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A Study of the Acidic Properties of Pure and Composite Oxides by Inverse Gas Chromatography at Infinite Dilution

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A family of *n*-alkanes and alkenes has been used in conjunction with the technique of inverse gas chromatography (IGC) to study the acidic properties of pure and composite oxides. Commercial and laboratory-prepared silica and alumina and alumina on silica composites derived from them were subjected to a modified Benesi titration scheme, and the results are compared to those obtained from IGC. We find that changes in acidity due to changes in composition of the samples can be determined from IGC data and the results are consistent with those obtained from the more conventional colorimetric titration. On the other hand, acidity changes due to dehydroxylation of the oxides can be easily monitored using IGC while the results from the modified Benesi titration are not sensitive enough to disclose any acidity changes. To our knowledge, this is the first application of IGC to study the surface acidity properties of composite oxides. The simplicity, sensitivity, and flexibility of IGC for study of catalysts and catalyst supports point toward its potential to add to the arsenal of techniques that characterize both commercial and laboratory prepared materials.

INTRODUCTION

Understanding the adsorptive properties of metal oxides is important in order to provide effective utilization of these materials in catalytic processes. Regardless of the nature of the interaction to be studied, the number, type, and strength of adsorption centers are the parameters that are sought from suitable experimental studies. Traditionally, when specific probes are used as the adsorbate, the type of adsorptive center is considered to be determined. The number and strength of these sites can, in principle, be ascertained from the adsorption isotherm.

When only physical interactions occur, the study of adsorption phenomena allows a quantitative description of the energetic properties of the solid surface. The relationship between the so-called adsorption energy distribution function, χ, and the experimentally measured quantity is expressed as

$$V(p,T) = \int_{\varepsilon_l}^{\varepsilon_m} \theta(\varepsilon,p,T)\chi(\varepsilon)d\varepsilon,$$

where V is the measured adsorption isotherm; $\theta(\varepsilon,p,T)$ is the local isotherm of adsorption on sites with adsorption energy ε; p and T are pressure and temperature; ε_l and ε_m are the minimum and maximum values of the adsorption energy of the adsorbate/solid system.

The acidic properties of metal oxides are generally thought to play an important role in determining the adsorptive and catalytic properties of these materials. Numerous experimental methods to determine the surface acidity of catalysts have been described. The differential titration of acid sites with *n*-butylamine in nonaqueous solutions became a standard method for de-

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termining the distribution of acid sites against Hammet and arylmethanol color indicators (*1–5*). Some methods have been proposed for selective determination of Lewis sites, based on adsorption of typical Lewis bases (*6, 7*) or on displacement of sterically hindered bases by *n*-butylamine (*8, 9*). Potentiometric (*10*) or calorimetric (*11, 12*) variants of *n*-butylamine titration have been reported. Various spectroscopic methods are available (*13–21*) that use IR, UV, or part of the visible spectrum either of adsorbed molecules (ammonia, pyridine) or of surface hydroxyl groups and that allow for a differentiation between Lewis and Brønsted sites. The methods based on adsorption from the gaseous phase, both under static or dynamic conditions, are of significance when the surface acidity of catalysts under conditions close to those of catalytic reactions is desired (*22*). The strength of the acid sites is generally characterized in these methods by the heat of adsorption, desorption temperature, or activation energy of desorption. The most commonly used adsorbate is ammonia, but pyridine, quinoline, carbon dioxide, alkenes, and hydrogen sulphide have also been used in various chromatographic methods to determine surface acidity.

A basic inconvenience of the above adsorption methods is the use of fairly strong bases that can adsorb also on weak acidic sites that may not participate in catalytic processes. In the general concept of acids and bases, protons (Brønsted sites) are hard acids, while transition metal ions (Lewis sites) are soft acids. The mechanism of adsorbate–adsorbent interactions in the former case is a charge transfer mechanism, with the latter implying an orbital controlled process (*23*). While the strength of Brønsted sites is conventionally measured, for example, in the scale of the Hammet function, no unique scale for Lewis acids is possible, since their activity depends strongly on the reaction considered. Moreover, the main difficulty in correlating the reaction rates in heterogeneous catalysis to acid strength of catalyst surfaces comes from the indirect evaluation of p*K* from *n*-butylamine titration and from the conventional meaning of this evaluation; only domains of acid strength are defined.

