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Determination of the hydroxyl group content in silica by thermogravimetry and a comparison with ^{1}H MAS NMR results

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Abstract

The hydroxyl group content in nine different types of silicas was determined by thermogravimetry (TG). The TG measurements were performed by heating the silica samples (15–30 mg) at a rate of 5°C min^{-1} from room temperature to 1250°C in an argon flow. The dehydration and dehydroxylation phenomena (two mass loss steps) were distinguished with the help of the differential TG curve (DTG). The temperature where physisorbed water was assumed to be totally released was dependent on the silica and was found to range from 100 to 130°C. The OH group content was calculated from the second mass loss step by assuming that there were only siloxane bridges left in silica at 1250°C. The total hydroxyl group content was calculated from the entire mass loss of the second step. The remaining amount of OH groups at any temperature below 1250°C could also be calculated and was done in this study at 550 and 1000°C. When comparing the total OH group content and the OH group content at 550°C determined by the TG method with the results of calcined samples measured by ^{1}H MAS NMR, they were found to be in a good agreement with each other. However, a significant difference was observed between the methods regarding the remaining OH group content at 1000°C. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silica; Hydroxyl; Silanol; Thermogravimetry; NMR

1. Introduction

The surface characteristics of silica and other catalyst supports are important in the study of reactions between the catalyst precursor and the support. The silica surface consists of a combination of different types of hydroxyl (i.e. silanol) groups and of siloxane bridges whose relative concentrations depend on the calcination temperature as well as on the ambient humidity and storage time. The distribution of silanols on the amorphous silica surface has been shown to be random by simulations based on the dehydration of crystalline β-cristobalite [1]. There are isolated and geminal silanols on the silica surface which can be linked through hydrogen bridges depending on the distance between the silanols and the local geometric structure [1,2]. The geminal silanols consist of two hydroxyl groups attached to one silicon atom, while the single isolated silanols consist of one hydroxyl per silicon atom. Hydrogen-bonded hydroxyls can be further divided into weakly and strongly bonded hydroxyls. The weakly bonded hydroxyls are also called internal or intraglobular hydroxyls which occur throughout the particle structure in almost all kinds of amorphous silicas [2,3]. These bulk silanols are said to be inaccessible to water even though the distinction between internal and surface silanols is ambiguous

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[2]. Hydrogen-bonded water molecules or physisorbed water may also be adsorbed onto all types of surface hydroxyl groups. In the preparation of heterogeneous catalysts by atomic layer deposition (ALD), also referred to as atomic layer epitaxy (ALE), controlled reaction conditions are achieved by first removing the adsorbed water from the silica surface [4]. After removal of the water, the surface reactions between the precursor and the silica depend, among other factors, on the hydroxyl group concentration on the silica surface.

The hydroxyl group content of silica can be determined by several different chemical and physical methods [2]. Thermogravimetry (TG) is an example of a simple and inexpensive physical method [5–7]. The most important parameters to be considered in the thermogravimetric measurements of silica are the heating rate and the end point of the measurement. It is usually preferred to keep the former as low as possible, while having the latter high enough to ensure a total dehydroxylation of silica. It has been stated that temperatures higher than 600°C are required to remove all intraglobular hydroxyls [2]. When heating silica samples at 1100°C, the amount of isolated hydroxyls diminishes considerably, but for the removal of the rest of the silanols temperatures higher than 1200°C are required [8,9]. In the TG method, it is also important to find an appropriate way to distinguish between the dehydroxylation and dehydration phenomena in the thermograms. The distinction can be made with the help of differential thermogravimetry (DTG) [2] or differential thermal analysis (DTA) [6]. Curve fitting of the DTG profile reveals that the desorption of physisorbed water from silica surface is complete by 120°C when heated at a rate of 10°C min^{-1} in a 150 ml min^{-1} nitrogen flow [2]. However, according to Zhuravlev [10,11], the threshold temperature corresponding to a complete of dehydration and the beginning of dehydroxylation is estimated to be 190 ± 10°C, so a small amount of physically adsorbed water remains on the surface up to ca. 200°C. In addition, it has been shown by NMR techniques [12] that drying at 110°C not only removes the physisorbed water but dehydroxylates some of the silanol groups. As a conclusion, it seems obvious that the dehydration and dehydroxylation reactions overlap to some extent.

A more complicated and expensive physical method for the determination of hydroxyl groups is solid-state NMR spectroscopy. Using a combination of silylation and ^{29}Si CPMAS NMR (^{29}Si cross-polarization magic-angle spinning), the total number of SiOH groups can be measured [13]. In addition, the relative amounts of single and geminal silanols can be determined [14]. ^{1}H MAS NMR is a more simple and direct way of measuring the total OH content, given a known reference sample, and can approximately separate the isolated and hydrogen-bonded SiOH groups [15]. ^{1}H MAS NMR is a bulk method able to detect all the OH groups in the sample.

Infrared spectra of silicas contain both qualitative and quantitative information on different types of OH groups. Quantitative analysis based on IR is complex, because distinguishing between peaks caused by different types of OH groups and also trapped water is difficult. Calibration and utilization of extinction coefficients are required for quantitative or semiquantitative analysis. We have recently used the same TG results as presented here for a multivariate calibration of diffuse reflectance infrared Fourier transform (DRIFT) spectra of silica samples to develop a model for the prediction of quantitative OH group content in an unknown silica sample [16]. In addition to actual quantitative analysis, the knowledge of a distinct change of reflectance of a particular band is also useful. For example, in the preparation of catalysts on silica, the decrease in reflectance of the DRIFT band of O–H stretching caused by adsorption can be observed and the stage of adsorption can be estimated.

