / %	$\delta_{27\text{Al}}$ / ppm	C_Q / MHz	η_Q
0.0 <i>o</i> -xylene/u.c.	P0	100	4	8.5	0.05
0.8 <i>o</i> -xylene/u.c.	P0	60	4	8.5	0.05
	P1	40	1	8.0	0.1
1.3 <i>o</i> -xylene/u.c.	P1	100	1	8.0	0.1
3.0 <i>o</i> -xylene/u.c.	P1	35	1	8.0	0.1
	P2	65	3	8.7	0.05
3.9 <i>o</i> -xylene/u.c.	P2	100	2	8.7	0.05
4.2 <i>o</i> -xylene/u.c.	P3	55	4	8.4	0.05
	P4	45	3	9.4	0.1
5.3 <i>o</i> -xylene/u.c.	P3	50	4	8.4	0.05
	P4	50	4	9.4	0.1
6.0 <i>o</i> -xylene/u.c.	P3	50	4	8.4	0.05
	P4	50	4	9.4	0.1

- Additional pattern P2 ($C_Q = 8.7$ MHz) on 3.0 and 3.9 molecules per u.c. (Figs. 3g and 3h), 2^{nd} structural change, similar to MIL-53*ht*. Single pattern P2, 2^{nd} plateau (Q2) on isotherm [4].
- Further loading of 4.2 (Fig. 3c), 5.3 (Fig. 3d), and 6.0 molecules per u.c., patterns P3 ($C_Q = 8.4$ MHz) and P4 ($C_Q = 9.4$ MHz), intensity ratio 1 : 1 (Fig. 3c and Tab. 1), change of local structure, possible contribution of P4 to Q2 [4].
- Spectra reproduced via desorption of *o*-xylene.

Summary

Adsorption of *o*-xylene on MIL-53*ht* was found to be accompanied by a stepwise change of the adsorbate mobility and of C_Q of framework aluminum. Upon adsorption of ca. 1.3 xylene molecules per u.c., the 1^{st} change of C_Q from 8.5 MHz (unloaded MIL-53*ht*) to 8.0 MHz occurred. The 2^{nd} change of C_Q to 8.7 MHz was finished after adsorption of ca. 4 xylene molecules per u.c. These two adsorbate-induced changes of C_Q of framework aluminum in MIL-53 can be correlated with the different steps of the double-sigmoidal isotherms observed for adsorption of *o*-xylene on MIL-53. Increase of the loading causes a 3^{rd} significant change of C_Q to 9.4 MHz, which is, however, limited to 50% of the framework aluminum atoms. The observation that the framework aluminum atoms of *o*-xylene-saturated MIL-53 exist in two local structures in an intensity ratio of 1 : 1 could be an indication for an alternating arrangement of $\text{AlO}_4(\text{OH})_2$ centers with very different electric field gradients in their local structure, which are caused, e.g., by different oxygen coordination symmetries. The occurrence of the $\text{AlO}_4(\text{OH})_2$ centers with low local symmetry ($C_Q = 9.4$ MHz) is accompanied by a significant decrease of the adsorbate mobility.

Literature

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