From the above, it is evident that in the field of heterogeneous catalysis there is a need for continuous improvement and development of experimental methods for characterization of reactant interactions on the surface of catalyst supports. The use of different adsorbates capable of probing a subtle scale of specific interactions with a given catalyst seems to be a better proposal than looking for one or several universal adsorbates. The correct choice of a probe molecule to be used as an adsorbate should take into account the need for a more comprehensive characterization of interactions between the strongest reactive sites of the catalyst surface and the reactant molecules. The use of polarizable molecules, like alkenes or aromatic hydrocarbons, or of polar molecules as adsorbates allows, in principle, for screening of a larger spectrum of specific interactions. The use of probing molecules with a weak basic (or electron donor) character allows for characterization of acceptor properties of the most reactive surface sites, presumably those that participate in catalytic reactions. A description of surface properties of catalysts in terms of acceptor/donor properties (*24*) in relation with a given class of adsorbates (homologous series of reactants) could be more useful than the usual approach to acid/base properties. It would also be desirable that the surface properties revealed by using different probe molecules could be quantified in terms of standard thermodynamic properties.

Chromatography is a fast, analytical method which is based on exchange between a stationary phase (solid or liquid) and a gaseous mobile phase and allows for the separation and identification of solutes. A variant of this technique is inverse gas chromatography (IGC), which allows for a detailed study of the stationary phase. In this method, gaseous or liquid probes are injected into a carrier gas in order to study the surface properties of the stationary phase. These experiments can be carried out under two extreme conditions: finite concentration and infinite dilution. In the former case, IGC at finite concentration has been developed to readily obtain adsorption isotherms. From these data, Jagiello *et al.* (*25*) have shown that the adsorption energy distribution function (Eq. (1)) can be determined for oxide surfaces (*26*). The use of IGC at infinite dilution allows for the determination of both the dispersive and specific components of the interaction between probe molecules and the stationary phase. When a suitable set of probes are selected to assess the acid/base properties of oxide surfaces, IGC provides an experimental vehicle whereby oxide surfaces can be studied with regard to their adsorption energy heterogeneity as well as their donor/acceptor adsorptive properties. These experiments have the advantage that they can be conducted rapidly, and the samples may be conditioned and treated *in situ*.

The objective of this study is to test the hypothesis that IGC at infinite dilution can be used to assess the acidic properties of a series of model oxide surfaces. To accomplish this objective, we compare the results from IGC at infinite dilution with those from a more conventional method of determining solid acidity, namely a variation of the Benesi colorimetric titration method. We find that the results from the IGC experiments are consistent with those of the more conventional method *and* the IGC technique is extremely sensitive, such that effects not detectable by the colorimetric method can be readily "seen" using IGC.

INVERSE GAS CHROMATOGRAPHY AT INFINITE DILUTION

This method is based on the study of interactions of gas molecules of known properties with solid surfaces. Small amounts of molecular probes are injected into the stream of the carrier gas flowing through the chromatographic column filled with the solid to be investigated. The net retention time, t_N, is measured as a difference between retention times of a given probe and a nonadsorbing gas used as a reference. The net retention volume, V_N, which is the fundamental quantity utilized in this method, is then calculated from the formula

$$V_N = jFt_N, \tag{1}$$

where j is the so-called James–Martin factor, and F is the flow rate of the carrier gas.

It is assumed, in the case of infinite dilution chromatography, that the adsorption is described by Henry's law, and hence we can write

$$V_N = mKS, \tag{2}$$

where m and S are mass and specific surface of adsorbent and K is Henry's constant. Since the surface of a catalyst is usually energetically heterogeneous, this constant is considered as a mean value of K° constants related to the different adsorption sites; this yields

$$K = \int_{\varepsilon_1}^{\varepsilon_m} K^\circ(\varepsilon)\chi(\varepsilon)d\varepsilon, \tag{3}$$

where χ is the distribution of adsorption energy ε in the domain (ε_1, ε_m) and K° is Henry's constant for adsorption sites having energy ε.

The standard free energy of adsorption at infinite dilution is directly related to the net retention volume

$$\Delta G^\circ = -RT\ln\frac{BV_N}{S_m}, \tag{4}$$

where R and T are the gas constant and temperature, B, is a constant related to the standard states of gas and adsorbed phases. ΔG° obtained under the conditions of infinite dilution is dependent on the interaction of probe molecules with the surface only; interaction beween adsorbed molecules is neglected.