Most of the silica used in chemical applications is synthetic and is generally amorphous. Depending on the method and specific parameters of preparation, certain physical properties such as surface area, pore volume, pore size and particle size are to some extent controllable. The number, size and morphology of the pores largely influence the water desorption [2]. The ratio between the quantities of surface and bulk OH groups depends on the pretreatment of the sample and on the size of the silica globules [17]. According to Zhuravlev's data [18] on over 100 different silica samples, the silanol number of totally hydroxylated silica is between 4.2 and 5.7 OH nm^{-2} regardless of the origin and structural characteristics of silica. Zhuravlev's measurements were performed using a deuterium-exchange method with mass spectrometric analysis which is able to distinguish between the surface and bulk hydroxyls [10,18]. Recently, De Farias and Airoldi [5] showed the TG method to be a satisfactory way to determine the hydroxyl group content of silica samples having different surface areas. They heated the silica samples at a rate of 5°C min^{-1} till 1100°C and calculated the remaining silanol groups attached to silica gel at 1100°C. The silanol numbers in their samples, which were untreated or were rehydroxylated by acid treatments, ranged from 4.3 to 6.7 OH nm^{-2}. The silanol numbers determined by the TG method are larger than the ones determined by deuterium-exchange, because both surface and bulk hydroxyls are included.

The aim of our study was to find a simple way to quantify the hydroxyl group content in an unknown silica sample. For this, the OH group content of a series of different types of silicas were measured by thermogravimetry. The results were compared with a reliable reference method for which ^{1}H MAS NMR was selected. In this work, we determined the total hydroxyl group content and the OH group content for the silica samples at two temperatures, 550 and 1000°C.

2. Experimental

2.1. The silica samples

Nine different types of silica samples were selected for the thermogravimetric study. The characterization of the silicas was done by determining BET surface area, BET pore volume, BET pore diameter and particle size distribution. The BET measurements were performed with a Micromeritics ASAP 2010 using nitrogen as adsorbate. Before the determinations, the samples were pretreated by heating to 150°C in vacuum in order to remove adsorbed species. The pretreatments took 15–20 h to ensure complete gas desorption. The results of the BET measurements in Table 1 are the average between two samples calcined

Table 1
Origin of the silica samples and the results of BET measurements of silicas calcined below 600 and at 1000°C

Technical product name of silica	Nature of silica	Supplier	BET surface area[a] ($\mathrm{m}^2\,\mathrm{g}^{-1}$)	BET pore volume[a] ($\mathrm{m}^3\,\mathrm{g}^{-1}$)	BET pore diameter[a] (nm)
SD 3216.20	Silica gel	Grace Davison	350 (<600°C) 38 (1000°C)	1.7 (<600°C) 0.1 (1000°C)	20 (<600°C) 6.5 (1000°C)
Sylopol	Silica gel	Grace Davison	330 (<600°C) 1 (1000°C)	1.7 (<600°C) 0.0004 (1000°C)	19 (<600°C) 11 (1000°C)
Kieselgel 40	Silica gel	Merck	790 (150°C) 720 (550°C) 0.4 (1000°C)	0.9 (<600°C) 0.01 (1000°C)	4.0 (<600°C) 61 (1000°C)
Kieselgel 60	Silica gel	Merck	495 (<600°C) 0.7 (1000°C)	0.9 (<600°C) 0.002 (1000°C)	5.9 (<600°C) 11 (1000°C)
EP 10	Silica gel	Crosfield	325 (<600°C) 80 (1000°C)	2.0 (<600°C) 0.2 (1000°C)	24 (<600°C) 11 (1000°C)
MS 3040	Spray-dried silica	PQ-Corp.	420 (<600°C) 320 (1000°C)	3.0 (<600°C) 2.1 (1000°C)	33 (<600°C) 22 (1000°C)
S 432	Spray-dried silica	Grace Davison	310 (<600°C) 0.8 (1000°C)	1.0 (<600°C) 0.002 (1000°C)	13 (<600°C) 37 (1000°C)
MCM-41	Precipitated[b], controlled pore size	–	1175 (<600°C) 11 (1000°C)	1.1 (<600°C) 0.03 (1000°C)	3.2 (<600°C) 9.5 (1000°C)
Aerosil 200	Pyrogenic, flame processed	Degussa	205 (<600°C) 164 (1000°C)	0.4 (<600°C) 0.3 (1000°C)	9.2 (<600°C) 8.6 (1000°C)

[a] BET measurements of silicas calcined below 600°C are the average between two samples calcined at 150 and 550°C (except for the BET surface area of Kieselgel 40).

[b] Synthesis of MCM-41 is described in [19].

at 150 and 550°C, because the surface area does not change significantly below 600°C for most of the silicas. Kieselgel 40 silica differs from the others, because its surface area diminishes already below 600°C. The average particle sizes were measured in aqueous solutions using a Malvern 2600 laser diffractometer and were found to be 20–100 μm, except for Aerosil 200 whose particle size was 12 μm. The nature and suppliers of the studied specimens of silica are listed in Table 1. All silica samples are mesoporous whose pore diameters lie in the range of 3.2–33 nm. Aerosil 200 silica differs from the others by having pores between small particles, while the others have actual pores in the structure. In addition, the surface area of Aerosil 200 is composed of the external surface area of those small particles, while the surface area of other silicas is mainly caused by the internal surface of the pores. The samples SD 3216.20, Sylopol, Kieselgel 40 and 60 and EP 10 are silica gels prepared by the sol–gel method, while MS 3040 and S 432 are spray-dried silicas. MCM-41 silica was precipitated using surfactant as a template so that a controlled pore size and shape could be achieved. After synthesis [19], the MCM-41 silica was calcined at 550°C in order to remove the surfactant. Aerosil 200 silica is pyrogenic and processed in flame. All the silicas had been stored in closed containers in air for an indefinite time. They were not rehydroxylated before use, i.e. the surface of every sample might not have been totally hydroxylated.

