Determination of the Concentration of Lewis Acid Centers in Surfaces of Mixed Oxides Containing Silica by Infrared Spectroscopy

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The number of accessible Lewis acid centers on the surfaces of several silica-containing oxides can be determined by infrared spectroscopy alone if some plausible assumptions are used. This is feasible by coupling the concentration of Lewis sites with the concentration of isolated surface hydroxyl groups (being known from other sources) *via* suitable characteristic adsorbate bands. The method works not only when the respective infrared bands belonging to the probe molecules adsorbed onto OH groups and Lewis acid centers are fairly well separated in the spectrum, but also when both bands are strongly overlapped. In the second case, the number of Lewis sites can be derived immediately from the parameters of a simple equation relating the frequency shift of the composite band to the adsorbate coverage. The effectiveness of the method is demonstrated for pyridine adsorption on silica–boria and silica–germania. Further possible applications are briefly discussed.

INTRODUCTION

The surfaces of many oxides are characterized by two main types of sites, namely, hydroxyl groups and Lewis acid centers with electron deficiency (Lacs) (*1, 2*). Several methods have been proved to be satisfactory for measuring the surface concentration of OH groups (*3–6*), above all the techniques of chemical analysis (*5, 6*), but up to now there has been a lack of gentle methods for obtaining the number of electron-accepting centers. Sometimes the concentration of Lacs has been ascertained by measurements combining spectroscopy and gravimetry (*7, 8*).

As will be shown in this paper, the number of Lewis sites can be determined in certain cases by infrared (ir) spectroscopy without other resources if both hydroxyls and Lacs are present on the surface, and the OH concentration is known. In any case, ir spectroscopy is one of the most

useful and widespread tools in surface chemistry (*1, 2, 9, 10*). The employment of ir spectroscopy includes another advantage in that the Lacs studied with it are really active and accessible for adsorbate molecules.

The aim of this paper is not so much to provide very exact data for particular adsorbents, but to demonstrate the applicability of the proposed procedures from the methodical point of view. To this end, results from ir measurements of pyridine adsorption onto chemically modified silica surfaces, described elsewhere (*11, 12*), have been used. Pyridine is known to be a very convenient probe for discriminating various types of surface sites (*2, 13, 14*).

METHODS

Theory

In many adsorption systems there are more or less distinct differences for the wavenumbers of characteristic ir bands belonging actually to the same vibrational mode ν, but to diverse types of adsorbed molecules. Such differences are caused by

variations in the strength (= electron-accepting power) of the binding sites and they especially occur between the adsorbates which we designate as HA and LA, the molecules of which are bound *via* hydrogen bonds and coordinate bonds, respectively. This fact is illustrated in Fig. 1 with pyridine (PY) used as an example for an adsorbate. The magnitude of the wavenumber separation, $\Delta\tilde{\nu}_A{}^\nu$, depends, in each case, on the adsorption system and the vibrational mode under investigation; it can amount to between a few and some decades of reciprocal centimeters. Provided that really one species of both HA and LA is formed, three patterns of spectra regarding the interrelation of the HA and LA bands can occur as demonstrated in Fig. 2:

(i) Both bands are extensively separated from each other (a).

(ii) The minor band is a shoulder of the major one (c).

(iii) Slighter variations in the maximum positions of the HA and LA bands result in the emergence of only one peak caused by total overlapping of the single bands (b).

Whereas at high $\Delta\tilde{\nu}$ (i) the characteristic band parameters can be taken immediately from the spectra, an expensive computer-aided band separation procedure is usually

FIG. 2. Infrared spectra of pyridine adsorbed onto surfaces of mixed oxides SiO_2–B_2O_3 (a) and SiO_2–GeO_2 (b + c). Spectra 1 refer in each case to the background of the adsorbent dehydrated 3 h *in vacuo* at 700°C. (a, 2–4): SiO_2–B_2O_3 covered with increasing amounts of adsorbed pyridine corresponding to θ_{OH} of 0.12, 0.27, and 0.67, respectively. (b + c, 2): SiO_2–GeO_2 after full PY adsorption followed by 2 h evacuation at 200°C (all HPY removed). (b + c, 3 + 4): SiO_2–GeO_2 fully covered with PY followed by 1 and 0.5 h adsorbate desorption at room temperature, respectively.

needed to obtain them in the other cases (ii, iii). Here we present simple formulas for the determination of the Lac concentration working not only in the first case (i), but also in the third case (iii).