Analysis of ΔG° values obtained for appropriate molecular probes can provide information about certain surface properties. In general, it can be assumed that adsorbate-absorbent interactions can be classified as dispersive (nonspecific) or polar (specific). Among probes that can undergo only dispersive interactions, *n*-alkanes are of great practical importance. It is well known that ΔG° for *n*-alkanes varies linearly with their number of carbon atoms, *n*. This behavior was adopted by Dorris and Gray (*27*) to calculate the dispersive component of the surface energy, γ_s, using

$$\gamma_S^D = \frac{1}{\gamma_{CH_2}}\left[\frac{\Delta G_{CH_2}}{4Na_{CH_2}}\right]^2, \qquad (5)$$

where ΔG_{CH_2} is the difference in the ΔG° of two subsequent *n*-alkanes, N is Avogadro's number, a_{CH_2} is the surface area of a CH_2 group, and γ_{CH_2} is the surface energy of a hypothetical surface made of CH_2 groups only (e.g., polyethylene). Despite some theoretical shortcomings, this method has the advantage of simple relationship with the well-established measured quantity, ΔG_{CH_2}. This quantity has simple physical meaning and is not affected by surface area of adsorbent or by its porosity. When chromatographic measurements are performed at several temperatures, the enthalpy of adsorption at infinite dilution, ΔH°, can be easily calculated. In the particular case of a homologous series of alkanes it is possible to describe the dependence of

$$\Delta H^\circ = R\frac{\partial \ln(V_N)}{\partial(1/T)} \qquad (6)$$

of $\ln(V_N)$ as a function of the number of carbon atoms and temperature using one simple equation

$$\ln(V_N) = -\frac{n\Delta H_{CH_2}}{RT} + na + \frac{b}{T} + c, \quad (7)$$

where n is the number of carbon atoms, and a, b, and c are empirical constants. Fitting this equation to the experimental data has the advantage of using more data points than in applying Eq. (6) to each hydrocarbon separately. Thus, the values of calculated enthalpies, with the aid of Eq. (7), should be more reliable.

The generally accepted way of separating dispersive interactions from specific (polar) effects is to compare the chosen probe with *n*-alkane (*28*). Providing both probes are of identical molar surface area, polarizability, and ionization potential, and they are able to exchange with the surface through identical dispersive interactions. The specific component ΔG^{sp} of total free energy, ΔG, can be simply evaluated,

$$\Delta G^{sp} = \Delta G - \Delta G^D, \qquad (8)$$

where ΔG^D is the value of ΔG of the *n*-alkane probe treated as a dispersive interacting reference. Practically, it is not a trivial problem to find a reference probe that fulfills the above given conditions. Instead, several empirical methods were proposed to estimate specific interaction parameters (*29*, *30*). The method proposed by Saint-Flour and Papirer (*29*) is based on the linear variation of the logarithm of the net retention volume V_N against the logarithm of the vapor pressure (P_0) of the *n*-alkane probes. This correlation is observed since alkanes at infinite dilution behave quite ideally. Assuming the additivity of the dispersive and specific component of energy, the alkane line may be taken as the reference line. By definition, the difference of ordinates between the alkane straight line and the point corresponding to the polar probe, having the same P_0 as a real or hypothetical alkane, gives the specific interaction parameter, I_{sp}. A similar method has been proposed by Schultz *et al.* (*30*), plotting $\ln(V_N)$ against $a(g_I)^{1/2}$, where a is the surface area of the probe and g_L its surface energy in the liquid state. In Saint-Flour and Papirer's approach, the proposed polar probes were chlorides, nitriles, ethers, aromatics, etc.

Recently it was proposed (*31*) to apply *n*-alkenes in comparison with *n*-alkanes to study the effects of a double bond placed in the hydrocarbon chain. This double bond (π electrons) interacts in a specific way with the surface, especially with electron acceptor sites, and this makes an additional contribution to the total energy of adsorption of alkenes. The specific interaction parameter, ε_π was defined as

$$\varepsilon_\pi = \Delta G_{\text{alkene}} - \Delta G_{\text{alkane}} \quad (9)$$

Also, other thermodynamic quantities related to the π bond interaction can be defined ($\Delta H_\pi, \Delta S_\pi$). The advantage of this method is that quantities like $\varepsilon_\pi, \Delta H_\pi$ are clearly defined (the definition is based on well-known chemical structure of alkanes and alkenes) and easily measured. These parameters can be taken as a measure of specific interaction capacity of the surface and especially of electron acceptor interactions.