2.2. Thermogravimetric measurements

Thermogravimetric measurements were made for untreated silica samples. The MCM-41 and Aerosil 200 silicas were too light to be placed straight into the crucibles as a powder. They were pressed to briquettes under 8 tonnes pressure in a pressing machine for several minutes and then the briquettes were crushed into smaller pieces for measurement. The other silica samples were measured without any pretreatment. Two measurements were made on each silica type.

TG measurements were made with a Perkin-Elmer TGA-7 instrument using standard platinum crucibles and sample sizes of 16–29 mg. The samples were heated at a rate of 5°C min^{-1} from room temperature to 1250°C in an argon flow of 110 ml min^{-1}. The weighing and stabilization of the weight of the silica samples were performed as quickly as possible, because fast dehydration of silicas took place in the argon flow even at room temperature. An accelerated start of the measurements without any delay would not have been necessary for the OH group determinations, but it was done in order to determine the physisorbed water content.

2.3. ^{1}H MAS NMR measurements

For the ^{1}H MAS NMR studies, the silica samples were calcined in a muffle furnace in air at 105, 550, and 1000°C for 16 h. The NMR samples received a further heat treatment at 105°C for 1 h in nitrogen flow in the ALD reactor where the pressure was 40–60 mbar. This was done in order to get the pretreatment conditions similar to the process conditions used in the catalyst support preparation. The procedure was necessary for the multivariate calibration performed with the same samples [16]. The samples were stored in an argon glove box between the treatments.

The experiments were made with a Chemagnetics CMX 400 Infinity spectrometer using a 5 mm NMR probe with zirconia rotors. The samples were loaded under dry nitrogen and run using a single 45° excitation pulse of 2.5 μs, 64 transients and pulse delay of 30–60 s. A spectrum of the empty rotor was subtracted from the spectrum of each sample to remove the background signal. A sample of EP 10 silica was used as a quantitative reference to determine the number of OH groups present in the samples [15]. We used this silica sample, because it has about the same number of OH groups per gram as our unknown samples. Another type of material with a low density of hydrogen, e.g. alumina, could have been used, but it might have led to more error in calculating the total intensity of the spectrum because of more intense spinning sidebands.

2.4. DRIFTS measurements

After the thermogravimetric measurements, DRIFT spectra were measured for the residues of the silica samples. The samples were collected from the TG crucible directly after the measurement, transported to the spectrometer in a desiccator and measured immediately. The DRIFTS measurements were made in Nicolet Magna IR 750 spectrometer equipped with a Spectra-Tech diffuse reflectance accessory. The spectrum obtained from a polished steel mirror was used as background. The samples were measured in a micro diffuse reflectance sampling cup. The spectra were collected in the 4000–3000 cm^{-1} region at a 2 cm^{-1} resolution over 64 scans.

3. Results and discussion

3.1. Interpretation of thermograms

The thermograms and DTG curves of the nine silicas studied are depicted in Fig. 1. As well established, there are two distinct mass loss steps in the thermograms of the silicas [2]. The first step is abrupt and is most probably due to the removal of physisorbed water from the silica surface. The second step is broader and is considered to correspond to slow condensation of silanols. According to the DTG curves of Fig. 1, the two mass loss steps in the thermograms seem to be discrete. Therefore, the dehydration and dehydroxylation reactions were assumed not to overlap.

From the literature [2], it is known that upon heating of silica, hydrogen-bonded hydroxyls are released first quite rapidly in the temperature range 200–400°C and isolated hydroxyls more slowly at higher temperatures.

