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Infrared Spectroscopic Study of Hydroxyl Group Acid Strength of Silica, Alumina, and Magnesia Mixed Oxides

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The acid strength of the hydroxyl groups of mixed oxides SiO_2/MgO, SiO_2/Al_2O_3, and Al_2O_3/MgO and their pure components was studied by ir spectroscopy. The shift of the hydroxyl bands after adsorption of acetone was taken as a measure of the acid strength. It increased with increasing Sanderson intermediate electronegativity of the oxide. Moreover, only one perturbed hydroxyl band was found to be due to a unique interaction between the hydroxyl groups and the acetone molecule. No relation was found between the appearance of Brønsted acid sites and the magnitude of the hydroxyl band shift.

INTRODUCTION

Catalytic activity is considered to depend strongly upon the acidity of hydroxyl groups (*1*). This is why the acidity of hydroxyl groups has been extensively studied. Titration with amines and indicator adsorption have been used and nowadays spectroscopic methods are increasingly applied. As acid strength is expected to depend upon the strength of the OH bond, ir spectroscopy, as far as it reflects bond strength, should be a powerful means of studying acid strength.

The infrared bands of free hydroxyl groups shift to lower wavenumbers during interaction with donor molecules. As many authors have pointed out, the shift increases with the basic strength of the electron pair donor (EPD) (*2*) and the acid strength of the OH group. The shifts of the hydroxyl bands of different oxides interacting with the same EPD molecule should therefore be an indicator of the acid strength of the hydroxyl groups of these oxides.

This was demonstrated by Hair and Hertl (*3*), who studied the OH groups on silica, magnesia, and silica–alumina. Vinek *et al.* (*4*), relating the product distribution of elimination reactions of alcohols to the O 1s XPS binding energy of the oxides, found the acid–base properties of mixed oxides to be in between those of the components.

In this work, the question is asked whether a similar monotonic variation is observed for the acid strength of hydroxyl groups of mixtures of SiO_2, Al_2O_3, and MgO. Furthermore, we tried to find out whether there is heterogeneity of the acid strength of the hydroxyl groups of these oxides. If so, more than one shift should be observed, indicating hydroxyl bondings of different strength.

EXPERIMENTAL

Adsorbents. The preparation methods used for the mixed oxides were those described by Vinek (*5*). The starting substances for the mixed oxides were SiO_2 (Degussa Aerosil 130), Merck $Mg(NO_3)_2 \cdot 6H_2O$, and Merck $Al(NO_3)_3 \cdot 9\,H_2O$.

MgO was produced by precipitating $Mg(OH)_2$ from a solution of $Mg(NO_3)_2$ with ammonia and converting the hydroxide to MgO at 500°C, and γ-Al_2O_3 was prepared according to MacIver (*6*).

The mixed oxides were obtained by impregnation, after which they were dried and calcined at 500°C for 10 hr. The BET surfaces of the oxides are listed in Ref. (*5*).

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Adsorptive. Acetone from Merck, Darmstadt (Uvasol quality) was dried over 4 Å molecular sieve and used without further purification.

Infrared measurements. The ir cell was constructed according to the description of Knözinger *et al.* (*7*). After the sample was placed in the cell, thermal treatment, adsorption, and recording of the spectra were carried out without removing the sample from the cell.

The oxides were pressed into thin self-supporting wafers ($10^8 - 3 \times 10^8$ Pa) and studied by transmission. It was assumed that the compacting pressure did not change the adsorption properties of the oxides. The spectra were recorded at room temperature using a Perkin Elmer (type 325) grating spectrograph in the range from 4000 to 1000 cm^{-1}. The speed of registration was 0,5 cm^{-1} s^{-1} using slit program 7, which corresponded to a resolution of 3 cm^{-1} at 3600 cm^{-1}.

RESULTS

Acetone was chosen as a donor molecule since it is a relatively weak donor (DN = 17) (*8*), e.g., in comparison with pyridine (DN = 33.1) (*8*) and no proton transfer occurred with the oxides we have studied here. Schulz and Knözinger (*9*) using ketones as test molecules stated that their high reactivity complicated their use as test molecules for determining acid strength. Since, in former studies, the interaction between acetone and the OH groups of the surface was found to be weak (and acetone molecules did not much change their ir spectra) we decided to use the magnitude of the perturbation of free hydroxyl bands as a measure of the interaction strength.