EXPERIMENTAL

Inverse Gas Chromatography at Infinite Dilution

The experiments were performed with an Antek 3000 gas chromatograph (from Antek Instruments Inc.) equipped with a flame ionization detector. The stainless-steel columns (30 cm long, 2.17 mm in diameter) were filled with sample particles with a particle size ranging between 0.2 to 0.4 mm. Helium was used as a carrier gas with flow rate of about 20 cm^3/min. Injector and detector temperatures were set at 475 K, i.e., a temperature above the measuring temperatures. The samples were conditioned at 475 K in the chromatographic column under helium gas flow for 12 h prior to the measurement. The hydrocarbons used in this work were HPLC grade (Aldrich Chemical Co.). Very small volumes of gaseous solutes were injected in order to approach conditions of Henry's region; it was checked that retention times did not depend on amount injected. It was also checked that the areas of the peaks were directly related to the amount injected (this ensures linear chromatographic processes) and that no chemisorption takes place. The solutes were injected using a 50-μl Hamilton syringe. Retention volumes were corrected for the gas compressibility. The precision of the measurements was 0.5%. The temperature was stabilized with accuracy at ±0.1°C.

Modified Benesi Titration for Lewis–Brønsted Site Distributions

A dual-sample technique for titration of Brønsted and Lewis acid sites of solid samples was used in this study. The method, proposed by Murrell and Dispenziere (*9*), combines the dry box technique with the Benesi method (*2, 3*) for titration of acid sites using color adsorption indicators. Murrell improved the method of establishing the titration end points by using small amounts of sample to which the indicator was added. Also, for a better equilibration of adsorbed bases, an ultrasonic treatment of the samples was used.

In the standard procedure adopted, two separate aliquots of samples of the support to be studied were dehydrated at 675 K for 16 h and sealed while still hot (520–570 K) in tightly capped glass bottles. Samples were then transferred into a dry box purged with purified nitrogen and 5 ml of dry benzene was added to each of them. After 30 min of equilibration, one of the samples was titrated with 0.1 *N* solution of *n*-butylamine in dry benzene for a determination of the total number of acid (Brønsted and Lewis) sites. After each addition of titrating *n*-butylamine solution, the samples were subjected to an ultrasonic treatment for 10 min to ensure that equilibrium was reached. To avoid any contact of samples with air, the ultrasonic treatment was done in the same dry box. Then a few drops containing the suspended powder were removed from the sample, and the color reaction with the Hammet indicators was checked. We used indicators for acid strength from ≤ -3.0 to ≤ -8.2, namely dicinamalacetone (pK_a -3.0), benzalacetophenone (pK_a -5.6), and anthraquinone (pK_a -8.2). By repeating the above procedure, the center strength distribution in the above range of H_0 function was obtained using only 1 g of sample.

The other 1-g sample was used for differential titration of Lewis sites only. The method is based on the fact that 2,6-disubstituted pyridine can bond strongly to Brønsted acid centers but are sterically hindered and bond only weakly to Lewis acid centers (*9*). Practically, an excess of 0.1 *N* benzene solution of 2,6-dimethylpyridine was added to the second dehydrated sample and equilibrated during a 10-min ultrasonic treatment. A subsequent titration with *n*-butyl amine gave an accurate estimation of the number of Lewis sites.

It was very important to keep dry all materials such as solvents, indicators, and samples, otherwise, the Lewis acid sites could not be detected because of water adsorption on these sites. In our colorimetric titration experiments, toluene,*n*-butylamine, and lutidine were freshly dried with a 4- to 5-Å molecular sieve. Indicators were dried in a desiccator using molecular sieve. The dry box was kept under a positive pressure of N_2 and maintained dry with activated molecular sieve, which was changed every day.

The accuracy of this titration method was estimated to be ±10 μmol/g. Reproducibility tests on the same sample gave differences lower than 10 μmol/g.

Materials

Two different silicas were used as starting materials. From these, alumina on silica composites were prepared.