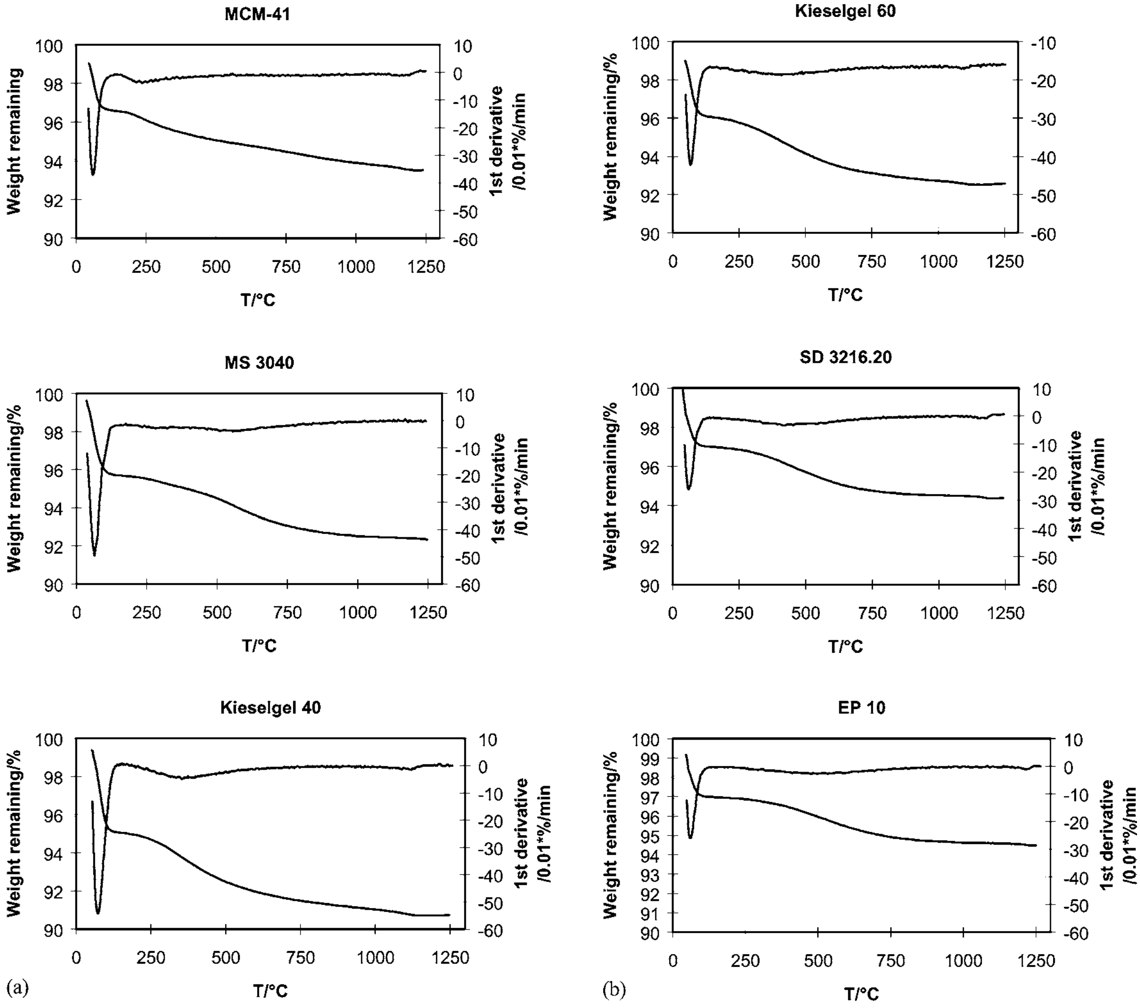

Fig. 1. TG and DTG curves of the silica samples recorded in a dynamic argon atmosphere at a heating rate of 5°C min^{-1}.

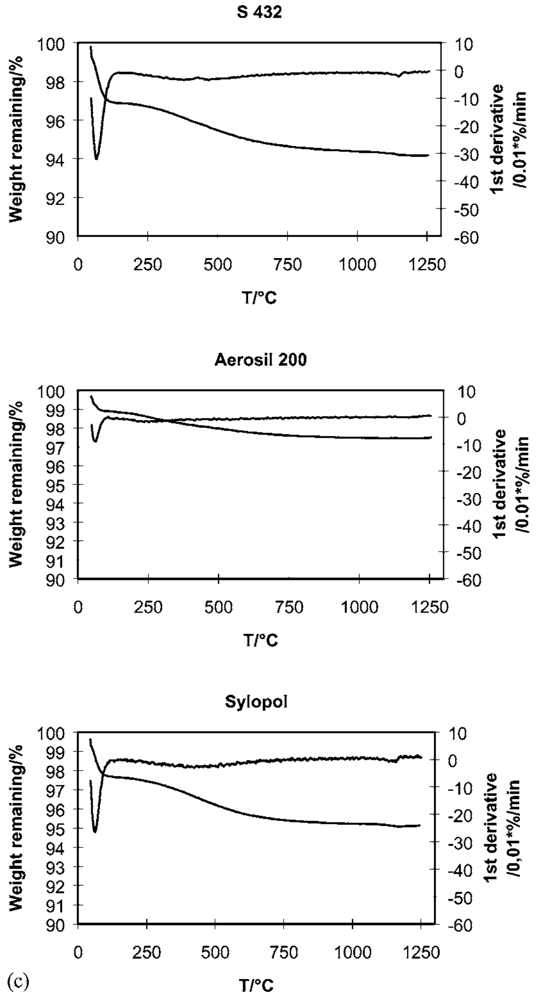

Fig. 1. (*Continued*).

Unfortunately, the removal of different types of hydroxyls, e.g. isolated and hydrogen-bonded, takes place during one continuous mass loss step so that distinguishing them is not possible from the thermograms. A third, rather flat peak at about 1100–1200°C can also be observed in the DTG curves of all the silicas, except for MS 3040 and Aerosil 200, but it is presumably not characteristic for any specific type of OH group. It might be due to the dehydroxylation of final OH groups before collapse of the porous structure after which no more OH groups are close enough and able to react on the external surface of the silica particles. This third DTG peak cannot be observed in the thermogram of Aerosil 200, because it is actually nonporous already before heat treatment.

