DESCRIPTION OF SURFACE STRUCTURES BY ADSORPTION MICROCALORIMETRY

B. FUBINI, V. BOLIS and E. GIAMELLO

Istituto di Chimica Generale ed Inorganica, Facoltà di Farmacia
Università di Torino, Via Pietro Giuria 9, 10125 TORINO (Italy)

ABSTRACT

   Three simple cases are discussed, in which adsorption calorimetry provides
information about the structure of the adsorbent surface: i) hydrophilicity and
hydrophobicity of various SiO_2; ii) occurrence of different types of crystal
faces on ZnO; iii) state of oxidation of Copper in a Cu/ZnO catalyst.

INTRODUCTION

   It is widely accepted that the knowledge of adsorption heats is vital in the

description of gas-solid interaction (ref.1). These obviously provide informa-

tion about the energetics of surface processes. In some simple cases, however, in-

ference can be made from adsorption heats on the structure of the surface

itself.

   We report three examples in which different possible aspects of a surface

are considered: i) hydrophobicity/hydrophilicity (various SiO_2); ii) occurrence

of different crystal faces (ZnO variously prepared); iii) oxidation state of a

transition ion (Cu on ZnO).

METHOD

   Heats of adsorption have been measured at 303 K by means of a Calvet micro-

calorimeter by contacting the solid with small successive doses of the adsorp-

tive (ref. 2). This allows the evolution of the interaction energy along the

coverage to be measured.

RESULTS AND DISCUSSION

Water on silica

   A large number of papers has been devoted to the surface structure of SiO_2

and to the adsorptive capacity towards H_2O (ref. 3). Upon dehydration, the SiO_2

surface develops an increasing hydrophobicity, related to the elimination of SiOH and the formation of SiOSi bridges: hydrophobicity corresponds to an adsorption energy. 44 kJ mol^{-1} (latent heat of liquefaction of H_2O) (ref. 4). There is, however, a lack of direct calorimetric measurements on this system.

As the dehydration process depends upon the crystallinity and the particle size of SiO_2, we have considered three samples: i) crystalline quartz, 5.2 m^2 g^{-1}; ii) Porasil, amorphous, 16.1 m^2 g^{-1}; iii) Aerosil, amorphous, 380 m^2 g^{-1}, all outgassed at 673 K for 4 hours.
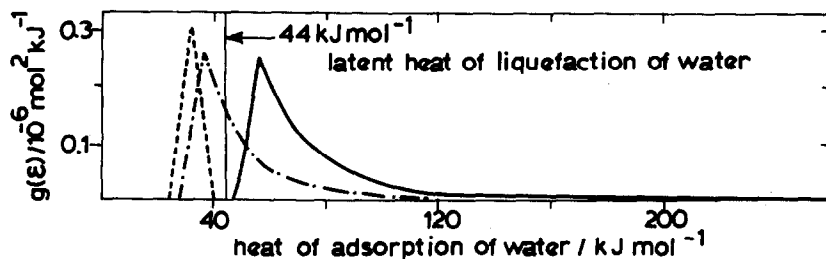

Fig. 1. Site energy distributions for the adsorption of H_2O_{vap} on SiO_2. — quartz; – – Porasil; – – – Aerosil.

Fig. 1 reports the site energy distributions. The extent of hydrophobicity is measured by the number of sites showing an adsorption heat 44 kJ mol^{-1} .Fig.1 suggests that quartz is completely hydrophylic and Aerosil completely hydrophobic. Porasil, with a texture similar to Aerosil, but with much higher particle size is in an intermediate situation. Structural reasons for such behaviours will be analyzed in the context of a more general paper concerning the energetics of the H_2O/SiO_2 system.

Occurrence of different crystal faces on ZnO

ZnO crystallizes in the hexagonal system so that its microcrystals may be described, with some oversimplification, as constituted of apolar prismatic faces terminating with hexagonal polar ones (0001). The distribution of the two kinds of faces depends upon the preparation route, but it is generally agreed that the active sites for methanol synthesis are located at the polar faces (ref. 5).

We have considered two ZnO samples: i) ZnO Kadox 25 obtained by ignition of Zn metal, (10 m^2 g^{-1}, K-ZnO); ii) ZnO obtained from thermal decomposition of