Magnesia

The adsorption of acetone on magnesia was described earlier (*10*). Here the question is considered of how to find the perturbed OH band indicative of the acid strength of hydroxyl groups if there are several perturbed OH bands.

After adsorption of acetone at 1300 Pa the band at 3740 cm^{-1} of free OH groups of magnesia disappeared and perturbed OH bands at 3680, 3590, and 3480 cm^{-1} appeared (Fig. 1). When the pressure was lowered to 10^{-1} Pa and the temperature raised to 473 K, only two bands (at 3675 and 3600 cm^{-1}) remained. These bands corresponded to the bands at 3680 and 3590 cm^{-1}, the frequency shift to lower wavenumbers probably being due to overlapping effects of the perturbed bands.

The band with the largest shift (3480 cm^{-1}), due obviously to the strongest interaction of acetone with OH groups, disappeared first and, together with it, the carbonyl band at 1710 cm^{-1}. Young and Sheppard (*11*) assigned this latter band to an acetone molecule adsorbed on a hydroxyl group. Provided the shift of the wavenumber increases with interaction strength, the acetone species of strongest interaction with an OH group is most readily desorbed, i.e., that species is more weakly bound than those associated with smaller shifts of OH frequency. This weak bonding is also evidenced by the small downward shift of the carbonyl frequency, from 1735 cm^{-1} in the gas phase to 1710 cm^{-1} only.

There were further carbonyl bands, at wavenumbers below 1700 cm^{-1}, which resisted the above temperature and vacuum treatment, indicating much more strongly bound acetone molecules. These bands were assigned to reaction products of acetone on the surface, with formation of carboxylic structures. Since no evolution of water was detected by the TPD technique (*10*), the persisting perturbed OH bands must be caused by these remaining molecules, which are considered to be mainly adsorbed via oxygen and a cation.

Strong interaction with the carbonyl group is associated with strong adsorption, but weak interaction with the hydroxyl group (lower shift). The shift of the OH bands depends not only upon the acidity of the OH group, but also the basicity of the

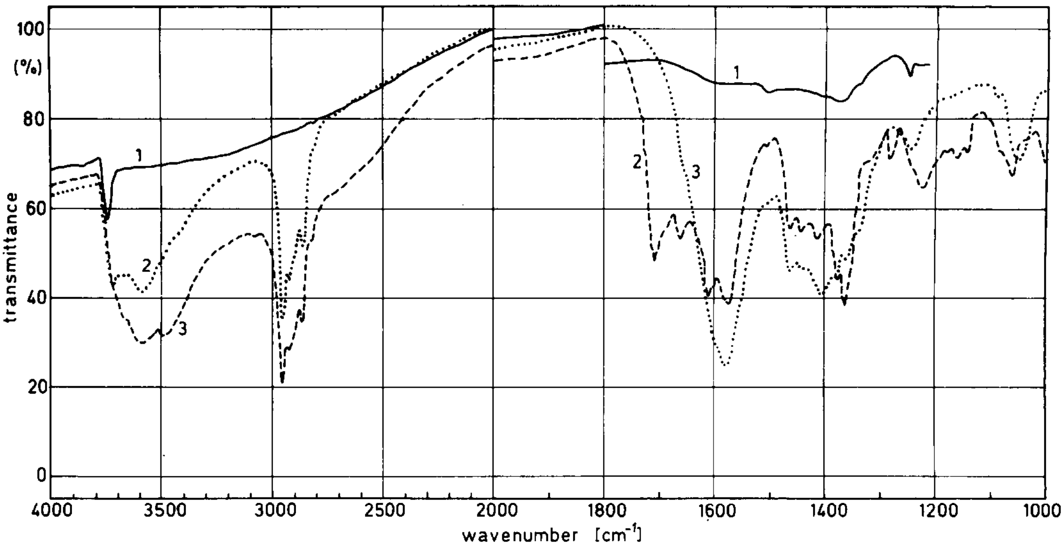

FIG. 1. Acetone on MgO. 1, Evacuation (10^{-1} Pa) at 873 K for 2 hr; 2, adsorption of acetone (1300 Pa) for 1 hr; 3, evacuation (10^{-1} Pa) at 373 K for 2 hr.

electron pair donor (EPD) molecule. Any further interaction (in addition to that with the hydroxyl group) of the molecule with an electron pair acceptor (EPA) site of the surface, which claims the EPD function of the molecule, should lead to a smaller shift of the OH band. This is why molecules which are bound via carboxylic structures caused a smaller shift of the OH frequency than those interacting only with an OH group.