3.2. Determination of physisorbed water of the silica samples by TG

The physisorbed water content was also calculated from the thermograms. Anyhow, it could not be entirely measured with the present technique, because some of the water was rapidly released in the gas flow before the mass of the sample had been stabilized and the measurement started. The amount of physisorbed water was calculated directly from the first mass loss in the thermograms by measuring the change in weight (in wt.%) up to the temperature where all the physisorbed water is released. The end point of the first weight loss is not quite unambiguous, but it can be considered to end where the DTG curve returns to zero. The starting point of the second mass loss is considered to be the same point where the first mass loss ends, so it is assumed that OH groups do not start to condensate before the physisorbed water is released. The temperature range where the physisorbed water is assumed to be totally released is 100–130°C for the samples studied. The results are in a good agreement with the literature [2] where the desorption of water is claimed to be complete at 120°C. Physisorbed water is removed at the low end of the 100–130°C range from Aerosil 200 (100°C), MCM-41 (110°C), and EP 10 (115°C). The precise end points of dehydration for all samples are presented in Table 2.

The physisorbed water contents of the silica samples are listed in Table 2. Honeycomb-structured MCM-41 silica calcined at 550°C has less than one molecule of physisorbed water per unit area adsorbed on the surface after calcination. Pyrogenic Aerosil 200 and silica gel Kieselgel 40 have only two water molecules per nm^2 and the other six silica types contain about the same amount of physisorbed water ($3\ H_2O\ nm^{-2}$).

3.3. Determination of hydroxyl groups of the silica samples by TG

The total hydroxyl group content in silica is calculated from the entire second weight loss which starts from the point where all physisorbed water is removed

Table 2
The masses of samples used in the TG measurements and physisorbed water content of the silica samples

Silica type	Mass of the sample[a] (mg)		Final temperature of first mass loss in thermogram (°C)	First mass loss[a] (%)		Physisorbed water[a] (mg g^{-1} SiO_2)		Physisorbed water[a] (mmol g^{-1} SiO_2)		Physisorbed water[a] (H_2O nm^{-2} SiO_2)	
SD 3216.20	20	19	125	3.0	3.2	30	32	1.7	1.8	2.9	3.1
Sylopol	19	16	130	2.7	2.3	27	23	1.5	1.3	2.6	2.2
Kieselgel 40	20	21	130	4.9	4.9	49	49	2.7	2.7	2.1	2.1
Kieselgel 60	20	19	130	4.0	3.9	40	39	2.2	2.2	3.1	3.0
EP 10	17	21	115	2.8	3.0	28	30	1.6	1.7	2.9	3.2
MS 3040	19	18	125	4.3	4.4	43	44	2.4	2.5	3.4	3.5
S 432	24	29	130	2.9	2.9	29	29	1.6	1.6	2.9	3.0
MCM-41	18	19	110	3.0	3.4	30	34	1.7	1.9	0.85	0.96
Aerosil 200	18	19	100	1.1	1.1	11	11	0.63	0.62	1.9	1.9

[a] The results of two measurements on each silica type are represented in separate columns.

and ends at the end point of the measurement ($T_{final} = 1250°C$). The amount of hydroxide groups left at a specific temperature below 1250°C can be calculated from the same thermogram. Then the change in weight between that temperature and the end point of the measurement is considered. All the hydroxyl groups from the pores are assumed to be released at the end point of heating, i.e. the residue of the sample is an oxide composed of only siloxane bridges.

The condensation of all kinds of silanol groups occurs by the reaction of two silanol groups on the silica surface resulting in the release of one molecule of water and the formation of one siloxane group. It is assumed that no other groups than water are released from the sample. The hydroxide group content, determined as moles of hydroxyls left per gram of silica at temperature T_0, can be calculated as follows:

$$n_{OH}(SiO_2) = 2n_{H_2O} = \frac{2(WL(T_0) - WL(T_{final}))}{100M_{H_2O}}, \qquad (1)$$

where $WL(T_0) - WL(T_{final})$ is the weight loss (wt.%) in the temperature region T_0–T_{final} and M_{H_2O} the molar mass of water.

The total hydroxyl group content of the silicas studied at room temperature are presented in Table 3. In addition, we calculated the hydroxyl group content of all the silicas at 550 and 1000°C (Table 3). Two measurements were made for each silica sample, but the deviation between them was <5%. The total OH group content of MCM-41 was not calculated, because it was calcined at 550°C. MCM-41 was rehydroxylated to some extent during storage, but the amount of rehydroxylation was not of particular interest.

3.4. The dehydroxylation stage of the silica samples at the end of the TG measurements and in samples calcined at 1000°C for ^1H MAS NMR

DRIFT spectra of the residues of the silicas after the TG measurements were measured in order to ensure total dehydroxylation at 1250°C. It has been shown in the literature [9,10] that the more completely the surface is dehydroxylated, the more hydrophobic the silica surface and the longer the rehydroxylation time. The silica surface of our samples is very hydrophobic, because the samples have been heated to 1250°C and should therefore not be rehydroxylated to large extent before the DRIFTS measurements. According to the DRIFT spectra in Fig. 2, the silicas Kieselgel 60, S 432, and Sylopol do not have any peaks due to OH groups, so they are almost totally dehydroxylated at the end of the TG measurement. In the DRIFT spectra of SD 3216.20, MCM-41 and particularly Kieselgel 40, a flat peak in the region 3680–3650 cm^{-1} can be observed which is probably due to weakly hydrogen-bonded hydroxyls. SD 3216.20 silica has also a weak peak due to isolated O–H stretching at about 3750 cm^{-1}, while MCM-41, Aerosil 200, EP 10, and MS 3040 silicas show strong reflectance at about the same wave number. The silicas Aerosil 200, EP 10, and MS 3040 have also

Table 3
The OH group content at 100–130 (the total OH groups), 550, and 1000°C of the silica samples determined by TG and ^{1}H MAS NMR