$ZnCO_3$, (37 m^2g^{-1}, C-ZnO). Adsorption and related heats of CO on these two samples have indicated that the number of coordinative sites for CO per unit area is 2.5 times greater on K-ZnO than on C-ZnO (ref. 6). As CO adsorption is known to occur onto cation exposed by anion vacancies on the polar faces, this was interpreted as evidence that on K-ZnO the extent of polar faces is larger than on C-ZnO. Hydrogen adsorption at r.t. involves heterolytic dissociation of H_2 and yields two separate species, named type I and type II (ref. 7),formed with different kinetics and heats of adsorption (ref.8). Type I is formed on the polar faces and is the adsorbed species active in the catalytic process.
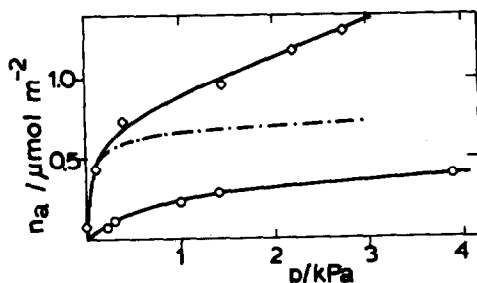

Fig. 2. Adsorption isotherms of H_2 on ZnO. - o -   C-ZnO;   - ◊ -   K-ZnO; -.-.-   Type I H_2 on K-ZnO

Fig. 2 compares the isotherms obtained for the adsorption of H_2 on K-ZnO (ref. 8) and on C-ZnO. The number of sites is much higher on K-ZnO than on C-ZnO: on K-ZnO the heat of interaction varies with coverage from 60 to 14 kJ mol^{-1} whereas on C-ZnO is 35 kJ mol^{-1} in the whole range examined. Comparing volumetric data on C-ZnO with those for the type I on K-ZnO (ref. 8) we found the same ratio 1:2.5 found for CO adsorption. Moreover, the heat value of 35 kJ mol^{-1} is very close to the one characteristic of type I, 37 kJ mol^{-1} (ref. 8).

These data indicate that: i) type II H_2 adsorption is negligible on C-ZnO; ii) the number of type I sites, related to the extention of polar faces, is larger on K-ZnO than on C-ZnO. C-ZnO monocrystals should thus be more elongated along the c-axis, K-ZnO more in the shape of platelets.

Carbon monoxide on Cu/ZnO

Copper and zinc oxide are the active components of the catalysts for methanol synthesis. The role of Cu is not yet fully understood, and in particular it

is still under debate whether Cu(0) or Cu(I) is involved in the active sites (ref. 5). CO interacts with ZnO and with Cu in both oxidation states. The heat of interaction, however, is very different from case to case so that we propose the adsorption heat as a probe for the detection of different adsorption sites. Coordination of CO on pure ZnO is so weak (ref. 6) that its contribution to the overall adsorption is almost negligible when some Cu is present. Fig. 3
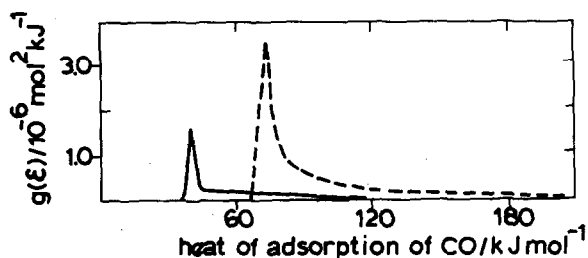

Fig. 3. Site energy distribution for the adsorption of CO on a Cu/ZnO catalyst (full line) and on Cu_2O/ZnO (dashed line).

compares the site energy distributions observed on a reduced Cu/ZnO (3% Cu) sample with that obtained on the same sample after conversion of surface layers into Cu_2O (ref. 9). A substantial fraction of the adsorption sites have energies of 40 kcal mol^{-1}, a value expected for adsorption of CO on Cu(0) (ref. 10); nevertheless some sites do exhibit a higher interaction heat, characteristic of the coordination of CO onto Cu(I). Most probably, these sites consist in incompletely reduced Cu(I) ions dispersed in the ZnO matrix, which some authors consider to be the active centers for the catalytic reaction (ref. 5).

REFERENCES
1. P.C. Gravelle, Catal. Rev. Sci. Eng., 16(1) (1977) 37.
2. B. Fubini, Rev. Gen.Therm., 18 (1979) 297.
3. H. Knözinger, in P. Schuster, G. Zundel and C. Sanderfy (Eds.), The Hydrogen Bond, North-Holland Publ. Co., Amsterdam, 1976, vol. 3, p. 1263.
4. K. Klier, J.H. Shen and A.C. Zettlemoyer, J. Phys. Chem., 77 (1973) 1458.
5. K. Klier, Adv. Catalysis, 31 (1982) 243.
6. E. Giamello and B. Fubini, J. Chem. Soc. Faraday Trans. I, 79 (1983) 1995.
7. A.L. Dent and R.J. Kokes, J. Phys. Chem., 73 (1969) 3781.
8. B. Fubini, E. Giamello, G. Della Gatta and G. Venturello, J. Chem. Soc. Faraday Trans. I, 78 (1982) 153.
9. E. Giamello, B. Fubini, P. Lauro, A. Bossi, J. Catalysis, 87 (1984) 443.
10. R.W. Joyner and M.W. Roberts, Chem. Phys. Letters, 29 (1974) 447.