Sample D was a Davison 952 grade silica which was used either as received (D) or after calcination at 875 or 1075K (samples D-875 and D-1075). Commercial gels of silica are normally prepared by reacting alkali metal/alkaline earth silicates with sulfuric acid. A low level impurity was expected for these samples because repeated contact with deionized water showed an unusually high value of the pH of the wash water. The manufacturer supplied us with a chemical assay that showed the only impurities to be sulfur, aluminum, sodium, calcium, magnesium concentrations SO_4 −0.005%, Al_2O_3 −0.036%, Na_2O −0.07%, Ca 0–0.17%, and Mg 0–0.05%.

Sample S-875 was a high-purity silica prepared by slowly hydrolyzing a tetraethyl orthosilicate (Aldrich Chemicals)–water–ethylic alcohol emulsion at room temperature. After drying at 385 K for 20 h, the resulting silica gel was calcined at 875 K for 16 h. The resulting silica had a value of 3.7 (determined by mass titration) for the point of zero charge (PZC).

Two sets of composite oxides were prepared from the above silicas, by dry impregnation with aluminum isopropoxide (Aldrich Chemicals) solutions in dried benzene. A dry box flushed with purified nitrogen was used in this step, in order to minimize the exposure of aluminum isopropoxide to moisture in the air before the impregnation of the silicas. The volume of the impregnation solutions was equal to the pore volume of the silicas (1.6 and 0.8 cm^3/g for samples D and S) and the concentration of aluminum isopropoxide was calculated to obtain composite oxides with 1% and 10% Al_2O_3. The impregnated samples were allowed to stand in air at room temperature for 24 h and then were dried at 385 K for 16 h. During this treatment, the organic aluminum compound was subjected to slow hydrolysis and subsequent oxidation. The final calcination of dried samples was done at 875 K for 16 h. The mixed oxides were designated according to their Al_2O_3 content and type of silica support. For example, a sample with 10% alumina supported on Davison silica was called 10A/D.

Sample A-875 was a pure alumina sample prepared for the sake of comparison from aluminum isopropoxide as the raw material. The hydrolysis product of aluminum isopropoxide at 330–350 K is bayerite. This sample was dried at 385 K for 24 h and finally calcined at 875 K for 16 h.

Sample A′ was a commercial alumina. It was included in this study to emphasize the differences in surface properties we find between commercial and laboratory-prepared

TABLE 1

Characterization of Pure and Composite Oxides

Sample	BET surface area m^2/g	Point of zero charge
D	288	—
D-875	280	—
1A/D	269	—
10A/D	240	—
S-875	577	3.80
1A/S	553	4.14
10A/S	541	5.08
A-875	192	8.30
A′	153	8.50

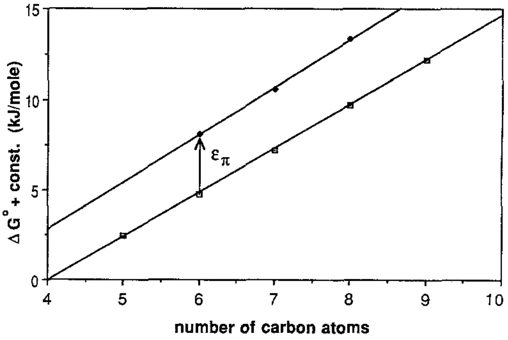

FIG. 1. Variation of $\Delta G°$ of alkanes (□) and alkenes (◆) as a function of number of carbon atoms for Davison silica (sample D) measured at 420 K.

catalyst supports. Details as to its manufacture were not made available to us.

The values of BET surface area of these materials, measured by the nitrogen sorption method using a Quantasorb system, are summarized in Table 1. Also shown are the values of the point of zero charge determined by mass titration. For samples based on the Davison silica, these values are not given because the presence of electropositive impurities in this silica denatured the results of the mass titration method.

RESULTS AND DISCUSSION

The $\Delta G°$ values for the homologous series of *n*-alkanes characterize the dispersive component of the surface energy, while $\Delta G°$ for *n*-alkenes contain the additional contribution of specific interactions of their π electrons with surface sites. A comparison between the $\Delta G°$ values for alkanes and alkenes for sample D is presented as an example in Fig. 1. It is seen that both straight lines are practically parallel. This behavior was observed for all other samples, except for the two composite oxides 1A/D and 10A/D. This effect is shown in Fig. 2 for sample 10A/D and suggests an influence of surface heterogeneity on adsorption on *n*-alkenes with different numbers of C atoms.

