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Characterization of silica gels by ^{29}Si MAS NMR and IR spectroscopic measurements

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Abstract

The solubility of commercial and synthesized silica gels in a solution of Tetra-Ethyl-Ammonium-Hydroxide (TEAOH) was investigated at room temperature. The state of parent silica frameworks was characterized by BET and SEM. The structural defects were identified both by the Q^n group analysis in ^{29}Si MAS NMR and IR spectroscopic investigation. It was found that the dissolution rate of the samples shows a tendency for growing up with an increasing BET surface. The increase of the internal surface was accompanied by formation of $Si(OSi)_3(OH)$ (Q^3) and $Si(OSi)_2(OH)_2$ (Q^2) structural units. The higher the number of Q^3 and Q^2 groups observed, the faster the samples were dissolved in TEAOH solution due to the attack of the hydroxide ions on the terminal OH groups of the framework. The asymmetrical TOT valence vibration of the IR spectra was systematically shifted to lower values with increase in the number of Q^3 and Q^2 structure groups.

Keywords: silica gel, preparation, solubility, ^{29}Si MAS NMR and IR spectroscopy

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Charakterisierung von Silicagelen mit Hilfe der IR- and ^{29}Si MAS NMR-Spektroskopie

Inhaltsübersicht.

Die Löslichkeit kommerzieller Silicagele und Gele eigener Herstellung in TEAOH-Lösung wurde bei Raumtemperatur untersucht. Die Löslichkeit stieg mit zunehmender Zahl von Strukturdefekten in der SiO_2-Matrix, die mit Hilfe der Q^n-Gruppen-Analyse aus ^{29}Si MAS NMR-Spektren charakterisiert wurden. Die Wellenzahl der asymmetrische TOT (T = Si) Valenzschwingung in IR-Spektren verschob sich mit Zunahme der Strukturdefekte systematisch zu niedrigeren Werten.

1 Introduction

Silica gels have been used in the chemical industry and laboratory technique as drying agents [1], feed stock of zeolite synthesis [2], and separation medium in chromatography [3] for a long period. More recently, they were applied also as wafer of optical sensors [4] and for heat storage by water sorption [5]. Pioneers reporting the physical and chemical properties of silica gels are Hauser [6], Sosman [7], or Hinz [8]. A general view about "The chemistry of silica" was published in 1979 by Iler [9].

Engelhardt and Michel [10] characterized the framework of silica gels by the Q^n group analysis (n = number of bridging oxygen atoms in the SiO_4-tetrahedron under study) and Cannes [11] reported on the surface properties by the characterization of silanol groups by means of ^{29}Si MAS NMR and CP MAS NMR experiments. IR spectroscopic measurements gave information about surface OH-groups [11, 12] and the SiO_2 framework [13].

The application of silica gels for the synthesis of zeolites was described in detail by Breck [1], Barrer [2], and Zhdanov [14]. The synthesis process of these aluminosilicates follows quite different recipes. The particle size, size distribution, and shape of the crystals obtained are decisively determined by the crystallization kinetics. All parameters depend on the temperature, alkalinity and composition of the synthesis batch, and, finally, the type of silica source. While in the classical synthesis of 4A (LTA) and X (FAU) zeolites water glass solution is used as silicate component, the synthesis of zeolites beta (BEA), mordenite (MOR), or ZSM-5 (MFI) involves the silica gels.

The reactivity of silica gels depends on their solubility in the alkaline mother liquors of the synthesis batches. Mechanism, kinetics and, consequently, the quality of the final products are thereby influenced by the size of SiO_2 particles as well as by the condensation state of the SiO_2 network. The crystal shape can be characterized by the scanning electron microscopic

investigation (SEM) and the solubility by chemical analysis of the liquid phase. ^{29}Si MAS NMR and IR measurements can give direct hints to the state of the SiO_2 framework.

This paper is aimed to demonstrate the applicability of the ^{29}Si MAS NMR as well as the IR spectroscopy as suitable methods for the efficient characterization of the framework state of silica gels, using two differently prepared sample series.

2 Experimental

Materials

Commercial silica gels used for different zeolite synthesis processes and shown in Tab. 1 as well as synthesized silica gels were investigated. The latter were prepared according to the following route. The aqueous solution of sodium silicate was transformed into acid silica sol using "Wofatit KPS 200" as ion exchanger resin. 220 ml silicate solution (1.8 M in SiO_2) was dropped into a stirred batch of 1000 ml resin and 200 ml water at 278 K within 10 minutes. The acidity of the as-synthesized silica sol with pH of 2 was adjusted to pH values between 3 and 8 by immediate adding of sodium hydroxide solution. SiO_2 xerogels were obtained by drying of the washed hydrogels at 383 K for 24 hours and subsequent crushing.

Solubility experiments

1 g silica gel was stirred at ambient temperature in 40 ml of a 15% aqueous solution of TEAOH for 15 – 60 minutes. Before ICP OES element analysis, the solution was separated from the solid by filtration over glass micro filters MF 100 (Fisherbrand) in a first step followed by the filtration using PTFE miro-membrans (0.2 μm) under pressure within 5 minutes. The separation period was part of the total treatment time. The solubility of the glass filter material does not exceed 3 mg/l and can be, therefore, neglected. Cellulose membranes were non-suitable for the separation procedure because the material dissolves itself under these conditions.

The filtrates were analyzed by use of a IRIS Intrepid High Resolution spectrometer (Thermo Elemental, USA). The ICP OES was calibrated within reference to synthesized solution standards. The accuracy of the measurements lies around 1-3 % within relative standard deviation (RSD) for values above background equivalent concentration (BEC).

Characterization of xerogels

The ^{29}Si MAS NMR spectra were recorded at room temperature on a Bruker Avance 400 spectrometer, operating at frequencies of 79.5 MHz. A 4 mm double tuned (^{1}H-X) MAS probe (Bruker Biospin) was used to perform MAS NMR measurements at spinning rates of 12 kHz. The spectra were obtained with a single pulse excitation consisting of 4 μs pulses (π/2 pulses) and recycle delays of 120 seconds to exclude saturation effects. Up to 700 FIDs were accumulated to obtain reliable signal-to-noise ratio. The spectra were externally referenced to liquid Me_4Si at 0 ppm. A detailed Q^n–group characterization includes the line shape analysis of the NMR spectra by use of an iterative deconvolution procedure with the help of dmfit software package [15].

IR absorption spectra were taken on a Shimadzu FTIR 8400S spectrometer with a resolution of ± 1 cm^{-1} by use of 30 scans. For analysis, 0.5 mg of the sample was pressed with 400 mg KBr into a pellet and measured in the IR range of 400 cm^{-1} to 4000 cm^{-1}.

Scanning electron microscopy (SEM) was performed on a Hitachi S2400 with W cathode at the accelerating potential of 15-20 kV. To produce the conductive layer, the particles were sputtered by a thin gold coating.

Chemical element analysis was measured by using XRF spectrometer PW2404 from Panalytical. 0,5 g of the sample were fused with 3 g lithium borate (Li4B6O11, Spectromelt A12 from Merck GmbH) in a platinum crucible to cast a 27 mm diameter glass disc.

The BET surface area was determined on basis of the volumetric nitrogen adsorption at p/p_0 = 0.075, 0.1, and 0.125 at –77.8 K on a Nova 1200 of the Quantachrome Corporation.

Results and discussion

The commercial and synthesized silica gels listed in Tab. 1 show similar dissolution behaviour in the TEAOH solution. The amounts of dissolved SiO_2 vary between 50 und 800 mg/l in dependence on time and sample type for both series (Figs. 1 and 2). The dissolution rate increases thereby with the absolute rising solubility of samples.