Figure 3 shows plots of the adsorbances of the characteristic adsorbate (PY) bands ($A_{HA}{}^\nu$, $A_{LA}{}^\nu$) at increasing coverage for various adsorbents. Some of the data originate from the spectra of Fig. 2. Surface coverage is indicated by $\theta_{OH} = 1$-$A_{OH}/A_{OH}{}^0$; A_{OH} and $A_{OH}{}^0$ are the absorbances of the Si–OH band at 3748 cm^{-1} at θ_{OH} and at zero coverage (i.e., before adsorption on hydroxyls), respectively (15). From Fig. 3b (which corresponds to Fig. 2a), the following equations result:
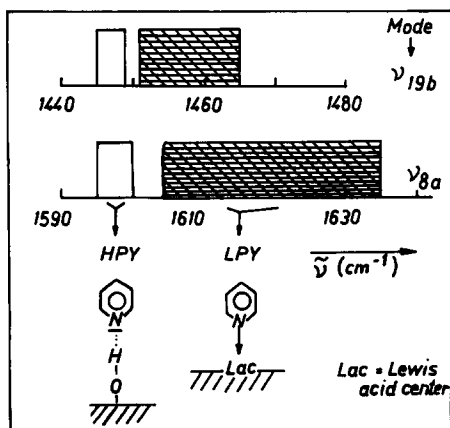

FIG. 1. Schematic representation of wavenumber regions characteristic for adsorbed pyridine molecules bound *via* hydrogen bonds (HPY) and Lewis acid centers (LPY on Lacs), respectively.
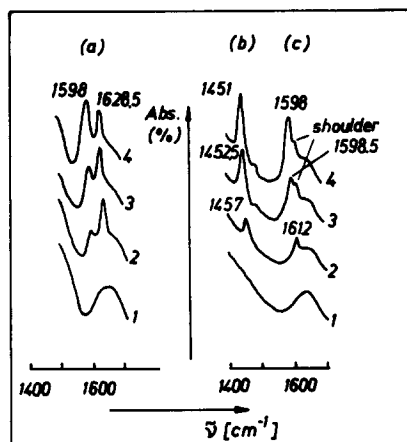
$$A_{HA}{}^\nu = a \cdot \theta_{OH}; \qquad (1a)$$

$$A_{LA}{}^\nu \simeq \text{const.} = b. \qquad (1b)$$

Equation (1b) meets the theoretical expectation that A_{LA} is independent of θ_{OH}. Furthermore, the plots illustrate the very pref-
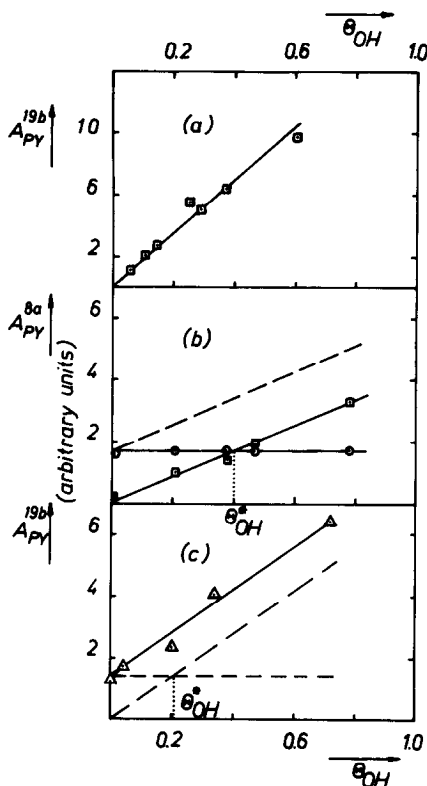
FIG. 3. Plots of the absorbances of characteristic bands of adsorbed PY against the coverage θ_{OH} which refers in each case to the silanol groups only. (a): SiO_2 (Aerosil)/PY, $\bar{\nu}_{PY}^{19b} = 1447$–$1448$ cm^{-1}; (b): SiO_2–B_2O_3/PY; squares originate from the HPY ν_{8a} band at 1598 cm^{-1}, circles from the LPY ν_{8a} band at 1628 cm^{-1}. The broken line is the resultant from both straight lines. (c): SiO_2–GeO_2/PY, $\bar{\nu}_{PY}^{19b}$ is about 1450 cm^{-1}. For an explanation of the broken lines see text.

