Langmuir **1987**, *3*, 316–318

Concentration of Hydroxyl Groups on the Surface of Amorphous Silicas[†,‡]

L. T. Zhuravlev

Institute of Physical Chemistry, the USSR Academy of Sciences, Moscow 117915, USSR

Received September 5, 1986. In Final Form: December 12, 1986

The present work studies a surface concentration of hydroxyl groups for a large number of amorphous silicas, viz., silica gels, aerosilogels, and porous glasses, differing in production conditions, surface area, and pore size distribution. It is shown that the surface density of OH groups (the silanol number) is a physicochemical constant for a fully hydroxylated surface and that the density as a function of temperature of vacuum treatment does not depend in a significant way on the type of silica.

Introduction

The adsorption and other properties of the surface of oxide adsorbents, particularly silicas, are known to depend frequently on the surface hydroxyl (silanol) groups.[1,2] By varying the concentration of hydroxyl groups on the surface of oxide adsorbents by one or another method, it is possible to substantially change the properties of such a surface.

Experimental Section

The researchers gave serious attention to the development of the methods for measuring the concentration of OH groups on the surface of oxide adsorbents. The author worked out the versions of the deuterio-exchange method with mass spectrometric analysis for determining small amounts of water and hydroxyl groups on the surface of dispersed oxide adsorbents.[3] The method of deuterio exchange is advantageous in that only surface hydroxyl groups enter into the reaction of isotopic exchange and the structural water (or OH groups) inside the silica particles does not.

The specific surface area of silica samples was determined by the BET method from low-temperature adsorption of krypton (the area covered by one krypton molecule $\omega_{\mathrm{m,Kr}} = 21.5\ \text{Å}^2$[4]). Nonspecific adsorption of Kr on the SiO_2 surface, determined by the dispersion interaction, is insensitive to a change in the hydroxylation degree. To reveal the structural specific features of amorphous silica samples, the following methods were used in this work as well: adsorption and capillary condensation by measuring the total adsorption isotherms of water, methanol, and benzene vapors, mercury penetration, electron microscopic, and other methods.

The surface concentration of OH groups (the silanol number) α_{OH}, expressed in OH groups nm^{-2}, is determined as

$$\alpha_{OH} = \delta_{OH}^{(s)} N_A \times 10^{-21} S^{-1}$$

where $\delta_{OH}^{(s)}$ is the concentration of OH groups on SiO_2 surface referred to the unit mass of the sample (mmol of OH/g of SiO_2) found by the deuterio-exchange method with mass spectrometric analysis, S is the specific surface area with respect to krypton adsorption ($m^2\ g^{-1}$) and N_A is the Avogadro number.

In addition to silanol groups, physically adsorbed water may be present on the surface of silica. In ref 5, 6 we have shown that preliminary treatment of amorphous silica under vacuum at 180–200 °C results in the removal of physically adsorbed water and complete retention of a hydroxyl cover.

Results and Discussion

We measured the silanol number α_{OH} by the deuterio-exchange method for the case of a fully hydroxylated state of the surface for 100 different samples of amorphous dispersed silica (S varied from 9.5 to 950 $m^2\ g^{-1}$).[5,7,8]

The following samples were studied: (a) initial, hydroxylated, laboratory and commercial silica gels obtained by the acidic method (26 samples); (b) initial laboratory silica gels obtained by the acidic method with the use of hydrothermal treatment at the stage of hydrogel or xerogel (nine samples); (c) laboratory silica gel obtained by hydrolysis of tetraethoxysilane (one sample); (d) hydroxylated laboratory and commercial silica gels obtained by the Bard ion-exchange method[9] from alkali and acid sols (14 samples); (e) laboratory aerosilogels obtained from water suspensions of aerosils (20 samples); (f) hydroxylated laboratory porous glasses obtained by leaching sodium borosilicate glass (10 samples); (g) rehydroxylated commercial silica gels (12 samples); (h) rehydroxylated laboratory and commercial aerosilogels (five samples); (i) re-

---

[†] The problem was stated in 1957 by Professor A. V. Kiselev. The data in this paper were obtained independently by L. T. Zhuravlev and jointly with A. V. Kiselev, A. A. Agzamkhodzhaev, R. L. Gorelik, K. Ya. Shengeliya, and others.