The kinetic curves of the commercial products given in Fig. 1 show higher concentrations of dissolved SiO_2 for Promeksil B12, Aerosil 200, and Sipernat 320 connected with the transformation of the solids into transparent hydrogels according to visual observation, while Silica 995and Aerosil OX 50 show lower dissolution degree, with a formation of SiO_2 nanoparticles.

The curves of the synthesized gels in Fig. 2 demonstrate increasing dissolution with decreasing pH-values of preparation. The remaining filter cakes of this series represent white gels for all the samples.

SEM micrographs of the commercial products provide the evidence that they are composed of primary particles with a significant surface roughness. In this case, particle size distribution is broad. In contrast, the synthesized samples have somewhat greater particles with a rather smooth surface. Their size lies between 10 and 910 μm (Tab. 1). Selected replicas of both series are shown in Fig. 3.

As it can be seen from Tab. 1 and Fig. 3, the particle size and the crystal shape do not influence the solubility of the gels in a systematic way. The reason consists in the fact that the size distribution of the primary particles is more uniform and does not differ in less than 0.1 μm for all samples (Tab. 1).

In opposite to the values of the secondary particle size, the BET surface of samples show a systematic change and coincides with the trend in solubility. Whereas the BET values of the commercial products vary between 42 and 413 m^2/g, the surface of the synthesized silica gels

ranges from 140 to 438m^2/g as shown in Tab. 1. As evident from Figs. 1 and 2, the amount of dissolved SiO_2 of the Aerosil OX 50 and SiO_2 (pH=8) is consequently lowest and for Promeksil B12 and SiO_2(pH=4) this parameter is observed as being highest. But in spite of the somewhat higher BET surface of the synthesized gels, their solubility does not reach higher values. For understanding of this phenomenon, the structure of the gel frameworks must be taken into consideration in more details.

The Q^n-group analysis on basis of the ^{29}Si MAS NMR spectroscopic measurements confirmed the dependence of the gel solubility on the state of the silica framework and, thus the structure of the internal surface. The NMR spectra of the commercial silica gels (see Fig. 4) normalized to 100% intensity show different line shape and chemical shifts of the peaks: Promeksil B12 and Sipernat 320 are characterized by different kinds of Q^n–signals. Firstly, there is Q^4 the main signal related to each Si atom which is linked over oxygen atoms with 4 Si neighbours. Additional signals such as Q^3 and Q^2 are also present in this spectrum. The first and the second are coming from 3 Si neighbours and 1 OH-group and 2 Si neighbours and 2 OH-groups, respectively. The chemical shift of the Q^4-peak appears at about -110 ppm and that of the Q^3-peaks is observed at -100 ppm. These values of chemical shift are near to those known for cristobalite rather than to tridymite or quartz. Only the Q^2-peaks strongly differ with values of -92,4 ppm and -95,3 ppm for Promeksil B12 and Sipernat 320, respectively. While the Q^4-groups characterize network with a perfect structure consisting of SiO_4-tetrahedrons, the Q^3– and Q^2–groups characterize an imperfect framework responsible for the formation of chemically active hydroxyl groups. In this consequence, commercial Aerosil 200, Silica 995 and Aerosil OX 50 contain only Q^3-groups related to defects in decreasing extent. However, their peak width is relative broad in comparison with crystalline silicate phases such as quartz, tridymite, and crystobalite because of non-perfect bond length and angles of their structural polyhedra.

For all the samples except Sipernat 320, the gel solubility increases with the rising degree of defects. In contrast to Silica 995, Sipernat 320 seems to be less soluble although it contains quite more defects. The reason could be associated with a relative high content of Na_2O of 2.1 weight-% (see Tab. 1) and especially contaminants of 0.15 weight-% Al_2O_3 which remarkably reduce the amount of dissolved of SiO_2. Sodium silicate and sodium aluminate which are formed under action of the TEAOH solution lead to a stronger condensation of $(SiO_2)_n$ units over -Si-O-Al-O-Si- bonds. Sipernat 320 produces, therefore, more hydrogel gel than Aerosil 200 and Promeksil B12.

As evident from Fig. 5, ^{29}Si MAS NMR spectra of the synthesized samples show Q^4-groups as well as Q^3 and Q^2-groups. The corresponding signals are centred at similar chemical shifts of about -111 ppm (Q^4), -101 ppm (Q^3), and –92-93 ppm (Q^2) as in the case of commercial products. But the line width of the signals observed are smaller. This could give a hint to the higher regularity in respect to the bond length and angle. This may compensate the greater number of defects which affect the dissolution behaviour, therefore the solubility becomes smaller than expected from the BET surface values.

IR spectroscopic measurements give also a direct hint to the state of the SiO_2 framework. For two selected samples, typical spectra are shown in Fig. 6. One could recognise peaks for the tetrahedron, the symmetrical TOT valence, and the asymmetrical TOT valence vibration in the range of wave numbers of 467-478 cm^{-1}, 802-812 cm^{-1}, and 1082-1121 cm^{-1}, respectively. Particularly, the asymmetrical TOT (T=Si) valence vibration shifts significantly to lower w_{TOT} values with a raising number of the framework defects as it is shown in Tab. 1.

This effect was extensively investigated for aluminosilicate zeolites, e.g. of the Y type [16, 17]. With change in the content of framework aluminium in Si/Al ratios from 2.4 to 139, w_{TOT} peak shifts from 1019 to 1082 cm^{-1} [18]. The reason could be in more regular bond angles when aluminium content is decreased owing to different bond length of the Al-O and the Si-O

units with 173 pm and 163 pm, respectively. A pure SiO_2 framework needs therefore higher activation energy for the vibrations which reflects in a higher wave number during IR spectroscopic measurements.

Although silica gels practically do not contain aluminium atoms, the shift of the TOT valence vibration depends also on the different bond length and angle in $Si(OSi)_4$, $Si(OSi)_3(OH)$ or $Si(OSi)_2(OH)_2$ tetrahedra. In contrast to the synthesized samples, the w_{TOT} values of the commercial silica gels are generally sligthly higher and differ, with values ranging from 1101 to 1120 cm^{-1} against values lying between 1082 and 1105 cm^{-1}. It means that commercial products have low degree of defects which fits nicely with data obtained by the ^{29}Si MAS NMR spectra. This is the reason why Aerosil OX 50 or SiO_2(pH=8) needs the highest and Promeksil B12 and SiO_2(pH=2) the lowest activation energies corresponding to the highest and the lowest IR wave numbers for each series as seen from Tab. 1. The solubility of the samples increases in the same tendency.

In the series of synthesized silica gels, a specific observation lies in the fact that the saturation of w_{TOT} begins with pH value equal to 6. In this range, the ^{29}Si MAS NMR is more sensitive than the IR spectroscopy. Nevertheless, synthesized silica gel products could be characterized by IR spectroscopic measurements with a high sensitivity over a wide range, too.

Conclusion

The solubility of silica gels in TEAOH solution depends on the internal BET surface of samples. In opposite to crystalline porous silicates such as zeolites, the surface of silica gels with irregular pore system contains, in addition to $Si(OSi)_4$ (Q^4), $Si(OSi)_3OH$ (Q^3) and $Si(OSi)_2(OH)_2$ (Q^2) structure units. The more the SiO_2 framework is disturbed, the stronger hydroxide ions of the TEAOH solution attack the silica framework at the terminal OH groups. In the case of commercial products, manufacturing process affects the formation of structural defects and cannot be exactly estimated. In the case of silica gels which were obtained from precipitation on basis of water glass solution (synthesized samples), it was observed that the number of defects increases with decreasing the pH value during precipitation process.

The Q^n group analysis of the silica gels was successfully employed with the help of ^{29}Si MAS NMR measurements. It appeared also that IR spectroscopic analysis could help with the reliable characterization of the structure under special consideration. In this case, the asymmetrical TOT valence vibration of the SiO_2 framework shifts sensitively to lower wave numbers with the raising degree of defects.