Hence, only the perturbed OH band with the largest wavenumber shift is indicative of the strength of interaction between acetone and the OH group. This band was considered to reveal the acid strength of the OH groups. On MgO this band was observed at 3480 cm^{-1}, which meant a shift of 260 cm^{-1}.

Alumina

The spectra of acetone adsorbed on alumina are more complicated. There were not only at least three free hydroxyl bands, but also three perturbed ones. The positions of the bands are listed in Table 1, and the spectra can be seen in Fig. 2. The wavenumbers agreed with those reported in the literature (*12, 13*).

After adsorption of acetone at 1300 Pa, bands at 3440, 3520, and 3680 cm^{-1} appeared. Those at 3440 and 3520 cm^{-1} were due to perturbed hydroxyl bands, while the third one seemed to be that of a (remaining) free OH group.

Evacuation at room temperature led to the disappearance of the OH band at 3440 cm^{-1} and bands at 3730, 3680, and 3560 cm^{-1} were observed. From this observation, we concluded that the perturbed hydroxyl band at 3440 cm^{-1} was due to interaction of acetone with the OH group at 3730 cm^{-1}.

Furthermore, weakly bound acetone molecules (ν_{CO} = 1715 cm^{-1}) were only observed as long as the hydroxyl band at 3440 cm^{-1} was present. Consequently the latter was the OH band which was due to the interaction of acetone exclusively with the OH group and hence indicative of the acid strength of that group according to Hair and Hertl (*3*). Again this band was associated with the 1715 cm^{-1} carbonyl band, which again indicated that the interaction was weak.

As with magnesia, bands were observed below 1700 cm^{-1} which were more resistant to heat and vacuum treatment than the band at 1715 cm^{-1}. The band at 1690 cm^{-1}

TABLE 1

Main ir Bands of Acetone Adsorbed on γ-Al_2O_3

Treatment	OH valence bands (cm^{-1})	CH valence bands (cm^{-1})	C=O valence bands (cm^{-1}) CH deformation bands (cm^{-1})
1 hr 873 K/evac.	3795, 3730, 3680	—	
1300 Pa acetone	3440, 3520, 3680	3000, 2965, 2920	1735, 1715, 1635, 1620 1440, 1365, 1228, 1215, 1205
1 hr 298/evac.	3730, 3560	2960, 2930, 2910, 2870	1680, 1615, 1585, 1450, 1382, 1370
1 hr 473 K/evac.	3790, 3720, 3670, 3565	2960, 2930, 2905, 2870	1690, 1615, 1580, 1465, 1450, 1380, 1330
1 hr 573 K/evac.	3790, 3720, 3680	2960, 2920	1690, 1570, 1470, 1370

was assigned to acetone molecules bound to cations (*10*), those at 1615 and 1580 cm^{-1} to carboxylic structures (*10, 14*). It is to these molecules, whose donor capacity was obviously reduced, that perturbed OH bands of higher wavenumbers (lower shifts) and higher thermal stability were assigned.

Mixed Oxides

The spectra of the mixed oxides were interpreted in a similar way to that described for the estimation of the OH band shifts on magnesia and alumina. The values of the shifts were always between those of the components and are represented in Fig. 3 as a function of the Sanderson intermediate electronegativity (as defined below).