[‡] Presented at the "Kiselev Memorial Symposium", 60th Colloid and Surface Science Symposium, Atlanta, GA, June 15–18, 1986; K. S. W. Sing and R. A. Pierotti, Chairmen.

(1) *Surface Chemical Compounds and Their Role in Adsorption Phenomena*; Kiselev, A. V., Ed.; MGU: Moscow, 1957 (Proceedings of All-Union conference, Moscow, 1955).

(2) Iler, R. K. *The Chemistry of Silica, Solubility, Polymerization, Colloid, and Surface Properties and Biochemistry*; Wiley-Interscience: New York, 1979.

(3) Zhuravlev, L. T.; Gorelik, R. L.; Zhuravlev, L. T. In *Experimental Methods in Adsorption and Molecular Chromatography*; Kiselev, A. V., Dreving, V. P., Eds.; MGU: Moscow, 1973; p 250. Zhuravlev, L. T. *Ibid.* p 266.

(4) Kiselev, A. V.; Korolev, A. Ya.; Petrova, R. S.; Shcherbakova, K. D. *Kolloidn. Zh.* **1960**, *22*, 671.

(5) Zhuravlev, L. T.; Kiselev, A. V.; Naidina, V. P.; Polyakov, A. L. *Zh. Fiz. Khim.* **1963**, *37*, 2258.

(6) Zhuravlev, L. T.; Guy, A. P.; Gerasimova, G. A. In *Adsorbents and Adsorption Processes in Solution of the Problem of Protection of Nature*; Kerdivarenco, M. A., Ed.; "Shteentsa": Kishinev, 1986, p 126 (Proceedings of All-Union conference, Kishinev, 1985).

(7) Akshinskaya, N. V.; Davydov, V. Ya.; Zhuravlev, L. T.; Curthoys, G.; Kiselev, A. V.; Kuznetsov, B. V.; Nikitin, Yu. S.; Rybina, V. V. *Kolloidn. Zh.* **1964**, *26*, 529. Davydov, V. Ya.; Zhuravlev, L. T.; Kiselev, A. V. *Zh. Fiz. Khim.* **1964**, *38*, 2047. Davydov, V. Ya.; Kiselev, A. V.; Zhuravlev, L. T. *Trans. Faraday Soc.* **1964**, *60*, 2254. Zhuravlev, L. T. Cand. Thesis, Moscow, 1965. Zhuravlev, L. T.; Kiselev, A. V. *Zh. Fiz. Khim.* **1965**, *39*, 453. Agzamkhodzhaev, A. A.; Zhuravlev, L. T.; Kiselev, A. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, *No. 6*, 1186. Zhuravlev, L. T. In *Main Problems of Physical Adsorption Theory*; Dubinin, M. M., Serpinskii, V. V., Eds.; "Nauka": Moscow, 1970; p 309 (Proceedings of All-Union conference, Moscow, 1968). Agzamkhodzhaev, A. A.; Zhuravlev, L. T.; Kiselev, A. V.; Shengeliya, K. Ya. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1969**, *No. 10*, 2111. Zhuravlev, L. T.; Kiselev, A. V. In *Surface Area Determination*; Everett, D. H., Ed.; Butterworth: London, 1970; p 155 (Proceedings of the International Symposium, Bristol, U.K., 1969). Gorelik, R. L.; Zhdanov, S. P.; Zhuravlev, L. T.; Kiselev, A. V.; Luk'yanovich, V. M.; Nikitin, Yu. S. *Kolloidn. Zh.* **1972**, *34*, 677. Gorelik, R. L.; Davydov, V. Ya.; Zhuravlev, L. T.; Curthoys, G.; Kiselev, A. V.; Nikitin, Yu. S. *Kolloidn. Zh.* **1973**, *35*, 456. Gorelik, R. L.; Davydov, V. Ya.; Zhdanov, S. P.; Zhuravlev, L. T.; Curthoys, G.; Kiselev, A. V.; Nikitin, Yu. S. *Kolloidn. Zh.* **1973**, *35*, 1153. Agzamkhodzhaev, A. A.; Zhuravlev, L. T.; Kiselev, A. V.; Shengeliya, K. Ya. *Kolloidn. Zh.* **1974**, *36*, 1145. Belotserkovskii, G. M.; Zhuravlev, L. T.; Kolosentsev, S. D.; Shengeliya, K. Ya. *Kolloidn. Zh.* **1974**, *36*, 1148. Grivstov, A. G.; Zhuravlev, L. T.; Gerasimova, G. A.; Bulatova, I. V.; Khazin, L. G. Preprint of the Institute of Applied Mathematics, the USSR Academy of Sciences, No. 142, 1983.