erential binding of basic adsorbates at Lacs which, as is well known, are substantially stronger adsorption sites than the OH groups (9). The finding of a straight line for the A_{HA} vs θ_{OH} plot with an intercept of zero is confirmed by the data from PY adsorption on virgin SiO_2 (Fig. 3a) having only hydroxyls as surface sites; i.e., the band at 1447–1448 cm^{-1} belongs only to HA (13, 16–18).

The shape of the curve in Fig. 3c obviously corresponds to the superposition of both straight lines experimentally obtained (see Fig. 3b, broken line). This close similarity supports the idea that A_{PY}^{19b} in the SiO_2–GeO_2/PY system is also composed of

portions of $A_{HA}{}^v$ and $A_{LA}{}^v$, and it encouraged us to separate the plot graphically into the two supposed underlying components in a reversed manner compared to Fig. 3b (see broken lines, Fig. 3c). The arbitrary action belonging to this procedure, especially to the fixation of $A_{LA}{}^v$, is indeed beyond question. At the points of intersection of both straight lines in Figs. 3b and c, θ_{OH}^*,

$$A_{LA}{}^v = (A_{HA}{}^v)_{\theta_{OH}^*}$$

is valid and, according to the Lambert–Beer law, we obtain

$$c_{LA} = (\epsilon_{HA}/\epsilon_{LA})_v \cdot (c_{HA})_{\theta_{OH}^*}. \qquad (2)$$

Here v represents the type of stretching fundamental (e.g., in Fig. 3b ν_{8a} of PY, or in Fig. 3c ν_{19b} of PY). Assuming 1:1 interaction (other stoichiometries can also be taken into consideration), the concentration of Lacs may be obtained from the coverage at the point of intersection, θ_{OH}^*, and the surface OH concentration:

$$c_{Lac} = (\epsilon_{HA}/\epsilon_{LA})_v \cdot \theta_{OH}^* \cdot c_{OH}. \qquad (3)$$

This formula reflects that c_{OH} can be used as a vehicle to determine c_{LAC} via the parameters of the respective adsorbate bands. Some difficulties restrict the applicability of Eq. (3): (i) in general, the extinction coefficients are unknown, and (ii) from the spectra with overlapping bands of HA and LA, the estimation of θ_{OH}^* is very rough.

These difficulties can be overcome by the following procedure based on the observed dependence of the wavenumber of the composite band belonging to both adsorbates, $\bar{\nu}_A{}^v$, on θ_{OH}. This opens up new possibilities for obtaining the parameters needed to determine θ_{OH}^*.

The first statement is founded on the reasonable assumption that $\bar{\nu}_A{}^v$ is a linear combination of the wavenumbers of the underlying single bands, $\bar{\nu}_{LA}{}^v$ and $\bar{\nu}_{HA}{}^v$ (presuming equal half-band widths for them):

$$\bar{\nu}_A{}^v = x_{HA} \cdot \bar{\nu}_{HA}{}^v + x_{LA} \cdot \bar{\nu}_{LA}{}^v, \qquad (4)$$

$$x_{HA} = \frac{c_{HA}}{c_A} = \frac{c_{HA}}{c_{HA} + c_{LA}};$$

$$x_{LA} = \frac{c_{LA}}{c_A} = \frac{c_{LA}}{c_{HA} + c_{LA}}. \quad (5)$$

Here x_{HA} and x_{LA} are the fractions of the indicated type of adsorbate, relative to the total amount of adsorbed molecules (c_A), i.e., $x_{HA} + x_{LA} = 1$. With $\Delta\tilde{\nu}_A^v = \tilde{\nu}_{LA}^v - \tilde{\nu}_{HA}^v$ it follows that

$$\tilde{\nu}_A^v = \tilde{\nu}_{LA}^v - \Delta\tilde{\nu}_A^v \cdot x_{HA}. \quad (6)$$