Silica type	Temperature (°C)	Second mass loss[a] (%)		OH group content[a] (mmol g^{-1} SiO_2)		OH group content[a] (mg g^{-1} SiO_2)		Silanol number (TG)[a,b] (OH nm^{-2})		Silanol number (^{1}H MAS NMR)[b,c] (OH nm^{-2})	OH group content (^{1}H MAS NMR)[c] (mg g^{-1} SiO_2)
SD 3216.20	125	2.8	2.7	3.1	3.0	52	51	5.4	5.2	5.4	53
	550	1.1	1.1	1.2	1.2	21	20	2.1	2.0	1.7	17
	1000	0.16	0.13	0.18	0.15	3.1	2.5	–	–	1.2	1.3
Sylopol	130	2.8	2.6	3.1	2.9	53	49	5.4	5.0	5.3	52
	550	0.81	0.84	0.90	0.93	15	16	1.7	1.8	2.0	18
	1000	0.14	0.11	0.16	0.12	2.7	2.1	–	–	NM[d]	NM[d]
Kieselgel 40	130	4.4	4.3	4.9	4.8	83	82	3.7	3.7	4.1	91
	550	1.50	1.4	1.7	1.5	28	26	1.4	1.3	1.2	24
	1000	0.30	0.26	0.34	0.29	5.8	5.0	–	–	0	0
Kieselgel 60	130	3.7	3.6	4.1	4.0	69	67	5.5	5.4	5.6	70
	550	1.3	1.3	1.5	1.4	25	24	1.6	1.6	1.4	22
	1000	0.17	0.16	0.19	0.18	3.3	3.1	–	–	0	0
EP 10	115	2.6	2.5	2.9	2.8	49	47	5.5	5.3	6.0	54
	550	1.2	1.2	1.3	1.3	23	22	2.4	2.4	2.2	20
	1000	0.09	0.13	0.09	0.14	1.6	2.4	0.71	1.1	1.1	2.4
MS 3040	125	3.7	3.7	4.1	4.1	69	70	5.8	5.9	6.7	80
	550	2.0	2.0	2.2	2.2	37	38	3.2	3.2	3.1	36
	1000	0.22	0.20	0.24	0.22	4.1	3.8	0.45	0.42	1.1	10
S 432	130	2.9	2.8	3.2	3.1	54	52	5.8	5.6	6.0	56
	550	1.1	1.0	1.2	1.1	20	19	2.4	2.3	2.0	17
	1000	0.20	0.19	0.22	0.21	3.8	3.5	–	–	–	0.2
MCM-41	550	1.5	1.4	1.6	1.6	28	27	0.84	0.82	1.3	42
	1000	0.36	0.39	0.40	0.43	6.7	7.3	–	–	2.3	0.7
Aerosil 200	100	1.3	1.3	1.5	1.5	25	25	4.4	4.4	4.3	24
	550	0.32	0.33	0.36	0.37	6.1	6.2	1.0	1.1	2.1	12
	1000	0	0	0	0	0.15	0	0	0	1.2	5.8

[a] The results of two measurements on each silica type are represented in separate columns.

[b] The calculated silanol number of some samples is very large because of the magnitude and uncertainty in the BET surface area measurements at 1000°C and therefore not presented here.

[c] The total OH group content was determined for the silicas calcined at 105°C independent on silica type.

[d] Not measured.

weak peaks at 3720 and 3520 cm^{-1} which have been assigned to hydrogen- and oxygen-perturbed O–H vibrations. These last-mentioned weak peaks and also the low-intensity peaks of weakly hydrogen-bonded hydroxyls observed in the DRIFT spectra might be due to rehydroxylation of silicas, because these types of hydroxyl groups should have been removed during the TG measurements. Isolated hydroxyls are most probably the remaining hydroxyls in the samples. Thus, the SD 3216.20 silica has some hydroxyls and MCM-41, Aerosil 200, EP 10 and MS 3040 have distinctly more remaining hydroxyls at the end of the TG measurement.

In practice, the knowledge of the OH group contents in silicas at 1000°C is not very useful in the preparation of catalysts, because catalyst supports are calcined at lower temperatures. In any case, the OH group content at high temperatures gives valuable information on the extent of dehydroxylation. According to the ^{1}H MAS NMR results, the OH group content in the samples calcined at 1000°C for 16 h is very small (Table 3 and Fig. 3). The silicas Kieselgel 40 and 60

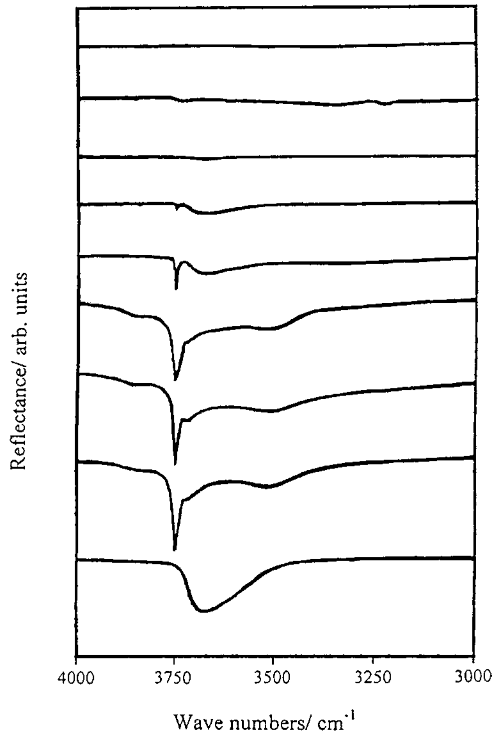

Fig. 2. DRIFT spectra of the silica samples after the TG measurements where they were heated to 1250°C in argon atmosphere at a heating rate of 5°C min^{-1}. From the top downwards: Kieselgel 60; S 432; Sylopol; SD 3216.20; MCM-41; Aerosil 200; EP 10; MS 3040; Kieselgel 40.

