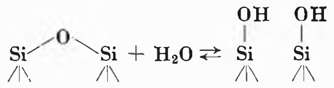
The Role of Surface Hydroxyl Groups in the Surface Chemistry of Metal Oxides *

P. W. Schindler **, E. Wälti and B. Fürst
Institut für Anorganische Chemie der Universität Bern

Summary

Hydroxylated oxides are polyelectrolytes whose properties are determined by the characteristics of the surface hydroxyl groups. Recent investigations on hydration numbers, protolytic behaviour and ligand properties of surface hydroxyl groups are summarized.

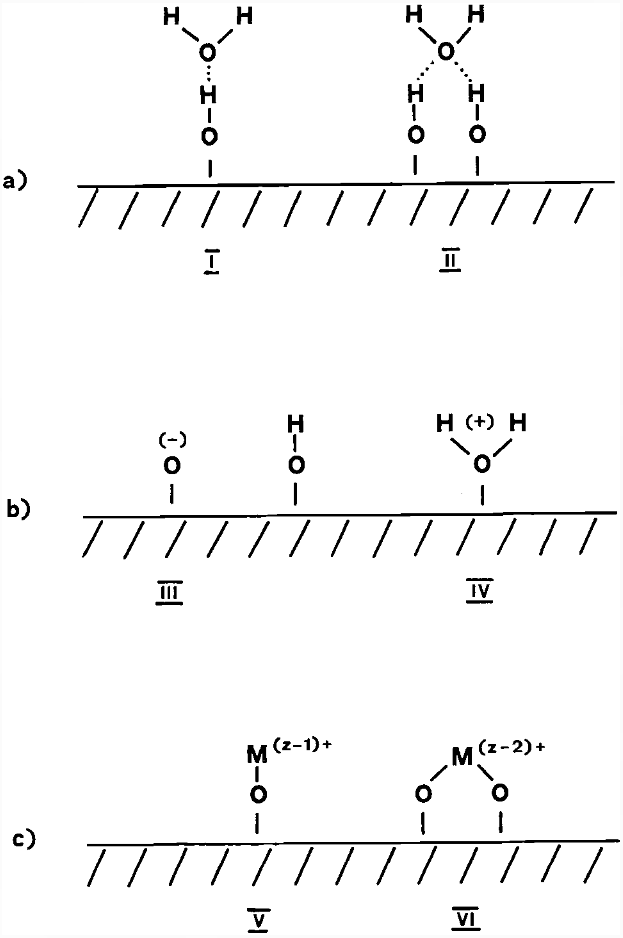
Oxide surfaces that are exposed to aqueous environments or humid air are generally covered with hydroxyl groups. Surface hydroxyl groups originate from chemical reactions between chemisorbed water and the oxide surfaces. In the case of silica this reaction is simply the hydrolysis of surface siloxane bridges as indicated by the scheme:



$$\underset{/|\backslash}{\mathrm{Si}}\overset{O}{\frown}\underset{/|\backslash}{\mathrm{Si}} + H_2O \rightleftarrows \underset{/|\backslash}{\overset{OH}{\mathrm{Si}}}\ \ \underset{/|\backslash}{\overset{OH}{\mathrm{Si}}} \tag{1}$$

The hydroxylation of oxide surfaces is reversible. Outgassing at elevated temperature reduces the surface concentration of hydroxyl groups. Eq. (1) shows the formation of "free" hydroxyl groups. IR spectra indicate, however, the possibility of hydrogen coupling between favourably oriented groups [1]. Moreover, the formation of geminal groups attached to one silicon atom has been suggested [2]. In the case of γ-Al_2O_3 five different types of hydroxyl groups were observed [3]. The observed differences in the frequencies of the valence vibrations are attributed to differences in the numbers of adjacent oxygen ions [4]. There is ample evidence that specific adsorption of molecules such as NH_3, amines, aliphatic and aromatic hydrocarbons is determined by surface hydroxyl groups [5].

The present article summarizes some recent work which shows that surface hydroxyl groups are equally responsible for the physisorption of water and the adsorption of hydrogen (hydroxide) ions and metal ions from aqueous solution at oxide water interfaces. The pertinent surface species are shown in the Figure.



Reactivity of surface hydroxyl groups. a) Hydration. b) Protolytic behaviour. c) Ligand properties

---

* Received: December 5, 1975

** Prof. P. W. Schindler, Institut für Anorganische Chemie der Universität Bern, Freiestrasse 3, CH-3012 Bern

1. The hydration of surface hydroxyl groups

The physisorption of water on hydroxylated oxide surfaces is equivalent to a hydration of surface hydroxyl groups. The first monolayer of physisorbed water thus forms the inner hydration sphere whereas the subsequent layers are attributed to the outer sphere. Hydration numbers are available from stoichiometric and thermodynamic informations related to the formation of the first monolayer. Recent figures derived from a study on the adsorption of water vapour on hydroxylated nonporous ZrO_2 (Baddeleyite) [6] are summarized in Table 1.