The shape of the secondary silica gel particles, characterized by SEM, does not influence the dissolution systematically. Different residual filter cakes such as white solids, transparent hydro-gels, and silica nano-particles can be observed. The contamination of the silica gel by traces of aluminium compounds leads to the increased formation of a secondary gel phase due to precipitation of the secondary $(SiO)_n$ particles containing -Si-O-Al-O-Si- bonds.

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Table 1

sample denotation	sample type	particle size μm secondary/primary	BET surface m^2/g	IR ν_{TOT}, cm^{-1}
commercial silica gels				
Promeksil B12	precipitated	< 10 / < 0.08	413	1101
Sipernat 320	precipitated	< 75 / < 0.06	196	1107
Aerosil 200	pyrogene	< 310 / < 0.09	210	1110
Silica 995	pyrogene	< 28 / < 0.07	61	1117
Aerosil OX 50	pyrogene	< 34 / <0.09	42	1120
synthesized silica gels				
SiO_2(pH 2)	precipitated	< 380 / < 0.12	538	1082
SiO_2(pH 3)	precipitated	< 283 / < 0.08	513	1088
SiO_2(pH 4)	precipitated	< 103 / < 0.09	507	1095
SiO_2(pH 5)	precipitated	< 94 / < 0.03	404	1101
SiO_2(pH 6)	precipitated	< 112 / < 0.06	352	1105
SiO_2(pH 7)	precipitated	< 910 / < 0.04	172	1103
SiO_2(pH 8)	precipitated	< 113 / < 0.06	140	1105

Fig. 1 Alkaline solubility of commercial silica gels

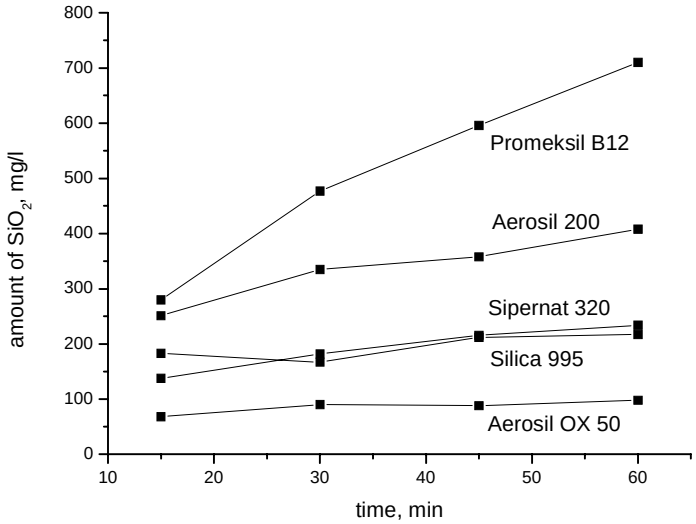


Fig. 2 Alkaline solubility of synthesized silica gels

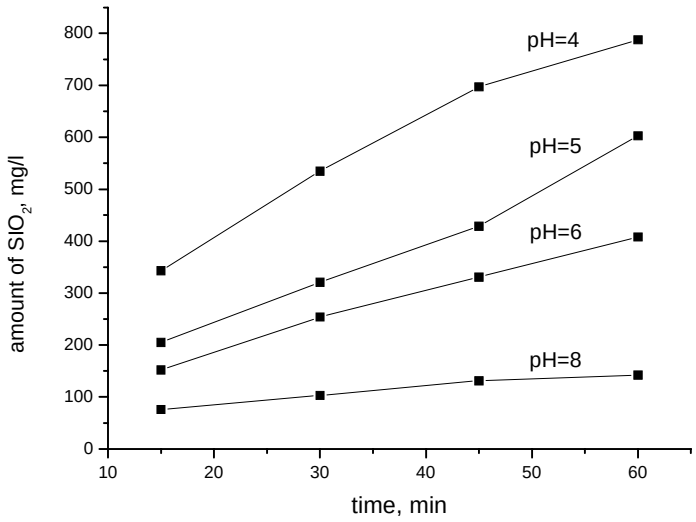


Fig. 3 Scanning electron micrographs of Aerosil 200 (a, b) and synthesized silica gel precipitated at pH = 2