To compare the surface properties of the samples studied, we present in Table 2 the values of γ_S^D and ε_π calculated from IGC data at 425 K. We have also calculated the enthalpies of adsorption of alkanes and alkenes using Eq. (6). In Table 2 are the selected values of ΔH(hexane) and ΔH(hexene) and also the difference between them $\Delta(\Delta H)$. These probes could be applied in all cases.

Silica Samples

It is known that, on the surface of amorphous silica, there is a considerable number of OH groups (silanol groups). These silanol groups can bond with strong bases like amines. They also can undergo reversible

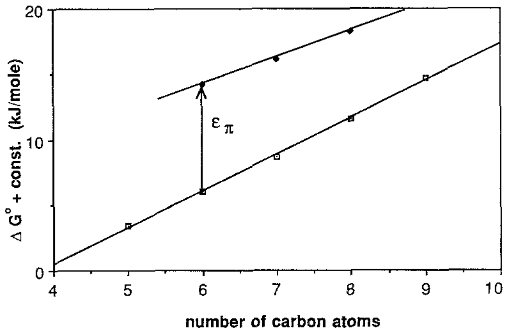

FIG. 2. Variation of $\Delta G°$ of alkanes (□) and alkenes (◆) as a function of number of carbon atoms for alumina–silica composite (sample 10A/D) measured at 420 K.

TABLE 2

Results of IGC at Infinite Dilution

Sample	γ_S^D	ε_π	$\Delta H°$(hexane)	$\Delta H°$(hexene)	$\Delta[\Delta(H)]$
D	41	3.3	44	47	3
D-875	38	2.8	39	42	3
D-1075	31	1.3	36	36	0
1A/D	67	5	44	73	29
10A/D	53	8.2	47	77	30
S-875	87	0.9	51	52	1
1A/S	91	1.0	53	56	3
10A/S	90	1.0	51	53	2
A-875	89	2.0	45	47	2
A′	72	3.7	39	57	18

physical interactions with polar and polarizable molecules having a much weaker electron donor character, like nonsaturated and aromatic hydrocarbons. Thus, a silica surface is considered a very weak acid according to its catalytic properties. However, it has been recognized as an electron acceptor that is related to the presence of surface silanol groups (*25*).

The electron acceptor properties of silica surfaces decrease with an increase in the calcination temperature because during this process silanol groups transform to siloxane groups. The dehydration process takes place in the temperature range from 775 to 1170 K, and the process is essentially irreversible. A fully hydroxylated surface of silica contains 4–5 SiOH/nm^2 after drying at 325 K (*32*). This figure decreases to 1.5 SiOH/nm^2 for a surface dehydrated at 875 K and to approximately 0.8 SiOH/nm^2 when the dehydration temperature is raised to 1075 K.

Data shown in the first three rows of Table 2 illustrate the sensitivity of the IGC method to quantify the changes in the energetic parameters for both nonspecific interactions (for alkanes) and specific interactions (for alkenes) induced by the thermal treatment of silicas. A continuous decrease of γ_S^D and of ΔH(hexane) with the temperature of the thermal treatment reflects the decrease of nonspecific (dispersive) interactions of probe molecules with the silica surface. There also is a decrease of ε_π and ΔH(hexene), which shows the decrease of the capacity for specific interactions with π electrons of alkenes with silanol surface sites. The thermodynamic quantity, which is related to the specific contribution of π electron interactions, $\Delta(\Delta H)$, becomes zero for sample D-1075. This demonstrates that this sample is almost completely dehydroxylated. We see that by using gas chromatography we can monitor the dehydroxylation processes due to the temperature treatment. The variation of electron acceptor properties accompanying this process is, however, too small to be seen by using the Benesi titration method as no changes in acidity were detected by this method (cf., Table 3).