Since

$$x_{HA} = \frac{A_{HA}^v}{A_{HA}^v + (\epsilon_{HA}/\epsilon_{LA})_v \cdot A_{LA}^v}, \quad (7)$$

we have using Eqs. (1a) and (1b)

$$\tilde{\nu}_A^v = \tilde{\nu}_{LA}^v - \frac{\Delta\tilde{\nu}_A^v \cdot a \cdot \theta_{OH}}{b \cdot (\epsilon_{HA}/\epsilon_{LA})_v + a \cdot \theta_{OH}}. \quad (8)$$

For practical use, this expression is transformed as follows:

$$Y = \frac{\Delta\tilde{\nu}_A^v}{(\tilde{\nu}_{LA} - \tilde{\nu}_A)_v} - 1; \quad X = 1/\theta_{OH}. \quad (9)$$

Consequently, Eq. (8) is converted into a linear relationship $Y = B \cdot X$ with the variables Y and X including the parameters $\tilde{\nu}_A^v$ and θ_{OH} implicitly. This function has the slope

$$B = (b/a)(\epsilon_{HA}/\epsilon_{LA})_v. \quad (10)$$

From Fig. 3b it results that $b/a = \theta_{OH}^*$ and, therefore, the concentration of Lacs is, following Eq. (3),

$$c_{Lac} = c_{OH} \cdot B. \quad (11)$$

This method yields the number of Lacs by a simple graphic procedure without any knowledge of the extinction coefficients. The only data needed now are a set of ir spectra in order to determine B, and the surface OH concentration, both easily accessible experimentally in suitable cases.

Experimental

All experimental procedures have been described in detail elsewhere (*11*).

The "surface mixed oxides," silica–boria (SiO_2–B_2O_3) and silica–germania (SiO_2–GeO_2), used as adsorbents were prepared by chemical reaction (chemical modifying, cf. (*19, 20*)) of Aerosil 380 (Si–OH groups as reactive sites) with the vapours of $B(OCH_3)_3$ and $GeCl_4$, respectively, at elevated temperatures, followed by hydrolysis with water vapour and dehydration. This process was repeated several times leading to a considerable amount of B_2O_3 or GeO_2 in the surface layer of the SiO_2 matrix. The surface area of the samples was about 300 m^2/g. PY was purified and dried by distillation in an argon atmosphere.

Small amounts of PY vapour were brought together *in situ* with discs of the adsorbents dehydrated for 3 h *in vacuo* at 700°C. After the surface had been fully covered, desorption experiments were also carried out.

Infrared spectra were recorded with the help of a UR-20 spectrophotometer using the programme for the maximum slitwidth as is usually done in adsorption measurements. The precision of the wavenumbers of the sharp PY bands in the region of C–C in-plane stretching vibrations was ±0.5 cm^{-1}.

RESULTS

Some of the primary results have already been shown in Figs. 2 and 3. The number of Lacs will be only roughly estimated if based
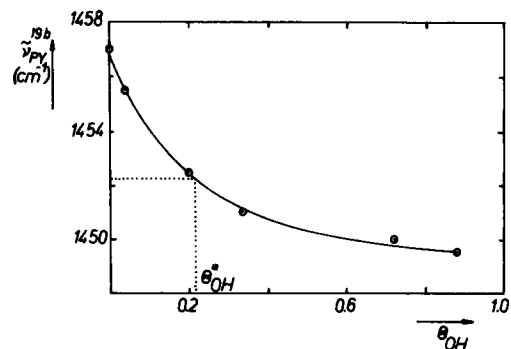

FIG. 4. Dependence of the wavenumber of the ν_{19b} band of PY adsorbed on the SiO_2–GeO_2 surface upon the PY coverage.