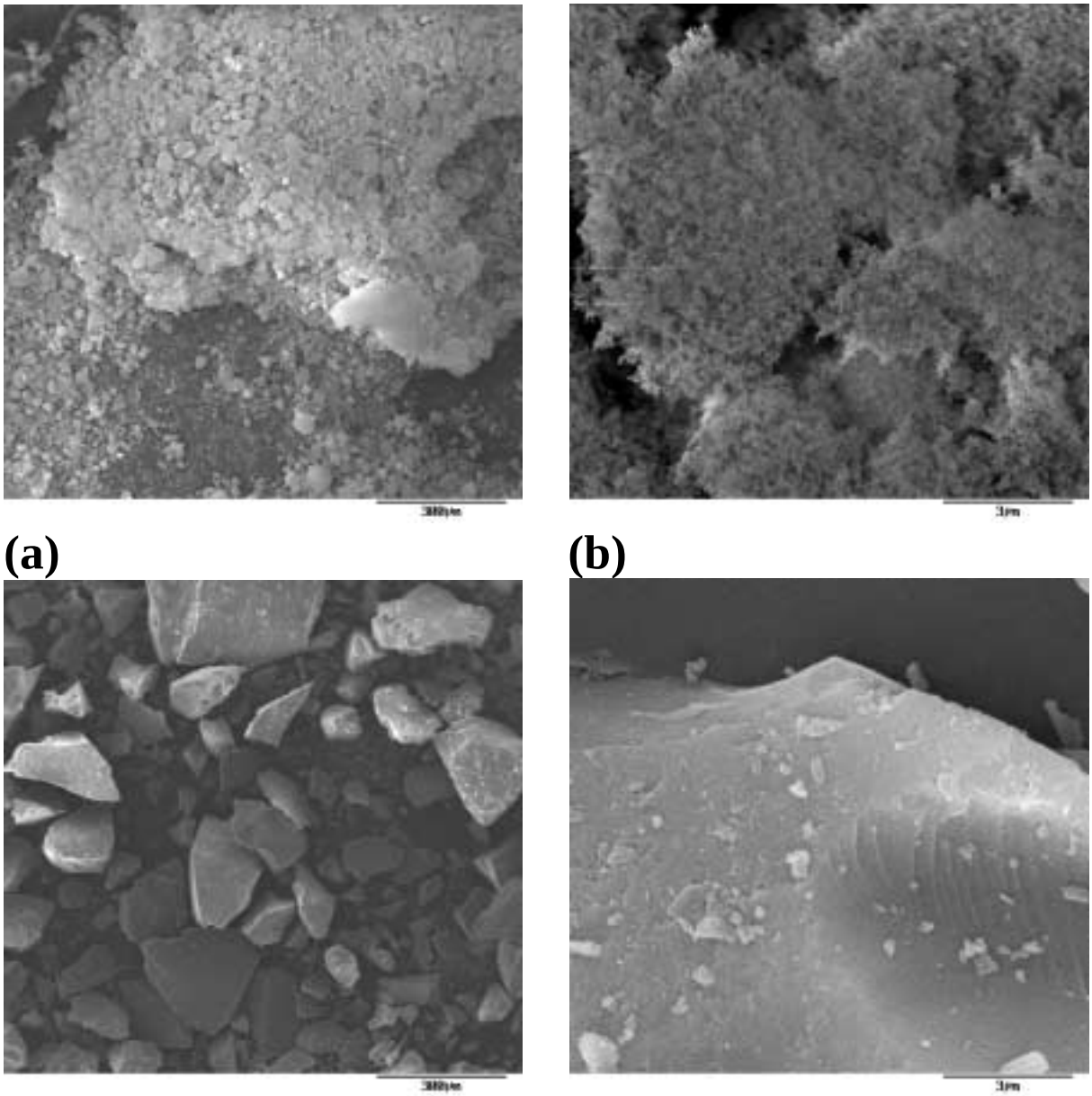


Abb. 4 ^{29}Si MAS NMR spectra of the commercial silica gels

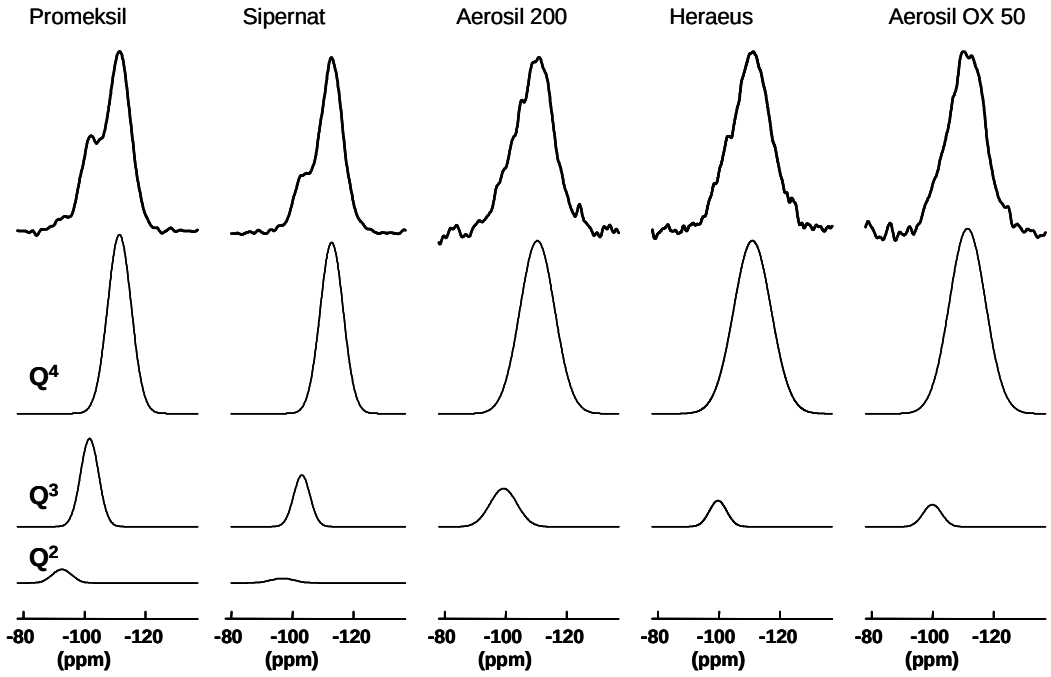


Abb. 5 ^{29}Si MAS NMR spectra of the synthesized silica gels in dependence of the pH value

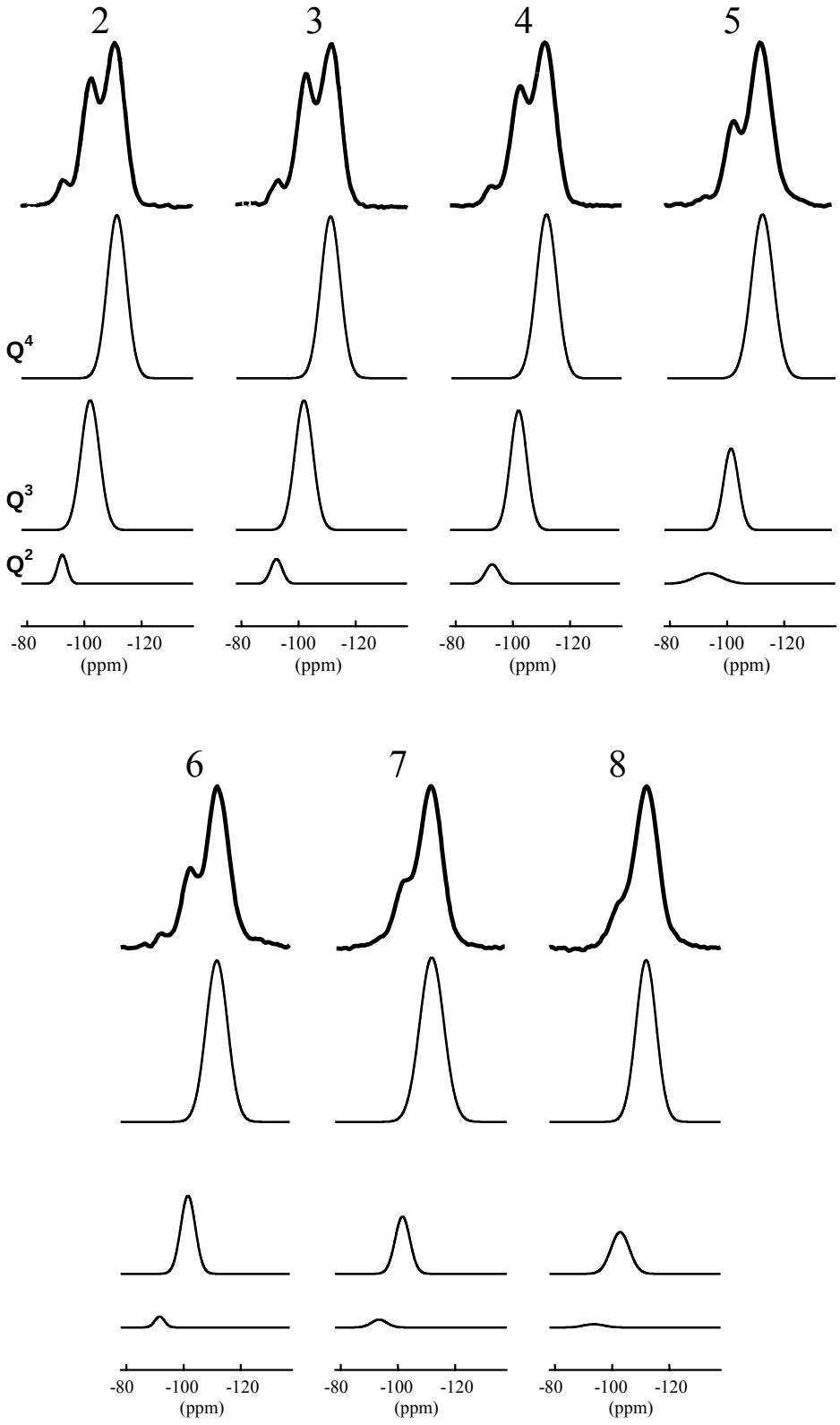
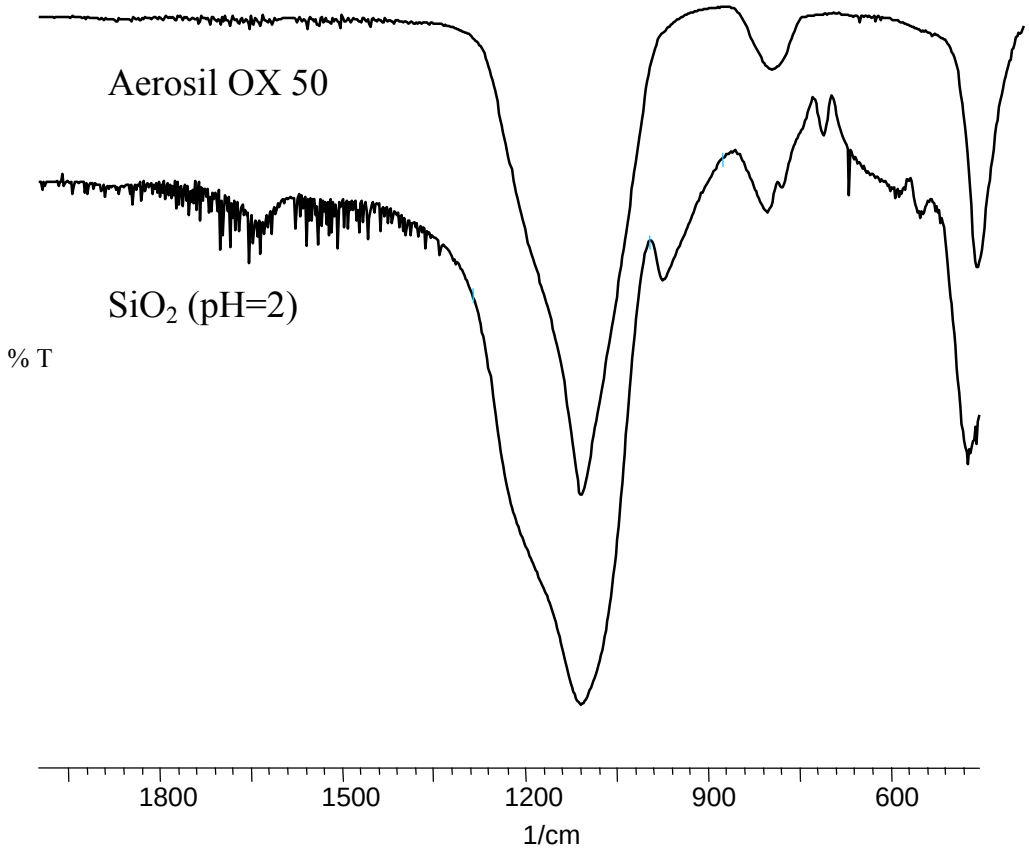


