Influence of silanol groups on adsorption mechanisms on silica-alumina gels

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Introduction

Silica-alumina gels are amorphous, predominantly mesoporous adsorbents used in chromatography, pharmacy, catalysis but mainly as drying agents. Their adsorption properties are strongly influenced by their surface chemistry. The surface of silica-alumina gels consist of silanol and siloxane groups which can be determined by combining ^{29}Si-nuclear magnetic resonance (NMR) and ^{1}H-NMR spectroscopy. As the silanol groups are the primary adsorption sites, the influence of each silanol group on the adsorption is studied by simultaneous volumetric and calorimetric measurements. Pyrrolidine is used as adsorptive because it can hydrogen bond as donor and acceptor and is thus expected to form specific interactions with silanol groups. Based on the measured load-dependent heat of adsorption, the strength of the prevailing interactions can be quantified. From the length of the formed plateaus the number of adsorbed molecules is determined. By combining these results with the distribution of the silanol groups obtained from ^{29}Si-NMR, ^{1}H-NMR and thermogravimetric analysis (TGA), an energetical value is assigned to the adsorption sites and adsorption mechanisms at each silanol group are proposed.

Materials and Experimental Methods

- Silica-alumina gel structure is formed by siloxane groups (Si-O-Si)
- Three different types of silanol groups (Si-O-H) represent primary adsorption sites

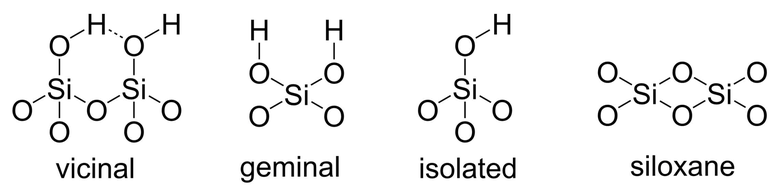
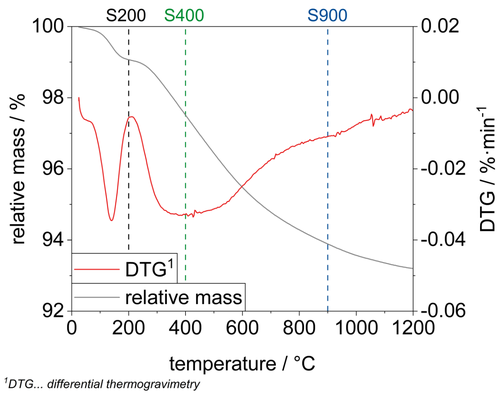


Figure 1: *Surface chemistry of silica-alumina gels*



[1]DTG... differential thermogravimetry

Figure 2: *Thermogravimetric analysis*

- The silica-alumina gel was pretreated at 200 °C (S200), 400 °C (S400) and 900 °C (S900)
- Two mechanisms during the pretreatment occur
  1. Dehydration for T < 200 °C: removal of physisorbed water
  2. Dehydroxylation for T > 200 °C: condensation of silanol groups
- The silanol number α_{OH} is determined according to Ek et al.[1]

$$c_{OH}\left[\frac{mol}{g}\right] = 2 \cdot c_{H_2O} = \frac{2\cdot(m_{rel}(T_s) - m_{rel}(1200\,°C))}{100\cdot M_{H_2O}}$$

$$\alpha_{OH}\left[\frac{OH}{nm^2}\right] = c_{OH} \cdot N_A \cdot \frac{10^{-18}}{S_{BET}}$$

m_{rel}... *relative mass*
T_s... *pretreatment temperature of the sample*

[1]Ek, S.: Determination of the hydroxyl group content in silica by thermogravimetry and a comparison with 1H MAS NMR results. Thermochimica Acta 379 (2001)