Recently, Connell and Dumesic (*33*) proposed the existence of a type of "anionic Brønsted" acidity that was suggested to be generated by highly electronegative impurity atoms. The pure silica sample, S-875, has surface properties different than those found for D-1075, namely higher γ_S^D and lower ε_π. We relate this to the different preparation methods and especially to the difference in impurity content. For samples of the D series we propose that impurities such as aluminum, sulfur, alkali metals, or alkaline earth independently affect dispersive and specific interactions. The presence of electropositive elements increases the

TABLE 3

Lewis–Brønsted Sites Distribution

Sample	Total number of Lewis and Brønsted sites (μmole/g)			Number of Lewis sites (μmole/g)
	$H_0 < -3$	$H_0 < -5.6$	$H_0 < -8.2$	
D	10	—	—	—
D-875	10	—	—	—
1A/D	70 ± 5	30 ± 5	—	10
10A/D	180 ± 10	100 ± 10	20 ± 5	40 ± 5
S-875	10	—	—	—
1A/S	10	—	—	—
10A/S	10	—	—	—
A-875	180 ± 10	—	—	90 ± 10
A′	279 ± 10	239 ± 10	209 ± 10	140 ± 10

specific interaction with probes containing π electrons, as would be expected. The aluminum and sulfur generate a type of Brønsted acidity that results in a lowering of the electron density of an OH bond due to inductive effects, thus effectively reducing the number and strength of interaction centers. Again, we note that these subtle nuances are not detectable by the more conventional Benesi-type measurement as no changes in acidity are apparent.

Alumina Samples

A different picture emerges by comparing the IGC data for alumina samples. After dehydration at 875 K, the surface of alumina has different types of isolated hydroxyl groups (*34*), that behave like Brønsted acids of different strength, and an increased number of coordinatively unsaturated Al ions that behave like Lewis acids. For the laboratory-prepared alumina sample studied here, the measurement of surface acidity by the modified Benesi method indicates a total of 180 μmol/g of acid sites, half of which (90 μmol/g) represent Lewis sites. The acid strength of Brønsted sites (90 μmol/g) is, however, lower than H_0 -3.0.

IGC data show that the parameter for specific interactions ranges from 2 to 3.7 for the aluminas, the higher value being found for the commercial sample. Also, $\Delta(\Delta H)$ confirms the same trend of specific interactions. The nonspecific interactions of alkanes is stronger with both aluminas than with silicas.

Composite Oxides

The composite oxides represent a new class of materials with special surface properties. They are usually prepared by mounting a low concentration of a hydrolyzable precursor of a second oxidic phase over the surface of a primary oxidic carrier. After a suitable fixing procedure (hydrolysis and calcination) the composite material has a well-dispersed second phase supported on the main carrier oxide. However, mutual interactions between the oxidic components will determine the degree of dispersion of the second phase, which, in turn, will likely depend on the preparation method. Of special importance is the reactivity of surface groups on the carrier oxide and the chemical intermediates developed during the impregnation and fixing steps. The acidic properties of the resulting composite oxides are greatly influenced by these factors. This is revealed by comparing the IGC data for alumina on silica composites prepared from D-875 and S-875 silica samples.

Data from Table 2 show a dramatic increase in both specific and nonspecific interactions on the surface of composite oxides based on Davison silica. Nonspecific interactions of alkanes, measured by γ_S^D and ΔH(hexane), are higher compared to the Davison silica. The increase of nonspecific interactions for these composites is explained by addition of alumina, which possesses sites of nonspecific interaction higher than that of silica.

A striking observation is the very large increase in specific interaction [measured by ε_π and ΔH(hexene)] with the increase of alumina content of the samples. The specific contribution of π electrons to the adsorption enthalpy, $\Delta(\Delta H)$, is 10 times larger on these composites than on the original silica. For the same samples, the results from the modified Benesi titration (Table 3) show an increase in both Brønsted and Lewis acidity as compared with the unmodified Davison silica. The number of Lewis sites, even though lower than that of pure alumina, increased with Al_2O_3 content in the composites, and strong Brønsted sites were formed on 1A/D and 10A/D samples, which do not exist on pure alumina.

The alumina on silica composites over the pure silica (samples 1A/S and 10A/S) show weak acidic properties, an unexpected result that is not fully understood. Previous work from our laboratory has shown that when a second phase oxide is dispersed on a primary phase, the PZCs of the composites formed lie between the values of the end members (*35*). This has been found here, also (Table 1). However, the results from the modified Benesi titration and those from IGC data show that both composites have properties that are very similar to those of the pure silica support.