Abb. 6 IR spectra of selected commercial and synthesized silica gels



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Inhaltsübersicht.

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In opposite to the values of the particle size which does not influence the solubility of the gels in a systematic way as can be seen from Tab. 1 and Figs. 1 and 2, the BET surface of samples show a systematic change and coincides with the trend in solubility. Whereas the BET values of the commercial products vary between 42 and 413 m^2/g, the surface of the synthesized silica gels ranges from 140 to 438m^2/g (in dependence also of sample milling). As evident from Figs. 1 and 2, the amount of dissolved SiO_2 of the Aerosil OX 50 and SiO_2(pH=8) is consequently lowest and for Promeksil B12 and SiO_2(pH=4) this parameter is observed as

being highest. Figs. 4 and 5 demonstrate this tendency by the dependence of the solubility on the BET surface of samples. But in spite of the somewhat higher BET surface of the synthesized gels, their solubility does not reach systematically higher values. For understanding of this phenomenon, the structure of the gel frameworks must be taken into consideration in more details.

The Q^n-group analysis on basis of the ^{29}Si MAS NMR spectroscopic measurements confirmed the dependence of the gel solubility on the state of the silica framework and, thus, the structure of the internal surface. The NMR spectra of the commercial silica gels in Fig. 6 normalized to 100% intensity show different line shapes and chemical shifts of the peaks: Promeksil B12 and Sipernat 320 are characterized by different kinds of Q^n–signals. Firstly, there is Q^4 the main signal related to each Si atom which is linked over oxygen atoms with 4 Si neighbours. Additional signals such as Q^3 and Q^2 are also present in this spectrum. The first and the second are coming from 3 Si neighbours and 1 OH-group and 2 Si neighbours and 2 OH-groups, respectively. The chemical shift of the Q^4-peak appears at about -110 ppm and that of the Q^3-peaks is observed at -100 ppm. These values of chemical shift are near to those known for cristobalite rather than to tridymite or quartz. Only the Q^2-peaks strongly differ with values of -92,4 ppm and -95,3 ppm for Promeksil B12 and Sipernat 320, respectively. While the Q^4-groups characterize network with a perfect structure consisting of SiO_4-tetrahedrons, the Q^3– and Q^2–groups characterize an imperfect framework responsible for the formation of chemically active hydroxyl groups. In this consequence, commercial Aerosil 200, Silica 995 and Aerosil OX 50 contain only Q^3-groups related to defects in decreasing extent. However, their peak width is relative broad in comparison with crystalline silicate phases such as quartz, tridymite, and crystobalite because of non-perfect bond length and angles of their structural polyhedra. A quantification of the volume fraction of all Q-groups is shown in Tab. 1.

For all the samples except Sipernat 320, the gel solubility increases with the rising degree of defects. In contrast to Silica 995, Sipernat 320 seems to be less soluble although it contains quite more defects. The reason could be associated with a relative high content of Na_2O of 2.1 weight-% (see Tab. 1) and especially contaminants of 0.15 weight-% Al_2O_3 which remarkably reduce the amount of dissolved of SiO_2. Sodium silicate and sodium aluminate which are formed under action of the TEAOH solution lead to a stronger condensation of $(SiO_2)_n$ units over -Si-O-Al-O-Si- bonds. Sipernat 320 produces, therefore, more hydrogel gel than Aerosil 200 and Promeksil B12.

As evident from Fig. 76, ^{29}Si MAS NMR spectra of the synthesized samples show Q^4-groups as well as Q^3 and Q^2-groups. The corresponding signals are centred at similar chemical shifts of about -111 ppm (Q^4), -101 ppm (Q^3), and –92 to -93 ppm (Q^2) as in the case of commercial products. But the line width of the signals observed are smaller. This could give a hint to the higher regularity in respect to the bond length and angle. This may compensate the greater number of defects which affect the dissolution behaviour, therefore the solubility becomes smaller than expected from the BET surface values.

IR spectroscopic measurements give also a direct hint to the state of the SiO_2 framework. For two selected samples, typical spectra are shown in Fig. 8. One could recognise peaks for the tetrahedron, the symmetrical TOT valence, and the asymmetrical TOT valence vibration in the range of wave numbers of 467 to 478 cm^{-1}, 802 to 812 cm^{-1}, and 1082 to 1121 cm^{-1}, respectively. Particularly, the asymmetrical TOT (T=Si) valence vibration shifts significantly to lower w_{TOT} values with a raising number of the framework defects as it is shown in Tab. 1. This effect was extensively investigated for aluminosilicate zeolites, e.g. of the Y type [16, 17]. With change in the content of framework aluminium in Si/Al ratios from 2.4 to 139, w_{TOT} peak shifts from 1019 to 1082 cm^{-1} [18]. The reason could be in more regular bond angles when aluminium content is decreased owing to different bond length of the Al-O and the Si-O

units with 173 pm and 163 pm, respectively. A pure SiO_2 framework needs therefore higher activation energy for the vibrations which reflects in a higher wave number during IR spectroscopic measurements.

Although silica gels practically do not contain aluminium atoms, the shift of the TOT valence vibration depends also on the different bond length and angle in $Si(OSi)_4$, $Si(OSi)_3(OH)$ or $Si(OSi)_2(OH)_2$ tetrahedra. In contrast to the synthesized samples, the w_{TOT} values of the commercial silica gels are generally sligthly higher and differ, with values ranging from 1101 to 1120 cm^{-1} against values lying between 1082 and 1105 cm^{-1}. Taking into consideration a sensitivity of the signals of ± 1cm^{-1} for the commercial as well as synthesized silica gels significant changes in their structure can be observed. The results mean that commercial products have low degree of defects which fits nicely with data obtained by the ^{29}Si MAS NMR spectra. This is the reason why Aerosil OX 50 or SiO_2(pH=8) needs the highest and Promeksil B12 and SiO_2(pH=2) the lowest activation energies corresponding to the highest and the lowest IR wave numbers for each series as seen from Tab. 1. The solubility of the samples increases in the same tendency.