Sanderson's Electronegativity Concept

Sanderson defines electronegativity as the power of an atom in a molecule to attract the electrons. "When two or more atoms initially different in electronegativity combine chemically, they become adjusted

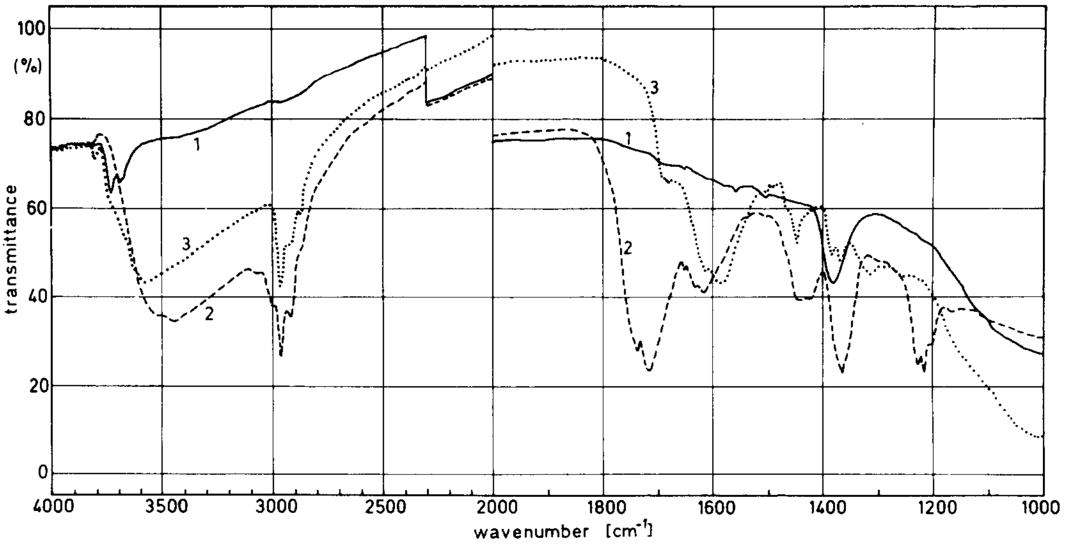

FIG. 2. Acetone on γ-Al_2O_3. 1, Evacuation (10^{-1} Pa) at 873 K for 2 hr; 2, adsorption of acetone (1300 Pa) for 1 hr; 3, evacuation (10^{-1} Pa) at 373 K for 2 hr.

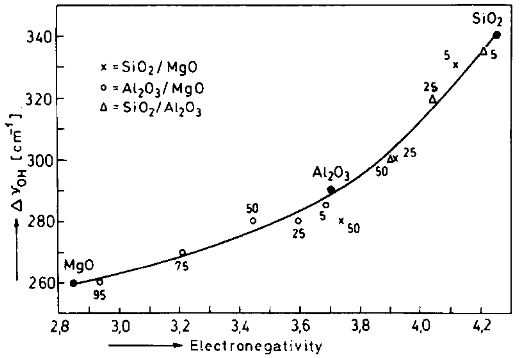

FIG. 3. Correlation of the shift of the stretching frequency of surface hydroxyl groups after adsorption of acetone with the Sanderson intermediate electronegativity of the adsorbents. The number indicates the content (mol%) of the component with the lower valency.

to the same electronegativity within the compound" (*15*). Therefore, in a molecule all the electrons should be distributed so that they are equally attracted by all nuclei. Sanderson postulated that the intermediate electronegativity of a compound was the geometric mean of the electronegativities (*15*) of the component atoms

$$S_{\text{int}} = (S_{\text{P}}{}^{p} \cdot S_{\text{Q}}{}^{q} \cdot S_{\text{R}}{}^{r})^{1/(p+q+r)}.$$

DISCUSSION

Determination of the Acid Strength of the OH Groups

The ir frequency of a hydroxyl bond is related only to its force constant. The force constant, however, is not indicative of the strength of this bond, but of the ease of varying the length of the bond. In other words, the frequency of the OH stretching vibration is not necessarily correlated with the depth of the OH potential curve, but with the radius of its curvature. Since, on the other hand, there should be a correlation between acidity and bond strength, it is obvious that the frequency of a free OH group should not be used as a measure of the acidity of the hydroxyl groups (*16*).

Searching for a method of measuring the acidity of OH groups, Hair and Hertl (*3*) found the shifts of the ir bands of oxidic hydroxyl groups interacting with donor molecules to increase with acid strength.

The larger shift was attributed to a stronger interaction of the donor molecule with the hydroxyl group. Using different electron donor molecules, Horill and Noller (*17*) found the hydroxyl band shift to increase with the donor number (*8*) of the adsorbed molecule. Cusumano and Low reported the hydroxyl band shifts on Vycor porous glass to be quantitatively related to the ionization potential of the adsorbed molecules (*18*). However, the shift of the OH groups was not correlated with the enthalpy of adsorption (*17*), leading to the assumption that there were strong adsorption centers in addition to hydroxyl groups.