Two factors must be considered in our analysis of these findings. First, the presence of dispersed alumina on silica should give rise to changes in acidity of the pure silica, assuming a pure acidity concept. Close examination of the results presented in Table 2 shows that both nonspecific and specific interaction parameters (γ_S^D and ε_π) increase with the addition of the second phase. Also, the thermodynamic properties show an increase. While the changes are small for 1A/S and 10A/S, but very large for 1A/D and 10A/D, they are consistent with probe molecules interacting with a dilute concentration of alumina moieties dispersed over an underlying silica surface. Recall that the objective of this study is to compare the results from IGC with those from conventional study of solid acidity. The modified Benesi titration data in Table 3 clearly indicate that they are not always sensitive to subtle changes in the surface properties of the composite oxides.

The second factor to be considered is related to the structural generation of acid sites due to the dispersion of the second phase. According to Connell and Dumesic (*33*), the introduction of Lewis and Brønsted acidity to silica by the fixing of a second oxide phase such as alumina is due to

> Lewis acidity: the presence of coordinatively unsaturated Al^{3+} cations
>
> Brønsted acidity: tetrahedral Al^{3+} cation substitution into the silica matrix at the surface, to produce a lattice proton bonded to the surface by ionic forces.

Assuming these assertions are correct, the composites formed by nonaqueous impregnation of aluminum isopropoxide onto the pure silica do not form these preferred geometries, while such configurations are produced by the Davison silica, which contains impurities. The nature of the processes, which result in the preferred geometries to induce Lewis and Brønsted acidity onto Connell and Dumesic's and our Davison silica during the fixing procedure, but not onto our pure silica, is not understood in detail. There are, however, significant differences in the preparation of these samples.

Connell and Dumesic prepared their composites using an inorganic precursor, $Al(NO_3)_3$, aqueous procedure, and a silica (Cabosil) which is likely to be as "pure" as that prepared by us. During aqueous impregnation, surface silanol groups are deprotonated and aluminum cations will exchange with these to give rise to –Si–O–Al– structures. The strongest Brønsted sites found on their samples were assigned to OH groups in bridge position between Al and Si atoms, namely –Si–OH–Al– (*33*).

Using nonaqueous techniques but with a silica sample having a part of its silanol groups exchanged with strongly electropositive elements, e.g. with sodium, similar structures may result by reaction of the aluminum isopropoxide precursor:

$$\text{–Si–O}^-\text{Na}^+ + \text{Al(OC}_3\text{H}_7)_3 \rightleftharpoons \text{–Si–O–Al(OC}_3\text{H}_7)_2 + \text{C}_3\text{H}_7\text{O}^-\text{Na}^+$$

After hydrolysis and calcination, the composite oxide formed will have a well-dispersed second phase with –Si–OH–Al– structures.

On the other hand, in nonaqueous conditions but in the absence of electropositive impurities, a similar reaction on the surface of our pure silica, namely

$$\text{–Si–OH} + \text{Al(OC}_3\text{H}_7)_3 \ldots \text{–Si–O–Al(OC}_3\text{H}_7)_2 + \text{C}_3\text{H}_7\text{OH}$$

is much less probable because of the lower degree of ionization of silanol groups. As a result, the 1A/S and 10A/S samples probably consist of small Al_2O_3 clusters in weak interaction with the silica beneath, whereas the 1A/D and 10A/D samples are much closer to a composite surface with Al cations intruded into the silica overlayer. According to the BET surface area of the two silicas, the density of Al cations (if uniformly spread on the surface) would be $4Al^{3+}/nm^2$ and $2Al^{3+}/nm^2$, respectively, for 10A/D and 10A/S samples. The corresponding figure for Connell and Dumesic's composite is $0.14Al^{3+}/nm^2$.

We propose therefore that the differences in the acidity of the composite oxides of this study and those studied by Connell and Dumesic are due to the existence of silicon–oxygen–aluminum linkages, which are necessary for the intrusion of aluminum cations into the silica lattice, which occurs during the fixing and calcination steps. These considerations are "plausibility" arguments that are provided to interpret some of the surface chemical effects that can occur during the preparation of composite oxides. Our central objective, however, has been demonstrated in that we have shown that the IGC technique employing infinite dilution can provide sensitive and accurate data related to the acidic (or electron acceptor) properties of oxides and, as such, offers advantages over more conventional procedures for measuring solid acidity. The use of the IGC technique at finite concentration to extract a quantitative measure of the energetic acidic heterogeneity of these oxides remains an on-going topic of our research.

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