In the series of synthesized silica gels, a specific observation lies in the fact that the saturation of w_{TOT} begins with pH value equal to 6. In this range, the ^{29}Si MAS NMR is more sensitive than the IR spectroscopy. Nevertheless, synthesized silica gel products could be characterized by IR spectroscopic measurements with a high sensitivity over a wide range, too.

3 Discussion

The solubility of silica gels in TEAOH solution depends on the internal BET surface of samples. In opposite to crystalline porous silicates such as zeolites, the surface of silica gels with irregular pore system contains, in addition to $Si(OSi)_4$ (Q^4), $Si(OSi)_3OH$ (Q^3) and $Si(OSi)_2(OH)_2$ (Q^2) structure units. The more the SiO_2 framework is disturbed, the stronger hydroxide ions of the TEAOH solution attack the silica framework at the terminal OH groups. In the case of commercial products, manufacturing process affects the formation of structural defects and cannot be exactly estimated. In the case of silica gels which were obtained from precipitation on basis of water glass solution (synthesized samples), it was observed that the number of defects increases with decreasing the pH value during precipitation process.

The Q^n group analysis of the silica gels was successfully employed with the help of ^{29}Si MAS NMR measurements. It appeared also that IR spectroscopic analysis could help with the reliable characterization of the structure under special consideration. In this case, the asymmetrical TOT valence vibration of the SiO_2 framework shifts sensitively to lower wave numbers with the raising degree of defects.

The shape of the secondary silica gel particles, characterized by SEM, does not influence the dissolution systematically. Different residual filter cakes such as white solids, transparent hydro-gels, and silica nano-particles can be observed. The contamination of the silica gel by traces of aluminium compounds leads to the increased formation of a secondary gel phase due to precipitation of the secondary $(SiO)_n$ particles containing -Si-O-Al-O-Si- bonds.

4 Experimental Part

Materials

Commercial silica gels used for different zeolite synthesis processes and shown in Tab. 1 as well as synthesized silica gels were investigated. The latter were prepared according to the following route. The aqueous solution of sodium silicate was transformed into acid silica sol using "Wofatit KPS 200" as ion exchanger resin. 220 ml silicate solution (1.8 M in SiO_2) was dropped into a stirred batch of 1000 ml resin and 200 ml water at 278 K within 10 minutes. The acidity of the as-synthesized silica sol with pH of 2 was adjusted to pH values between 3 and 8 by immediate adding of sodium hydroxide solution. SiO_2 xerogels were obtained by drying of the washed hydrogels at 383 K for 24 hours and subsequent crushing.

Solubility experiments

1 g silica gel was stirred at ambient temperature in 40 ml of a 15% aqueous solution of TEAOH for 15 – 60 minutes. Before ICP OES element analysis, the solution was separated from the solid by filtration over glass micro filters MF 100 (Fisherbrand) in a first step followed by the filtration using PTFE miro-membrans (0.2 μm) under pressure within 5 minutes. The separation period was part of the total treatment time. The solubility of the glass filter material does not exceed 3 mg/l and can be, therefore, neglected. Cellulose membranes were non-suitable for the separation procedure because the material dissolves itself under these conditions.

The filtrates were analyzed by use of a IRIS Intrepid High Resolution spectrometer (Thermo Elemental, USA). The ICP OES was calibrated within reference to synthesized solution standards. The accuracy of the measurements lies around 1-3 % within relative standard deviation (RSD) for values above background equivalent concentration (BEC).

Characterization of xerogels

The ^{29}Si MAS NMR spectra were recorded at room temperature on a Bruker Avance 400 spectrometer, operating at frequencies of 79.5 MHz. A 4 mm double tuned (^{1}H-X) MAS probe (Bruker Biospin) was used to perform MAS NMR measurements at spinning rates of 12 kHz. The spectra were obtained with a single pulse excitation consisting of 4 μs pulses (π/2 pulses) and recycle delays of 120 seconds to exclude saturation effects. Measurements in the high power decoupling mode (HPDEC) brought no higher resolution of the signals. Up to 700 FIDs were accumulated to obtain reliable signal-to-noise ratio. The spectra were externally referenced to liquid Me_4Si at 0 ppm. A detailed Q^n–group characterization includes the line shape analysis of the NMR spectra by use of an iterative deconvolution procedure with the help of dmfit software package [15].

IR absorption spectra were taken on a Shimadzu FTIR 8400S spectrometer with a resolution of ± 1 cm^{-1} by use of 30 scans. For analysis, 0.5 mg of the sample was pressed with 400 mg KBr into a pellet and measured in the IR range of 400 cm^{-1} to 4000 cm^{-1}.

Scanning electron microscopy (SEM) was performed on a Hitachi S2400 with W cathode at the accelerating potential of 15-20 kV. To produce the conductive layer, the particles were sputtered by a thin gold coating.

Chemical element analysis was measured by using XRF spectrometer PW2404 from Panalytical. 0,5 g of the sample were fused with 3 g lithium borate ($Li_4B_6O_{11}$ - Spectromelt A12 from Merck GmbH) in a platinum crucible to cast a 27 mm diameter glass disc.

The BET surface area was determined on basis of the volumetric nitrogen adsorption at p/p_0 = 0.075, 0.1, and 0.125 at –77.8 K on a Nova 1200 of the Quantachrome Corporation.

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Table 1 Chemical and physical data of used commercial and synthesized silica gels

sample denotation	sample type	particle size[1] µm	BET surface m^2/g	IR ν_{TOT}, cm^{-1}	^{29}Si MAS NMR groups, % portion of Q^4	of Q-Q^3	Q^2
commercial silica gels							
Promeksil B12	precipitated	≤ 10	413	1101	70	26	4
Sipernat 320	precipitated	≤ 75	196	1107	80	17	3
Aerosil 200	pyrogene	≤ 310	210	1110	85	15	0
Silica 995	pyrogene	≤ 28	61	1117	93	7	0
Aerosil OX 50	pyrogene	≤ 34	42	1120	94	6	0
synthesized silica gels							
SiO_2(pH 2)	precipitated	≤ 380	538	1082	54	41	5
SiO_2(pH 3)	precipitated	≤ 285	513	1088	56	39	5
SiO_2(pH 4)	precipitated	≤ 105	507	1095	61	34	5
SiO_2(pH 5)	precipitated	≤ 95	404	1101	71	24	5
SiO_2(pH 6)	precipitated	≤ 110	352	1105	74	24	2
SiO_2(pH 7)	precipitated	≤ 910	172	1103	81	17	2
SiO_2(pH 8)	precipitated	≤ 115	140	1105	80	19	1