Table 1: Adsorption of water vapour on ZrO_2

Chemisorbed water:	0.249 cm^3/g (STP)
First (statistical) monolayer:	0.515 cm^3/g (STP)
Isosteric heat of adsorption:	25 kJ/mole (25°)
(Heat of liquefaction of water:	44.01 kJ/mole [25°])

Eq. (1) shows that chemisorption of one molecule of H_2O results in the formation of two hydroxyl groups. Hence the stoichiometric observations suggest hydration number 1. The arrangement (I) is further supported by an unusually low value for the isosteric heat of adsorption which suggests that each H_2O molecule exhibits but one hydrogen bond. Hydration number 1 is also observed for hydroxyl groups on ZnO [7] and η-Al_2O_3 [8] whereas hydration number 0.5 (II) was found on TiO_2 (Rutile) [9], α-Fe_2O_3 [10] and ThO_2 [11]. So far it is not known whether the preference for a given hydration number is an inherent property of the particular hydroxyl groups or a consequence of their density and geometric arrangement on the particular surface.

2. The protolytic behaviour of surface hydroxyl groups

Oxide surfaces adsorb H^+ and OH^- ions what in turn leads to positive or negative surface charges. This behaviour is a consequence of the ampholytic properties of the surface hydroxyl groups. Adsorption of OH^- leads to deprotonated groups (III), adsorption of H^+ to protonated groups (IV). Applying the law of mass action two acidity constants may be defined:

$$Ka_1^s = \{R{-}OH\}\,[H^+]\,/\,\{R{-}OH_2^+\};$$

$$Ka_2^s = \{R{-}O^-\}\,[H^+]\,/\,\{R{-}OH\}$$

[ ] : Moles/dm^3 of the aqueous phase
{ } : Moles/kg of the solid oxide

These constants exhibit a charge dependence that shows a striking similarity to the well known examples in the field of natural and synthetic organic polyelectrolytes. Extrapolating *Ka* values to zero charge conditions leads to the intrinsic microscopic acidity constants of the surface hydroxyl groups $Ka^s_{1(\text{int})}$ and $Ka^s_{2(\text{int})}$ (Table 2).

Table 2: Intrinsic microscopic acidity constants of surface hydroxyl groups (25°C)

Reactive group	Solid phase	Electrolyte solution	$pKa^s_{1(\text{int})}$	$pKa^s_{2(\text{int})}$	Ref.
Si—OH	Silicagel	0.1 M $NaClO_4$	(−3)	6.8	[11]
	Silicagel	1.0 M $NaClO_4$	(−3)	6.71	[12]
Ti—OH	Anatase	3.0 M $NaClO_4$	4.98	7.80	[13]
	Rutile	1.0 M $NaClO_4$	4.46	7.75	[14]
Th—OH	ThO_2	1.0 M $NaClO_4$	5.15	7.90	[6]
Al—OH	γ-Al_2O_3	0.1 M $NaNO_3$	6.51	8.43	[15]
	γ-$Al(OH)_3$	3.0 M $NaClO_4$	6.9	9.5	[12]

The data suggest a correlation between the protolytic behaviour of metal ions in homogeneous medium and the surface properties of the corresponding oxides. The acidity of the metal ions increases in the order $Al^{3+}_{aq} < Th^{4+}_{aq} < Ti^{4+}_{aq} < Si^{4+}_{aq}$. The same order is observed for the acidity of the surface hydroxyl groups.

3. Ligand properties of surface hydroxyl groups

From Table 2 it is further seen that deprotonated surface hydroxyl groups are Brönsted-bases of considerable strength. They may therefore behave as Lewis-bases in reactions with metal ions. Recent work [16, 17, 18] has actually proved that adsorption of metal ions from aqueous solution at oxide-water interfaces is based on the formation of surface complexes (V, VI):

$$R{-}OH + M^{z+} \rightleftarrows R{-}O{-}M^{(z-1)+} + H^+$$

$$^*K_1^s = \{R{-}O{-}M^{(z-1)+}\}\,[H^+]\,/\,\{R{-}OH\}\,[M^{z+}]$$

$$2\,R{-}OH + M^{z+} \rightleftarrows (R{-}O)_2M^{(z-2)+} + 2\,H^+$$

$$^*\beta_2^s = \{(R{-}O)_2M^{(z-2)+}\}\,[H^+]^2\,/\,\{R{-}OH\}^2\,[M^{z+}]$$

The so far obtained values of $^*K_1^s$ and $^*\beta_2^s$ (Table 3) are but little dependent on the surface charge.