(8) Gorelik, R. L.; Zhuravlev, L. T.; Kiselev, A. V.; Nikitin, Yu. S.; Oganesyan, E. B.; Shengeliya, K. Ya. *Kolloidn. Zh.* **1971**, *33*, 51.

(9) Bard, P. G. U.S. Patent 2 244 325, 1941.

0743-7463/87/2403-0316$01.50/0

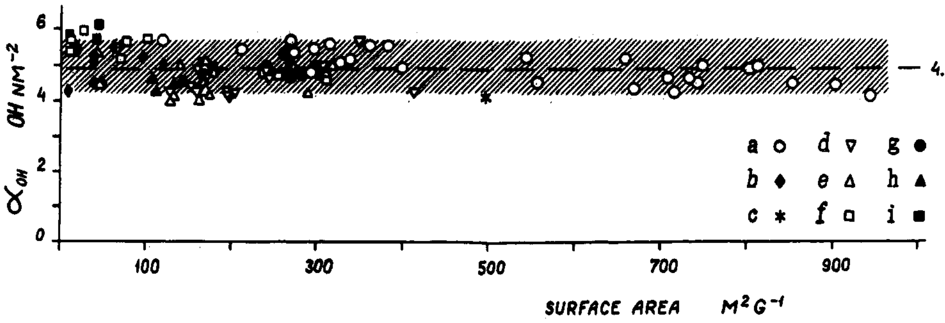

Figure 1. Concentration of surface hydroxyl groups for silicas (the silanol number) of different surface areas. (a)–(i): The different types of amorphous silicas (see text). Shaded area: range of data on a variety of types of silica (100 silica samples with different specific surface areas: from 9.5 to 950 m^2 g^{-1}). Dashed line is the average meaning of the silanol number (231 independent determinations): $\alpha_{OH,av}$ = 4.9 OH groups nm^{-2}.

hydroxylated laboratory porous glasses (three samples).

The silanol number α_{OH} was found on the surface of pores accessible to krypton molecules (according to Dubinin's classification):[10] macropores, $d > 2000$–4000 Å; mesopores, 30–32 Å $< d <$ 2000–4000 Å; supermicropores, 12–14 Å $< d <$ 30–32 Å (d is a diameter of pores). When a biporous SiO_2 sample contained, in addition to large pores (mesopores), very small pores (ultramicropores[8,11]), it was considered as large porous but the thinnest pores were not taken into account. The ultramicropores are commensurable in their diameter with the size of water molecules. So only water molecules penetrate into the ultramicropores. The presence of ultraporosity in some silica samples has been detected by the adsorption and isotope-exchange kinetic experiments.[3,8,11] The OH groups in the thinnest pores were classified not as surface silanol groups but as intraskeleton structural water.

For a fully hydroxylated state of the surface the values of the silanol number α_{OH} of the above amorphous silica samples lie within the range 4.2–5.7 OH groups nm^{-2}, although the samples were prepared in a different way and had different structural characteristics (specific surface area, type of the pores, size distribution of the pores, particle packing density, structure of SiO_2 skeleton).

In Figure 1 the values of the concentration of surface hydroxyl groups are given for 100 silica samples of different surface areas.[5,7,8] An average meaning of the silanol number (231 independent determinations) is α_{OH} = 4.9 OH groups nm^{-2}.