[1] estimated from SEM with an error of ± 5%

Fig. 1 Alkaline solubility of commercial silica gels in dependence on time

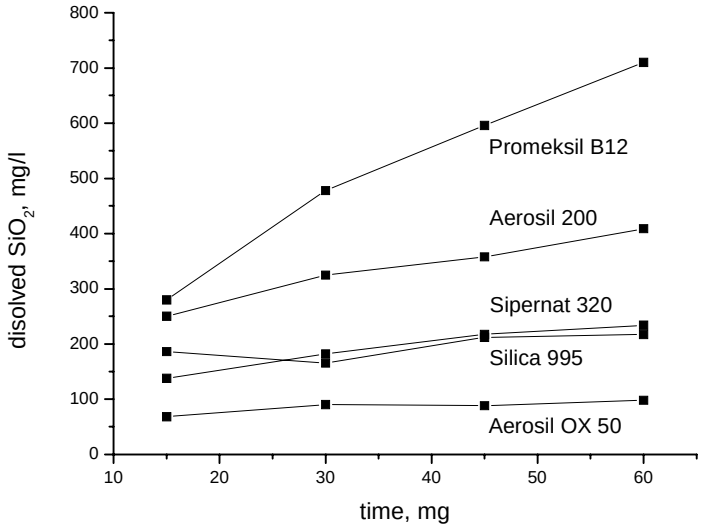

Fig. 2 Alkaline solubility of synthesized silica gels in dependence on time

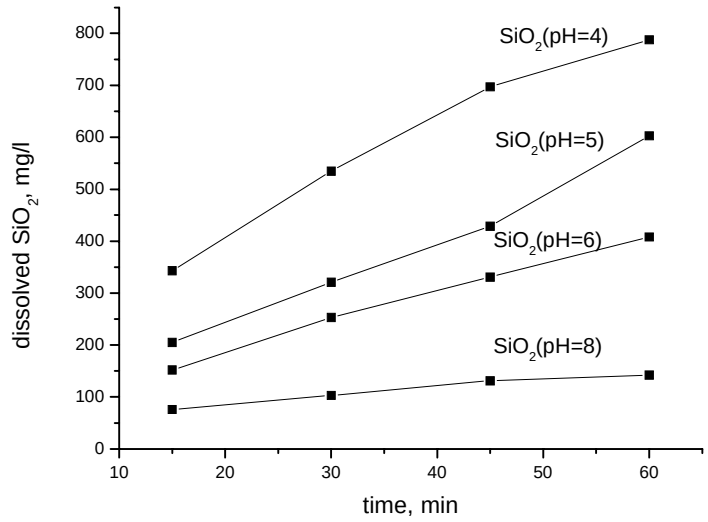

Fig. 3 Selected scanning electron micrographs of a commercial (Aerosil 200 - a, b) and a synthesized silica gel (SiO_2(pH=2) – c, d) with typical different particle habit

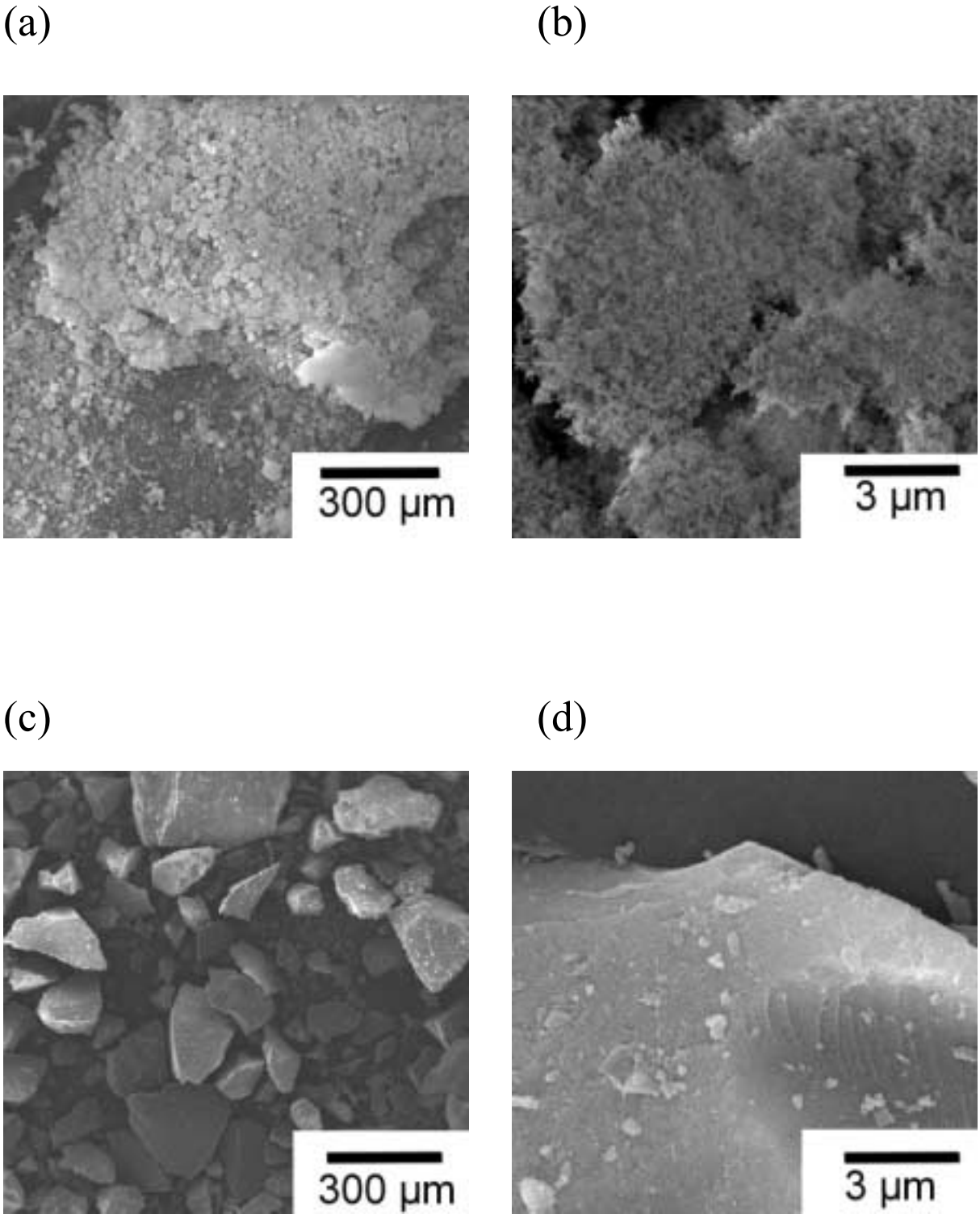

Fig. 4 Influence of the BET surface on the alkaline solubility of commercial silica gels after 60 min stirring

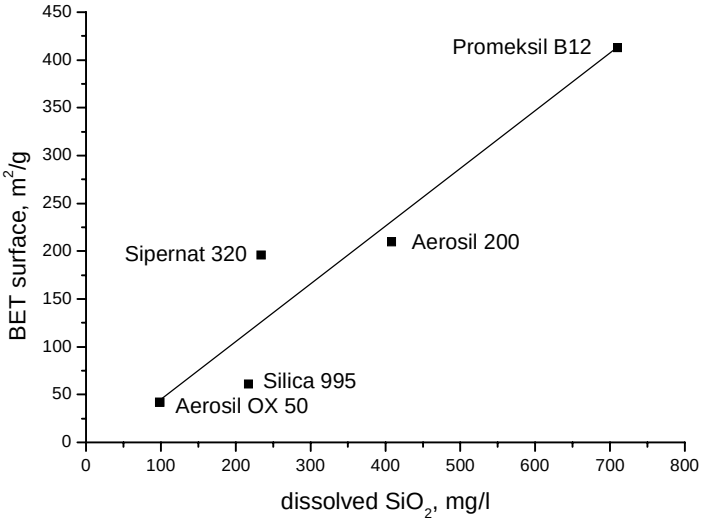

Fig. 5 Influence of the BET surface on the alkaline solubility of synthesized silica gels after 60 min stirring

