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THE RELATIONSHIP BETWEEN HYDROXYL GROUPS ON OXIDE SURFACES AND THE PROPERTIES OF SUPPORTED METALS

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RESEARCH SCOPE AND OBJECTIVES

Supported metal catalysts are commonly prepared by depositing catalytic precursors from aqueous solutions of electrolytes onto high surface area oxides. A general conclusion of our previous studies was that the performance of the finished catalyst depends on the characteristic properties of the hydroxyl inventory on the surface of the oxide support, both in wet and in (pseudo)-dry conditions. Hydroxyl groups serve as adsorption or exchange sites during catalyst preparation. On the other hand, the configuration of hydroxyl groups still remaining on oxides after dehydration determines the acid-base characteristics of the catalyst, which is an important catalytic property.

The purpose of the investigation is to characterize the relationship between the complex inventory of hydroxyl groups at oxide surfaces, the acid-base properties of oxides (both in aqueous solution and in the pseudo-dry state) and the resultant effects on the properties of catalytic materials formed by adsorption/impregnation onto these hydroxylated supports during catalyst preparation. We use a common crystallographic model to describe the local configuration of hydroxyl groups on both the pseudo-dry oxide surface and the oxide/aqueous solution interface. This allows us to extend the concept of structurally determined intrinsic heterogeneity of pseudo-dry surfaces (as already known from the IR spectra of isolated surface hydroxyls) to the oxide/solution interface. We examine the consequences of that heterogeneity upon the impregnation step during catalyst preparation.

DESCRIPTION OF RESEARCH EFFORT

The Model

The surface heterogeneity of oxides results from differences in coordination of oxygen atoms; they differ from each other by the number and type of surrounding metal cations. These differences determine the occurrence of various types of hydroxyls on partially dehydrated surfaces, as identified in IR spectra and characterized by their acid/base properties. Assuming that rehydration does not perturb the atomic order on oxide surfaces, the same categories of surface hydroxyls exist at the oxide/solution

interface. They associate or dissociate protons according to their own proton affinity, which is structurally dependent.

Method

We assume that the heterogeneity of acid/base properties at the oxide/aqueous solution interface can be accurately accessed from proton adsorption isotherms. To this end we use the method of potentiometric titration and collect a large number of data points over as broad a pH interval as allowed by the oxide sample being titrated. Although this experimental method was used for a long time to study the charging behavior of oxides in electrolyte solutions, now it is for the first time combined with a powerful computational method that allows for the deconvolution of experimental isotherms.

The 1-pK/multisites model - employed by us for the first time for the oxide/solution interface - pictures the surface as consisting of nonequivalent oxygen groups which are characterized by a continuous distribution of proton affinities. A smoothing spline procedure was used and a criterion for optimal smoothing was proposed and tested.

Results

As a first approximation, we neglect the electrostatic effects in the calculation of proton affinity constants. The distributions obtained in this way (so-called apparent distributions), though not exactly related to intrinsic properties, reflect the conditions under which the interface was studied and are free from the ambiguity of any particular electrostatic model. Using this simple approach, we were able to extract meaningful information about the acid-base properties of oxides studied. The proton affinity distributions were successfully correlated with the available structural models.

The apparent distribution spectra for oxides, with electrostatic effects neglected, showed well-defined peaks that were assigned to protonation/deprotonation processes of distinct -O(H) and -OH(H) groups in various surface configurations. A correlation was obtained between the evaluated $\log K$ values for proton association equilibria and values predicted by structural models. These results confirm that proton adsorption isotherms are sensitive to the heterogeneity existing at oxide surfaces. We found that ionic strength effects on apparent distributions were minor when compared with effects of surface structure and chemical composition.

Because of its importance either as a support for commercial catalysts or as an adsorbent in purification of waste water, the proton binding properties of surface hydroxyls at the alumina/solution interface were comprehensively characterized. Figure 1 shows an experimental proton adsorption isotherm together with the calculated proton affinity distribution. Three well-defined peaks are apparent in the $f(\log K)$ distribution and were assigned to different types of surface hydroxyls which were identified in the IR spectrum of the same sample after dehydration at 875 K (Figure 2). The positions of the peaks were relatively invariant with respect to variations in ionic strength but showed a characteristic dependence on temperature. This observation was used to determine, separately, the thermodynamic functions (enthalpy and entropy) for proton adsorption on distinct surface sites. The results showed that adsorption of protons on structurally different sites at the alumina/water interface is both enthalpically and entropically driven.

Doping alumina with either electronegative (F^-) or electropositive (Na^+) ions is used for fine tuning of its surface properties as a catalyst support. We studied the effect of both dopants on the proton affinity distribution (PAD) of surface hydroxyls for a series of variously doped aluminas. The changes observed in PAD were compared with the changes recorded in the hydroxyl region of infrared spectra collected after dehydration of the same samples. The comparison between the two is based on the assumption that the local configuration of OH groups at the oxide/solution interface is similar to that of hydroxyls on partially dehydrated surfaces, as used for the assignment of IR bands of isolated surface hydroxyls. A common structural model was then used to correlate the changes observed in proton affinity distributions with those recorded in IR spectra after doping alumina with either F or Na.