Results and Discussion

Surface Chemistry

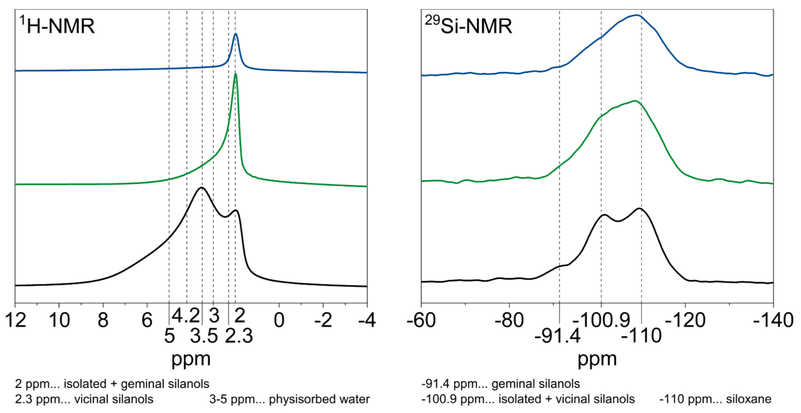


Figure 4: *NMR spectra of pretreated samples S200, S400 and S900*

- Proportion of each silanol group determined by peak deconvolution
- Quantification of silanol groups by combination with silanol number α_{OH} determined by TGA

	α_{OH} OH·nm^{-2}	isolated OH·nm^{-2}	geminal OH·nm^{-2}	vicinal OH·nm^{-2}
S200	6.0	1.3	1.9	2.8
S400	4.5	3.3	1.2	0
S900	1.1	1.1	0	0

Energetic characterization

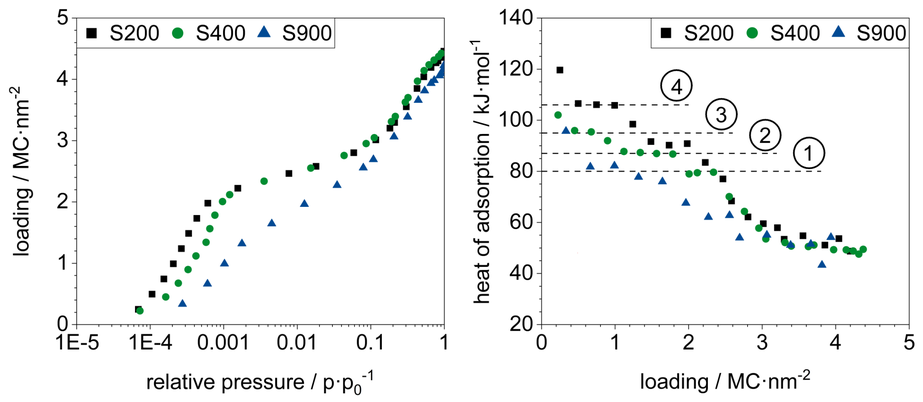


Figure 5: *Adsorption isotherms and heats of adsorption of pyrrolidine at 25 °C*

- Load-dependent heat of adsorption shows four plateaus at 80 ①, 87 ②, 95 ③ and 106 kJ·mol^{-1} ④
- Depending on the pretreatment temperature these plateaus are formed to different extents
- Equal values for the heat of adsorption indicate the same strength of interactions and thus adsorption at a specific adsorption site, i.e. a specific silanol group
- From the plateau length the number of adsorbed molecules can be determined

Combination of NMR and calorimetry

Table 1: *Number of adsorbed pyrrolidine molecules (MC·nm^{-2})*

Plateau	① MC·nm^{-2}	② MC·nm^{-2}	③ MC·nm^{-2}	④ MC·nm^{-2}
S200	0	1.0	0	1.0
S400	0.7	1.0	0.7	0
S900	1.0	0	0	0

Plateau ① present in S400 and S900

- S900 has only isolated silanol groups → adsorption at isolated silanol groups assigned to plateau 1 at 80 kJ·mol^{-1}

Plateau ② present in S200 and S400

- S400 has only isolated and geminal silanol groups → since adsorption on isolated silanol groups already result in plateau 1, adsorption at geminal silanol groups assigned to plateau 2 at 87 kJ·mol^{-1}

Plateau ③ only present in S400

- Heat of adsorption of 95 kJ·mol^{-1} suggests a hybrid adsorption site with an energetical value between plateau 2 and 4

Plateau ④ only present in S200

- S200 is the only material with vicinal silanol groups → adsorption at vicinal silanol groups assigned to plateau 4 at 106 kJ·mol^{-1}