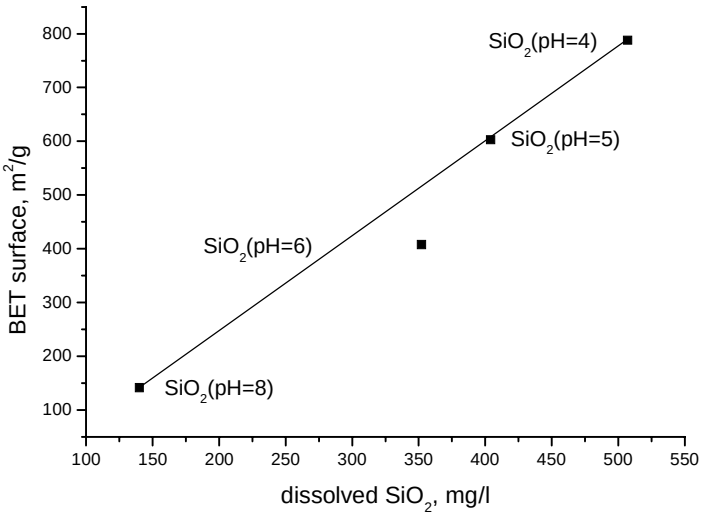

Abb. 6 ^{29}Si MAS NMR spectra of the commercial silica gels

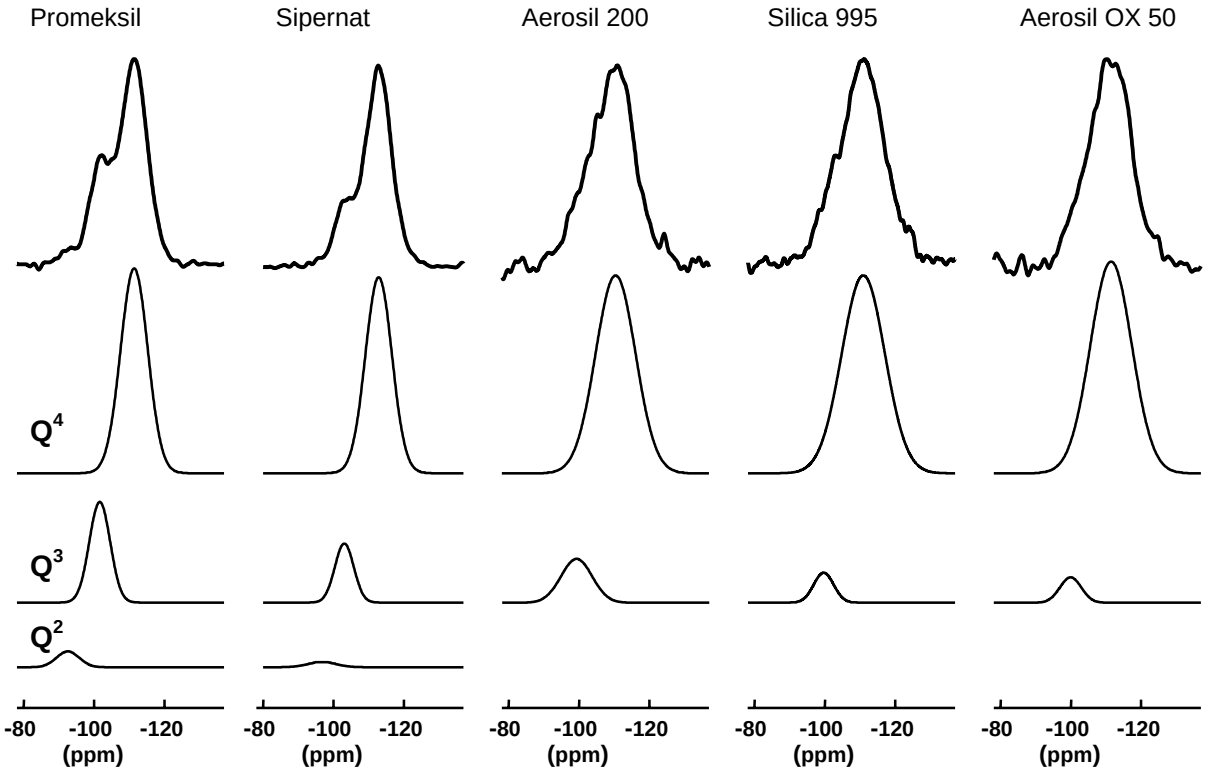

Abb. 7 ^{29}Si MAS NMR spectra of the synthesized silica gels in dependence of the pH value

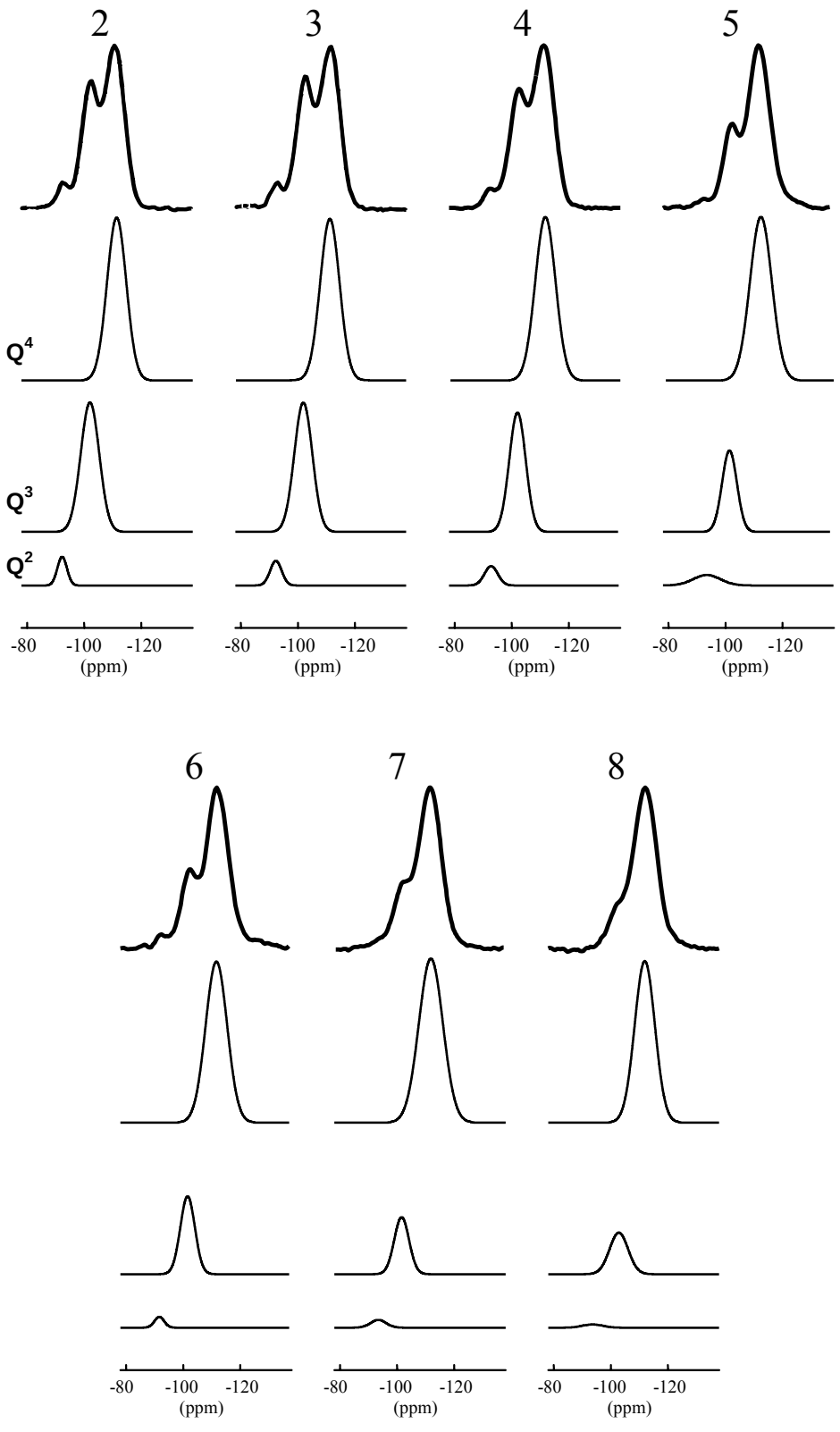

Abb. 8 IR spectra of two selected commercial and synthesized silica gel samples