The Pd(II)-tetraamine ion is a precursor commonly used in preparation of Pd/alumina catalysts. We used the 1-pK multisite model for the description of charge development at the aqueous alumina interface and for analysis of equilibrium adsorption of $Pd(NH_3)_4^{2+}$ ions on alumina. According to the assumptions of the 1-pK model for the oxide surface, the proton adsorption isotherm represents a sum of local proton binding isotherms for various types of surface sites. The total isotherm could be recomposed with the calculated parameters for local isotherms. We found that the models that picture the dry alumina surface consisting of low index planes may also be used for the aqueous surface. The development of surface charge as a function of pH has completely different characteristics on different surface planes.

We developed a model which combined the charging mechanism of the surface with adsorption results for Pd(II)-amine complexes measured at fixed ionic strength

and varying pH and initial concentration. Although the pH dependence of adsorbed amounts could be predicted on this basis, the effects of concentration could not be described exactly. In conjunction with results from temperature-programmed reduction and UV-VIS spectroscopy we propose the concept of geometrical constraints during adsorption-impregnation of precursor ions on the manifold of charged sites revealed by proton-transfer reactions.

Oxide monolayers supported on oxide supports form a general class of catalysts that have recently attracted the interest of both experimental and theoretical characterizations. Alumina-supported tungsten oxide is a typical example in this class. We used the same method to characterize the proton binding processes at the oxide/solution interface for alumina, tungsten oxide and a series of alumina-supported tungsten oxides.

A comparison with reference compounds showed that the reactivity towards protons of composite oxides with low loading of tungsten oxide is close to that of the alumina support, while for highly loaded samples the surface chemistry is better described by the aqueous chemistry of tungstate/isopolytungstate solutions rather than of crystalline tungsten oxide. At surface densities close or above monolayer, supported tungsten species show a definite tendency to form polymeric surface aggregates in solutions with $\text{pH} < 6$, and more extensively below $\text{pH} 4$. We found that this behavior has important consequences on the equilibrium adsorption of cationic activators (Co, Ni) introduced in a second step on preformed tungsten oxide/alumina composites during preparation of complex ternary catalysts.

Implications and future studies

The above examples prove the existence of particular proton binding sites on the hydroxylated surface of commonly used supports; they act specifically in adsorption of catalyst precursors during the wet impregnation step. The results also show that the above sites are related to the intrinsic hydroxyl inventory of the surface.

These findings have very important implications related to supporting metals or oxides on catalyst supports for catalyst preparation. A comprehensive description of the intimate mechanism leading to the binding of catalytic precursors or additives on the surface of supports is still needed and recent literature continues to focus on this subject. Our results show that adsorption of anions (F^- , Cl^-) and cations ($\text{Pd}(\text{NH}_3)_4^{2+}$) from acidic and basic solutions, respectively, occurs on different types of surface sites, i.e. basic sites for anions and acidic sites for cations.

In future studies the effect of various additives on the proton affinity distributions of selected supports will be systematically studied. In this manner we will observe the inventory of hydroxyl groups on the surface which did not react with the adsorbed components. We plan to extend the systems investigated by including systems where the catalyst support is either co- or sequentially impregnated with the catalyst precursors both in anionic and cationic forms, e.g. MoO_4^{2-} and Co^{2+} . A direct confirmation of the location of adsorbed species on oxide surface will come in future studies from comparison of the infrared spectra of the stretching modes of surface hydroxyls of the original and modified supports.

PUBLICATIONS AND MANUSCRIPTS IN PREPARATION/IN PRINT

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6. J. A. Schwarz, Cr. Contescu, J. Jagiello
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7. J. A. Schwarz, Cr. Contescu
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MEETING PRESENTATIONS

Cr. Contescu, J. Jagiello, J.A. Schwarz
 "PROTON BINDING DISTRIBUTIONS: A METHOD OF STUDYING THE
 HETEROGENEITY OF OXIDE SURFACES"
 Gordon Research Conferences, Catalysis, New London, June 27 - July 2, 1993.

J.A. Schwarz
 "THERMODYNAMIC PROPERTIES OF HYDROXYL GROUPS ON OXIDE
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 RELATIONSHIP TO CATALYST PREPARATION"
 13-th North American Meeting of the Catalysis Society, Pittsburgh, PA, May
 2-6, 1993.

Figure 1: Experimental proton binding isotherm for a reference alumina support, $Q(\text{pH})$, and the corresponding proton affinity distribution, $f(\log K)$, calculated in the RJ approximation.

Figure 2: A typical IR spectrum of hydroxyl stretching vibrations on the reference alumina support.

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