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Surface Nonuniformity Effects on Metal Oxides in Going From Proton Adsorption Equilibria to
the Kinetics of Acid Catalyzed Reactions

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by

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Proton transfer processes at the solid oxide / aqueous interface are controlled primarily by the structure and composition of the solid surface; these processes can be accessed from potentiometric titration data. A research effort was proposed which sought to exploit this simple "ready-to-use" technique for catalyst characterization in terms of proton affinity spectra.

Case studies demonstrate that in the case of mixed oxides, and provided their extent of dehydration is not too severe, the number and strength of Bronsted acid sites that participate in the linear isomerization of 1-butene can be obtained from the proton affinity spectrum of the oxide. On the other hand, equilibria of hydrolytic polycondensation within surface oxide overlayers (e.g. WO_3 , MoO_3) deposited on alumina are pH dependent and thus are revealed in their affinity spectra as a signature of surface structures. Case studies demonstrate that these signatures, obtained from materials in their oxide state, can be correlated with the catalytic activity for HDS of the same materials in their sulfided state. Despite the seemingly disparate conditions of these catalytic reactions, the common element of the research was the "yardstick" which can access the relevant catalytic properties and whose results can be correlated to the reaction performance of the materials studied.

Oxide surfaces are composed of non-equivalent oxygen groups that differ in their coordinative configuration and thus in proton binding properties. This results, even for mono-component oxides with well defined chemical and phase composition, in a heterogeneous distribution of sites able to bind or release protons at the interface between a solid oxide and the surrounding medium. In some instances, the heterogeneity of proton binding sites on real oxide surfaces is so complex that a continuous description, rather than a discrete one, is appropriate.

The property of a non-uniform surface to bind or to release protons at specific values of H^+ concentration in the surrounding environment can be quantified. Proton affinity at the oxide/water interface is dependent on the structure and composition of the oxide. Either property may give rise to actual proton dissociation steps or they may involve complex hydrolysis equilibria.

In general terms, a distribution function of proton lability for a non-uniform oxide surface, $f(pK)$, can be defined as the mole fraction of surface sites with acidity constants in the interval $(pK, pK+d pK)$. For a system composed of several groups of proton bindings sites, the total concentration of deprotonated sites is given by

$$\Theta = \int_{pK_1}^{pK_2} [\theta ([H], pK)] f(pK) d pK \quad (1)$$

where the bracketed term in the integral takes the form of a Langmuir local isotherm with the corresponding proton binding constant, K^{-1} . It corresponds to proton transfer processes between amphoteric surface hydroxyls and the aqueous electrolyte solution, usually described by simple local equilibria which are structurally dependent:

When complex protolytic equilibria are involved, such as

which for $M = W$ or Mo depicts the octahedral-to-tetrahedral transformation of aggregates generated by these network forming oxides, an apparent hydrolytic equilibrium constant can still be defined in terms of the hydrolysis quotient, Q_β , as $K_{hydr} = (Q_\beta)^{1/\beta}$.

All proton-transfer processes described above are pH dependent. In accordance with the above description, it appears that there is a simple and versatile experimental method which is well suited for evaluation of surface structures on solid samples which undergo proton transfer to- or from- the aqueous environment: potentiometric titration.

In 1993 we were successful in deconvoluting potentiometric titration data and characterizing the heterogeneity of proton binding sites on alumina (1). Although the picture of a heterogeneous distribution of proton binding sites at the oxide/water interface pre-existed in the literature (2) and methods for an a priori prediction of the point of zero charge (3) and proton binding constants (4) have been previously proposed, this was the first time, to our knowledge, that the pK spectrum of an oxide surface was measured and the result confirmed and complemented earlier theoretical predictions. Since then, we continued to explore proton transfer at the surface of various solid samples, including catalyst supports (5, 6), doped supports (7), supported oxides (8), mixed oxide xerogels (9) and aerogels (10).

Two levels of analysis have been applied. The first deals with those systems in which the kernel of the integral equation, i.e. the overall proton isotherm in eq. (1), is described by a Langmuir isotherm. This is the case of oxide surfaces, where the proton binding equilibria can be ascribed to protonation of amphoteric surface hydroxyls at the oxide/electrolyte interface, as depicted by scheme (I) above. In the second case, the proton binding/release is due to hydrolysis of surface compounds on the oxide support and may be accompanied by polycondensation equilibria, as shown by general equilibria (II) above. The latter case applies to supported transition metal oxides such as MoO_3 and WO_3 (network former oxides), on traditional catalyst supports (network modifiers or intermediate type oxides).

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