The average α_{OH} = 4.9 OH groups nm^{-2} is in a good agreement with the values of surface concentration of silicon atoms on an octahedral face of β-cristobalite (α_{Si} = 4.55 Si atoms nm^{-2}) and with other values of α_{Si} calculated by De Boer and Vleeskens[12] for cristobalite and tridymite, which represent crystalline modifications of silica and have a density close to that of amorphous silica.[2]

Thus, the experimental data obtained by us[5,7,8] show that in the fully hydroxylated state of the surface of amorphous silica, approximately one OH group corresponds to one Si atom of the surface and, hence, a silanol group $\equiv$Si—OH is the most probable compound. The α_{OH} value independent of the origin and structural characteristics of amorphous silica is considered as a physicochemical constant.[5,7,8]

The data obtained by the deuterio-exchange method[5,7,8] have shown that many varieties of amorphous dispersed silica contain silanol groups not only on the accessible surface but inside the particles. The distribution of OH groups between the surface and bulk depends on the processes of silica preparation and treatment.

Table I. Average Concentration of Hydroxyl Groups α_{OH} on the Surface of Amorphous Silica after Vacuum Treatment at Different Temperatures[a]

temp of vacuum treatment, °C	$\alpha_{OH,av}$, OH groups nm^{-2}	coverage of the surface of amorphous silica with OH groups, θ
180–200	4.9	1.0
300	3.6	0.7
400	2.3	0.5
500	1.8	0.4
600	1.5	0.3
700	1.1	0.2
800	0.7	0.15
900	0.4	0.1
1000	0.2	0.05
1100	<0.15	<0.02

[a] Initial state is the fully hydroxylated surface.

It is of interest to consider the dependence of the silanol number on the temperature of preliminary vacuum treatment of amorphous silica samples fully hydroxylated in the initial state. The dependence was studied in ref 5–8. Table I gives the most probable values of the silanol number α_{OH} which can be used for evaluating an average concentration of OH groups on the surface of amorphous silica at different temperatures of vacuum treatment of the initial fully hydroxylated samples.[6] Numerical values (Table I) were obtained as an average for 16 various amorphous silicas (silica gels, aerosilogels, porous glasses), whose specific surface area varied from 11 to 905 m^2 g^{-1}. The experiments were conducted within the temperature range from 200 °C (fully hydroxylated state of the surface) to 1000–1100 °C (strongly dehydroxlyated state of the surface). Although SiO_2 samples differed considerably by structural characteristics and method of preparation, the values of α_{OH} proved to be close at certain temperature of vacuum treatment and a decrease in α_{OH} under similar heating conditions for different samples follows approximately the same pattern.[5-8]

Conclusions

By the deuterio-exchange method with mass spectrometric analysis, the concentration of hydroxyl groups (the silanol number) α_{OH} has been estimated on the fully hydroxylated surfaces of 100 samples of amorphous silica (silica gels, aerosilogels, porous glasses). The silanol number α_{OH} is about 5.0 OH groups nm^{-2}, independent of the origin and structural characteristics (specific surface area, type of the pores, size distribution of the pores, particle packing density, structure of SiO_2 skeleton). The

---

(10) Dubinin, M. M. In *Adsorbents, Their Preparation, Properties, and Application*; "Nauka": Leningrad, 1978; p 4 (Proceedings of All-Union conference, Leningrad, 1976).

(11) Zolotarev, P. P.; Zhuravlev, L. T.; Ugrozov, V. V. *Kolloidn. Zh.* **1984**, *46*, 247.

(12) De Boer, J. H.; Vleeskens, J. M. *Proc. K. Ned. Akad. Wet., Ser. B: Phys. Sci.* **1958**, *61*, 2. De Boer, J. H. *Angew. Chem.* **1958**, *70*, 383.

α_{OH} value is considered as a physicochemical constant. A silanol group $\equiv$Si—OH (one OH group per one surface Si atom) is the most probable compound on the fully hydroxylated surface of amorphous silica.

The deuterio-exchange method was used for measuring the silanol number of 16 samples of amorphous silica with different specific surface areas (from 11 to 905 m^2 g^{-1}), depending on the temperature of vacuum treatment. The values of α_{OH} at a certain temperature of vacuum treatment are close for all samples under study and lowering of the concentration of hydroxyl groups on the surfaces of different silicas under similar conditions of the heat treatment also proceeds similarly.