Table 3: Selected stability constants of surface complexes (25°C)

Solid phase	M^{z+}	Electrolyte solution	$\log {}^*K_1^s$	$\log {}^*\beta_2^s$	Ref.
$SiO_{2(am)}$	Fe^{3+}	3.0 M $NaClO_4$	−1.77	−4.22	[17]
	Cu^{2+}	1.0 M $NaClO_4$	−5.52	−11.19	[17]
	Cd^{2+}	1.0 M $NaClO_4$	−6.09	−14.20	[17]
	Pb^{2+}	1.0 M $NaClO_4$	−5.09	−10.68	[17]
TiO_2	Cu^{2+}	1.0 M $NaClO_4$	−1.52	−4.96	[14]
(Rutile)	Cd^{2+}	1.0 M $NaClO_4$	−3.17	−10.48	[14]
	Pb^{2+}	1.0 M $NaClO_4$	−0.15	−1.96	[14]
γ-Al_2O_3	Pb^{2+}	0.1 M $NaClO_4$	−2.2	−8.1	[18]

There is no obvious correlation between Lewis- and Brönsted-basicity of deprotonated hydroxyl groups. With $SiO_{2(am)}$ there is, however, for various metal ions an excellent correlation between the stability constants of hydroxo complexes and surface complexes [17].

4. "So what?"

So far this article is concerned with some aspects of—as it seems to be—a rather narrow field of limited relevance. We would therefore like to present to our readers three arguments that demonstrate that the surface chemistry of metal oxides is closely related with some fields of general importance:

- The overwhelming part of the crust of our planet consists of simple or complex solid oxides. It is the surface of these oxides that is exposed to the atmosphere and the hydrosphere. Geochemical interactions such as weathering, soil formation and sedimentation are governed by the surface chemistry of these metal oxides. Surface reactions make an important contribution to hydrogeochemical transport processes. The concentrations of trace elements in aquatic systems are preponderantly controlled by adsorption-desorption equilibria [19].
- Metal oxides are powerful catalysts in many processes of technological importance. The catalytic activity is a consequence of an enhanced reactivity of adsorbed species. We presume that a systematic study of adsorbed species and the nature of adsorbent-adsorbate interaction may contribute to a deeper understanding of the fascinating field of heterogeneous catalysis.
- Hydroxylated metal oxides are polyelectrolytes. They differ from the more familiar organic polyelectrolytes inasmuch as they have but one kind of functional groups and that they do not suffer from conformational changes. They thus permit model studies of phenomena such as hydration, effects of charge and potentials, binding of cations and anions that might be of some interest for those working in the field of biopolymers. It is this latter aspect that relates our present activities to the scientific work of Professor Hans Nitschmann.

Acknowledgement

The work was financially supported by the Swiss National Foundation (Project Nr. 2.0460.73).

Literature

1 *A. V. Kiselev* and *V. I. Lysin:* Kolloidn. Zh. *21* (1959) 581.
2 *J. B. Peri:* J. Physic. Chem. *70* (1966) 2937.
3 *J. B. Peri:* J. Physic. Chem. *69* (1965) 211.
4 *J. B. Peri:* J. Physic. Chem. *69* (1965) 220.
5 *A. V. Kiselev* and *V. I. Lysin:* Infrared Spectra of Surface Compounds, Keter Publishing House Ltd., Jerusalem 1975.
6 *E. Wälti:* Untersuchungen über die Grenzfläche Oxid–Wasser, Dissertation, Bern 1974.
7 *M. Nagao:* J. Physic. Chem. *75* (1971) 3822.
8 *H. P. Boehm* and *R. Sappok:* Disc. Faraday Soc. *52* (1971) 257.
9 *E. McCafferty* and *A. C. Zettlemoyer:* Disc. Faraday Soc. *52* (1971) 239.
10 *C. M. Hollabaugh* and *J. J. Chessick:* J. Physic. Chem. *66* (1962) 2597; *T. Morimoto, M. Nagao* and *F. Tokuda:* ibid. *73* (1965) 243.
11 *P. Schindler* and *H. R. Kamber:* Helv. Chim. Acta *51* (1968) 1781.
12 *P. Schindler* et al.: unpublished results.
13 *P. Schindler* and *H. Gamsjäger:* Kolloid-Z. *250* (1972) 759.
14 *B. Fürst:* unpublished results.
15 *W. Stumm, C. P. Huang* and *S. R. Jenkins:* Croat. Chim. Acta *42* (1970) 223.
16 *C. P. Huang* and *W. Stumm:* J. Coll. Interface Sci. *43* (1973) 409.
17 *P. Schindler, B. Fürst, R. Dick* and *P. Wolf:* J. Coll. Interface Sci. (in press).
18 *H. Hohl* and *W. Stumm:* J. Coll. Interface Sci. (in press).
19 *P. Schindler:* Great Lakes J. (in press).

Redaktionelle Bemerkung

Der erweiterte wissenschaftliche Teil dieses Heftes enthält ausschliesslich Herrn Professor Hans Nitschmann gewidmete Arbeiten. Die Redaktionskommission ad hoc dankt den folgenden Donatoren für ihre grosszügigen finanziellen Beiträge:
Schweizerischer Chemiker-Verband; Blutspendedienst des Schweizerischen Roten Kreuzes, Bern; Emserwerke AG, Domat-Ems; Galactina AG, Belp; Haco AG, Gümmligen; Nestlé Alimentana S.A., Vevey, und Firma Wander AG, Bern.

sig. *E. Rickli* *C. H. Schneider* *P. Zahler*