and S 432 seem to be totally dehydroxylated consisting of only siloxane bridges, while MCM-41, SD 3216.20, and EP 10 are not quite dehydroxylated. In addition, MS 3040 and Aerosil 200 differ from the other silicas by having distinctly some OH groups left on the surface. The remaining hydroxyls might be trapped in the structure or temperatures higher than 1000°C are required to remove all hydroxyls by calcination.

According to the TG results, there is still a significant number of hydroxyls left in silicas at 1000°C, and thus 1000°C is not high enough as final temperature for TG measurements when heated at a rate of 5°C min^{-1}. According to the DRIFT spectra (Fig. 2), there are still some hydroxyl groups left in some silicas even at 1250°C. Because the weight of the silicas has been stabilized before 1250°C, these remaining OH groups may be the ones captured in the pores of the silica which cannot be removed by heat treatment. It seems not necessary to have temperatures higher than 1250°C or to lengthen heating times in order to have these OH groups to react and to be released from the sample and thus to achieve satisfactory results for the OH group assessment.

3.5. Comparison of the hydroxyl group content determined by TG with ^{1}H MAS NMR results

When comparing the total OH group content determined by TG with the ^{1}H MAS NMR results, the TG results seem to be in a good agreement with the NMR results (Fig. 3a). The relative difference between the OH group contents (mg g^{-1} SiO_2) determined by these two methods is 2–15%, depending on the silica type, the NMR technique giving systematically slightly higher values. This is probably due to the fact that in NMR all hydroxyl groups are detected, while in TG some hydroxyls might remain unreacted. The OH group contents of EP 10, MS 3040, and Kieselgel 40 silicas determined by TG differed from the NMR results most. The difference is probably explained by the presence of hydroxyls remaining at the end point of the TG measurement.

The silanol numbers of the silica samples are also presented in Table 3. The silanol number of the samples taken out of the containers, i.e. the total OH group content, is in the range of 3.7–5.9 OH nm^{-2} (TG) and 4.1–6.7 OH nm^{-2} (NMR). The calculated silanol numbers contain also inaccessible internal silanols which are not useful concerning adsorption studies. Nevertheless, our TG and NMR results are close to those of Zhuravlev's [18], where the silanol number of totally hydroxylated silica, including only surface silanols, was found to be in the range 4.2–5.7 OH nm^{-2} in over 100 different silica samples.

The OH groups of the silicas remaining at 550°C (Fig. 3b) also correlated well with the ^{1}H MAS NMR results, the relative difference being 4–17%, except for the MCM-41 and Aerosil 200 silicas, where the differences were 53 and 95%, respectively. Regarding MCM-41 and Aerosil 200, the TG method gave distinctly lower OH group contents compared to the NMR results. The low amount of OH groups calculated from the thermogram at 550–1250°C means that a larger amount of OH groups have already reacted before 550°C. It is worth noting that the total number of OH groups in Aerosil 200 (not measured for