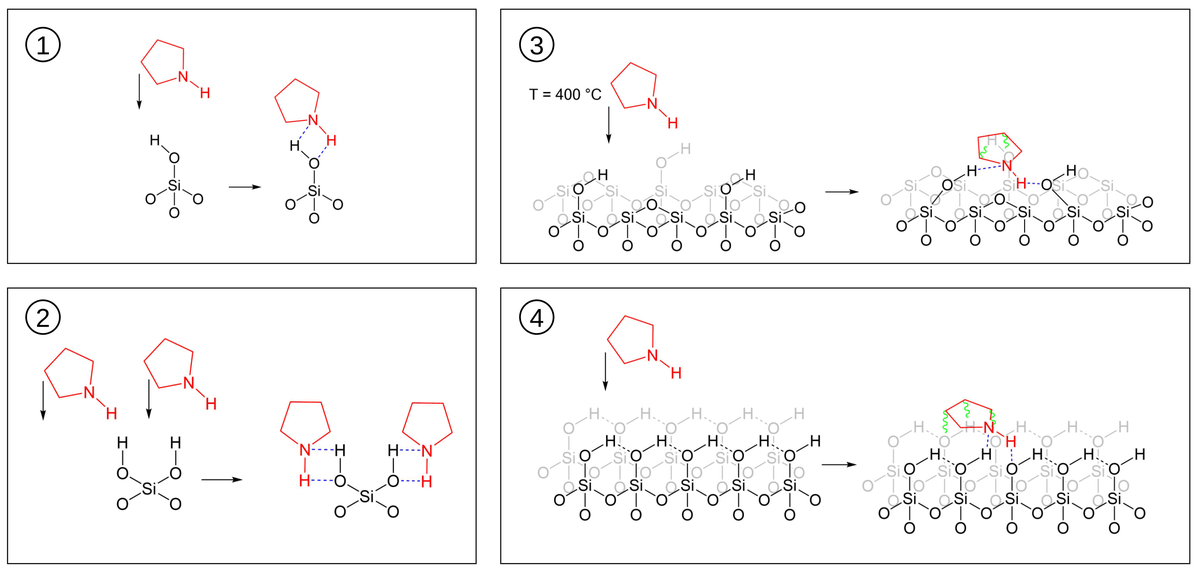
Proposed adsorption mechanisms

① S900
- Number of isolated silanol groups (1.1 OH·nm^{-2}) and adsorbed molecules (1.0 MC·nm^{-2}) indicate stochiometric adsorption

② S400
- Number of geminal silanol groups (1.2 OH·nm^{-2}) and adsorbed molecules (1.0 MC·nm^{-2}) indicate stochiometric adsorption

③ S400
- 0.7 isolated OH·nm^{-2} are involved in stochiometric adsorption at plateau ①, so the number of remaining isolated silanol groups (2.6 OH·nm^{-2}) and adsorbed molecules (0.7 MC·nm^{-2}) indicate that one pyrrolidine molecule interacts with at least three silanol groups
  - At 400 °C condensation of the vicinal silanol groups leads to spatially close isolated silanol groups. If an idea by Saengsawang et al.[2] is applied, pyrrolidine forms strong hydrogen bonds as electron donor and acceptor with two isolated silanol groups while the C_4H_8 ring forms additional induction and dispersion interactions with a neighboring isolated silanol group and thus stabilizing the complex.

④ S200
- Number of vicinal silanol groups (2.8 OH·nm^{-2}) and adsorbed molecules (1.0 MC·nm^{-2}) indicate that one pyrrolidine interacts with an average of about three silanol groups and a similar adsorption mechanism as suggested in ③ can be applied, the only difference being the interaction with vicinal silanol groups



[2] Saengsawang, O., Remsungnen, T., Fritzsche, S., Haberlandt, R. u. Hannongbua, S.: Structure and energetics of water-silanol binding on the surface of silicalite-1: quantum chemical calculations. J. Phys. Chem. 109 (2005)

Summary and Outlook

The silica-alumina gels pretreated at 200 °C, 400 °C and 900 °C were analyzed using NMR and TGA measurements in order to determine the number and distribution of silanol groups. Using calorimetric measurements the load-dependent heats of adsorption exhibit four plateaus depending on the pretreatment temperature and therefore on the number and distribution of silanol groups. For each adsorption site an adsorption mechanism is proposed. While the adsorption on isolated silanol groups (80 kJ·mol^{-1}) and on geminal groups (87 kJ·mol^{-1}) are stochiometric, adsorption on vicinal groups (106 kJ·mol^{-1}) and spatially close silanol groups (95 kJ·mol^{-1}) includes hydrogen bonding to two silanol groups and stabilization through induction and dispersion interaction of the C_4H_8 ring with a third silanol group. In order to verify the proposed adsorption model and to investigate other factors, micro and mesoporous materials with different pore size distributions and varying Al_2O_3 content will be investigated.

Acknowledgement

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