The Uniformity of the Acid Strength of OH Groups

In good agreement with other authors, the maxima of the perturbed hydroxyl bands were found to be broad. With most of the studied oxides (especially with mixed oxides) only one maximum of a perturbed OH band was observed. Provided that only one OH band was observed, this result is indicative of only one acid strength of OH groups occurring on these oxides.

Uniform acid strength does not mean that there is no difference at all between the (observed) hydroxyl groups, but that there exists only one maximum in the distribution curve of acid strength. However, that result disagrees with the distribution of acidity found with indicator adsorption and amine titration methods (*19, 20*).

Nevertheless, there are cases where not only one perturbed OH band was found (as on MgO) and more than one free hydroxyl band existed before acetone adsorption (as on Al_2O_3). As we pointed out before, mainly one type of OH groups was involved and only one perturbed hydroxyl band was due to exclusive EPD–OH interaction.

Moreover, the OH band shift seemed to be an overall property which was independent of the texture of the oxide. It only had a correlation with the content and type of cation as well as the Sanderson intermediate electronegativity (Fig. 3).

The Acid Strength of the Mixed Oxides

Using Sanderson's intermediate electronegativity the following order of acid strength of OH groups is expected: $SiO_2 > Al_2O_3 > MgO$. Since other authors reported maxima of acid strength in series of mixtures of these oxides (*21, 22*), we were surprised to find almost monotonic variation of the strength of the hydroxyl groups of Al_2O_3/MgO, SiO_2/MgO, and SiO_2/Al_2O_3 mixed oxides.

The hydroxyl band shifts of these mixtures were always between those of their components. This was in agreement with basicity measurements (*5*) and the mixing rule (*4*) which suggested that the strength of acidic and basic sites in mixed oxides should always be between the values of the components. Moreover, the values of the mixed oxides showed a good correlation with the value of Sandersons's intermediate electronegativity. The higher the value of the intermediate electronegativity, the larger was the shift of the hydroxyl group.

The question now arises as to why this discrepancy exists between titration results and infrared data. One possible answer could be, as mentioned earlier, that titration and indicator adsorption measurements cover not only the strength of the hydroxyl groups, but also that of the cations. Adsorption of EPD molecules on cations is much stronger than on hydroxyl groups and therefore the acid strength of cations must be assumed to be higher. A higher accessibility of cations could change the acid strength (total acid strength) drastically and lead to maxima of acidity, which cannot be explained with only the help of this acidity estimation or the mixing rule.

Brønsted Acid Sites

Brønsted sites are defined as centers able to donate protons. On oxide surfaces these sites can only be hydroxyl groups. Brønsted centers are detected by adsorption of pyridine or ammonia, which will be protonated in the presence of abstractable protons. Usually pyridine is used and the criterion for the presence of Brønsted centers is the appearance of a band at 1540 cm^{-1} in the spectrum of pyridine adsorbed on the oxide.

Silica, which exhibited the largest shift of the OH bands of the investigated oxides, has been found not to have Brønsted acidity (*23*). The band at 1540 cm^{-1} has not been found on Al_2O_3 either (*23*). However, bands at 1540 cm^{-1} could be detected on mixed oxides of SiO_2 and Al_2O_3 (*23*). Nevertheless, the shifts for these oxides were in between those of the components, in agreement with their intermediate electronegativity, and this shows that the occurrence of Brønsted centers is not due to higher intermediate electronegativity or higher overall OH acid strength. The ability to transfer a proton to a pyridine molecule requires a high facility to lengthen the hydroxyl bond. As was found in preliminary experiments (*24*), some structural requirements appear to be necessary for such a proton transfer. OH groups which fulfil these requirements show a much higher band shift than reported here. As the concentration of these groups (Brønsted acid sites) in amorphous silica–alumina is probably very small, we cannot exclude that our oxides contained a small amount of such groups, the perturbed OH band of which would be expected around 2800 cm^{-1}.

The 1540 cm^{-1} band from pyridine was not found with silica–magnesia mixed oxides with about the same intermediate electronegativity as silica–alumina mixtures, which showed this pyridine band.

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