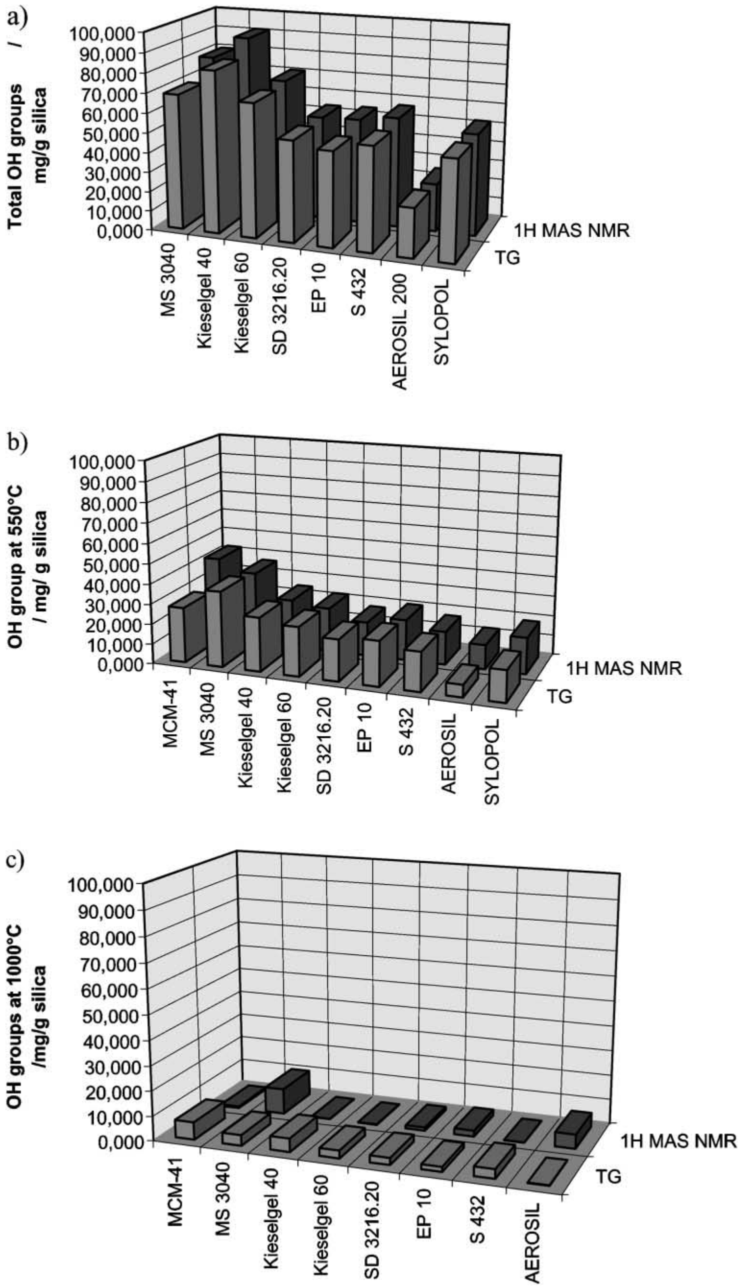

Fig. 3. (a) The total OH group content, (b) the OH group content at 550°C, and (c) at 1000°C as determined by TG and ^{1}H MAS NMR for the silica samples.

MCM-41) determined by TG correlated well with the NMR results, so approximately the same amount of OHs are removed both during the TG measurements and calcination of samples for NMR. Thus, there are less OH groups left at 550°C, i.e. dehydroxylation is faster in TG than in the same silica samples calcined for the NMR. The preparation method of the samples might have an effect on the fast dehydroxylation of

MCM-41 and Aerosil 200, because dehydroxylation might be faster and might occur at lower temperatures in the briquettes than in the calcined powder samples. Nevertheless, this conclusion is contrary to the general effect of packing on the thermal behavior of samples when reactions shift to take place at higher temperatures. By looking at the DRIFT spectra in Fig. 2, it can be noted that there are still OH groups left in the structure of MCM-41 and Aerosil 200. These OH groups might be too far from each other for a reaction between them to occur or they might be captured in the structure, unable to react and to be removed from the sample.

The hydroxyl group content at 1000°C determined by TG differs clearly from that obtained by ^{1}H MAS NMR (Fig. 3c). Nevertheless, when comparing the remaining hydroxyls after the TG measurements at 1250°C and in the samples calcined at 1000°C for NMR, they seem to be similar, because there are remaining hydroxyls in the same silica types, i.e. SD 3216.20, MCM-41, Aerosil 200, EP 10, and MS 3040. Even though, there are no OH groups remaining in the TG samples of Kieselgel 40 and 60, S 432, and Sylopol at 1250°C (determined by DRIFTS) and in the same NMR samples calcined at 1000°C, the TG samples contain more hydroxyls at 1000°C than the NMR samples (Fig. 3c). Thus, in the region 1000–1250°C, the last hydroxyls of the last-mentioned silicas are removed during dynamic TG measurements which is reasonable from the kinetic point of view.

As shown above, the best results were obtained when calculating the total OH groups and the OH groups at 550°C. The reason for the difference between the TG and NMR methods of silicas at 1000°C is probably due to the residual OH groups at the end point of the TG measurements. These remaining OH groups cause a relatively higher difference in samples at 1000°C than in the total OH group content. In addition, at higher temperatures the time taken for the equilibrium to be reached may be longer than at lower temperatures due to the time taken for the OH groups to migrate along the surface and condense. Therefore, the calcined samples for NMR have reached equilibrium, but the samples for the TG have not, even though the weights in the thermograms seem to have stabilized before 1250°C. Nevertheless, MS 3040 and Aerosil 200 silicas distinctly have some OH groups left at 1000°C according to the NMR results (not observed in TG), so they are most probably hydroxyls which cannot be removed by heat treatment. In addition, even though the Aerosil 200 surface is totally dehydroxylated by 1000°C in TG but not in the NMR samples MCM-41 show quite opposite behavior. Thus, it seems that sample preparation is profitable for pyrogenic silicas, like Aerosil 200, when measuring the total OH group content. The OH group content at some other temperature calculated from the thermogram, in this case at 550°C, is not so reliable. The OH group contents of MCM-41 silica at both 550 and 1000°C were not accurate enough, so it seems that mesoporous silicas belonging to the M41S family cannot be reliably measured by the present technique.

4. Conclusions

Thermogravimetry proved to be a simple and satisfactory method to determine the hydroxyl group content of silica. A slow heating rate (5°C min^{-1}) and high end point (1250°C) for the TG measurement were found to be good measurement parameters in order to achieve almost total dehydroxylation of silica. Nevertheless, according to the DRIFT spectra measured after the TG measurements for the residues of the silica samples, the dehydroxylation was still found to be incomplete in some cases. The reason may be that the remaining OH groups are captured in the structure of silica because of the collapse of porous structure. Some OH groups may also be too far from each other to react and be removed from the sample. Most of the OH group contents determined by dynamic TG measurements were in a good agreement with the results obtained by ^{1}H MAS NMR which were obtained from samples calcinated under a static air atmosphere in a muffle furnace for 16 h. The total hydroxyl group content especially, but also the hydroxyl group content at 550°C, determined by TG were very close to the ^{1}H MAS NMR results. However, the difference between the methods was much larger in the remaining OH group content at 1000°C, which is probably due to a combination of dynamic and steric effects. Thus, the TG method described above can be easily applied, especially for the determination of the total OH group content and the silanol number, but not so reliably for the determination of OH groups at temperatures higher than 550°C.

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