Acknowledgment. I express deep gratitude to Prof. A. V. Kiselev for the statement of the problem and constant attention. I also thank A. A. Agzamkhodzhaev, R. L. Gorelik, K. Ya. Shengeliya, and others for their help in this work.

Registry No. SiO_2, 7631-86-9.

Reversible Adsorption of Carbon Monoxide on Copper Oxide[†]

A. V. Larin

Institute of Physical Chemistry, Academy of Sciences of the USSR, Leninsky Prospect, 31, 117915 GSP, Moscow, USSR

Received September 5, 1986

The reversible adsorption isotherm of CO on active sites of CuO at 293 K was measured by the ideal chromatography method. This isotherm of weak adsorption is satisfactorily approximated by the Langmuir equation with the constants a_m = 0.0003 mol/kg and b = 370 m^3/mol.

Introduction

The study of catalysts by adsorption techniques enables one to obtain the necessary information on the formation, location, and nature of active sites. It is known that carbon monoxide is irreversibly sorbed on CuO. This is evidenced by the results of the studies carried out by using various methods, mainly spectroscopic[1] and adsorption[2] methods. At the same time, the reversible physical adsorption or the weak adsorption of CO on CuO has been inadequately studied. The purpose of the present paper was to study the interaction of CO with CuO by employing gas chromatography.

Experimental Section

In this study we used CuO deposited on activated carbon AC-40 in an amount of 8% by decomposing cupric ammonium carbonate at ~130 °C. The geometric micropore area of AC-40 is 455 m^2/g, and the mesopore specific area of AC-40 is 100 m^2/g. Into glass chromatographic columns with an inside diameter of 6 mm were packed up to 3 g of the prepared catalyst (the layer length was up to 20 cm). As the carrier gas we used air when working with a thermochemical detector and helium when working with a katharometer. Concordant results were obtained here. The sample volume varied from 5×10^{-3} up to 5×10^{-2} cm^3 (NTP). The relative error of the measurements was determined mainly by the accuracy of adding the CO dose with a syringe and did not exceed ±10%. The experiment was conducted at 293 ± 1 K.

Results and Discussion

The deposition of copper oxide on activated carbon did not significantly change the adsorption capacity of nonpolar krypton and methane. The values of their specific retention volumes decreased less than 10% of the mass of the initial activated carbon, and the shape of chromatographic peaks remained almost unchanged and close to Gaussian distribution.

When CO was introduced into the carrier-gas flow passing through the catalyst, the irreversible adsorption of its first impulses was observed. The irreversible adsorption of 0.0003 mol/kg stands in quantitative and qualitative correlation with spectroscopic[1] and adsorption[2] measurements.

With more CO added, the complete elution of the samples was observed together with the sharp increase in CO adsorption in the low concentration region as compared with the starting activated carbon. The asymmetrical peaks are due to the nonlinear isotherm of physical adsorption.

To evaluate the contributions of the nonlinear isotherm and the adsorption rate to the smearing of the chromatographic peak, the experiments with two size fractions of the catalyst (0.8–1.0 and 0.4–0.5 mm) in the air and helium flow were conducted in accordance with recommendations.[3,4] The space velocity of the mobile phase varied within 20–80 cm^3 (NTP)/min. In all cases the back boundaries of elution curves coincided (Figure 1). This proves that the relative length of the chromatographic column is too big and peak smearing is mainly determined

---

[†] Presented at the "Kiselev Memorial Symposium", 60th Colloid and Surface Science Symposium, Atlanta, GA, June 15–18, 1986; K. S. W. Sing and R. A. Pierotti, Chairmen.

(1) Stobie, R. W.; Dignam, M. J. *Can. J. Chem.* **1978**, *56*, 1088.

(2) Kholjavenko, K. M.; Rubanic, M. Ya.; Barishevskaya, I. M.; Chernukhina, N. A. *Catalysis and Catalysts*; Naukova Dumka: Kiev, 1965; p 187.

(3) Kiselev, A. V.; Yashin, Ya. I. *Gas Adsorption Chromatography*; Nauka: Moscow, 1967.

(4) Larin, A. V. *Izv. Akad. Nauk SSSR, Chem. Ser.* **1984**, 1914.

0743-7463/87/2403-0318$01.50/0