TABLE 1

Number of Lewis Sites on $SiO_2-B_2O_3$ and SiO_2-GeO_2

Fig.	Adsorbent	$\left(\dfrac{\epsilon_{HPY}}{\epsilon_{LPY}}\right)_v$	v_{PY}	θ^*_{OH}	c_{OH} (nm^{-2})	c_{Lac} (nm^{-2})
3b	$SiO_2-B_2O_3$	~1 [a] 0.54 [b]	v_{8a}	0.40	~1.2	~0.48 ~0.26
3c,4	SiO_2-GeO_2	~1 [a]	v_{19b}	0.21	~1.7	~0.36

Note. Results are evaluated according to Eq. (3) together with the data which are necessary for it.

[a] From Ref. (*17*).

[b] From Ref. (*21*) for two bands at 1600 and 1630 cm^{-1} found for PY adsorbed on Al_2O_3.

on the θ^*_{OH} values (see Figs. 3 and 4). In Table 1 the data required according to Eq. (3) are listed for the adsorption of pyridine (A = PY) onto the two different adsorbents. The concentration of surface hydroxyls was evaluated following the data of Davydov *et al.* (*5*) and Borello *et al.* (ϵ_{OH} = 35 liters/mol · cm) (*3*), thus bringing our figures into good agreement with each other. The quotients of the extinction coefficients were taken from the literature (*17, 21*); they were found to be rather divergent, e.g., for the 8a mode of PY. This also leads inevitably to rather discrepant Lac concentrations (cf. last column of Table 1). Compared to this, the c_{Lac} determination using the shift of $\bar{v}_A^v$ should be based on a detailed fit of observations. The primary data obtained from the spectra of the silica–germania/PY system (cf. Fig. 2c) are given in Table 2. A significant broadening of the 1450-cm^{-1} band from $\Delta\bar{v}_{1/2}$ of 12 up to 19 cm^{-1} occurs with increasing coverage, confirming the assumption that this band is composed of HA and LA single bands. At the same time, the observed half-band widths of 12 cm^{-1} for the LPY band and 14 cm^{-1} for the HPY band (taken from the SiO_2/PY system) of the v_{19b} mode, respectively, do approximately fulfil the prerequisite of equal half-widths for both bands as needed for the validity of Eq. (4).

In Fig. 4 a plot of $\bar{v}_A^v$ vs θ_{OH} is shown corresponding to the hyperbola expected according to Eq. (8).

Including the fact that only one type of Lewis sites (electron-deficient Ge centers) occurs on the SiO_2-GeO_2 surface, $\bar{v}_{LPY}^{19b}$ and $\Delta\bar{v}_{PY}^{19b}$ can be regarded as constants which were obtained as follows. The wavenumber of the LPY band was found to be 1457 cm^{-1} at $\theta_{OH} = 0$ from the spectrum of silica–germania/PY after degassing the sample at 200°C in order to remove all HPY (see Fig. 2b, Curve 2). On the other hand, it is impossible to produce a "pure" HPY specimen within this system because of the preferential binding of PY molecules at the Lewis sites. Since the acidity of the hydroxyls on SiO_2 and SiO_2-GeO_2 is almost the same (*11*), we can transfer the HA value $\bar{v}_{HPY}^{19b}$ = 1447.5 cm^{-1} from the PY adsorption on pure silica, consequently obtaining a $\Delta\bar{v}_{PY}^{19b}$ of 9.5 cm^{-1}. From these data and those

TABLE 2

Infrared Spectroscopic Data from the SiO_2-GeO_2/PY System Together with Their Empirical Errors

No.	A_{OH} (%)	$\bar{v}_{PY}^{19b}$ (cm^{-1})
0	$100 = A_{OH}^0$	$1457.0 = \bar{v}_{LPY}^{19b}$
1	96	1455.5
2	80	1452.5
3	66	1451.0
4	28	1450.0
5	12	1449.5

Note. $s(A_{OH})$ = ±1%; $s(\bar{v}_{PY}^{19b})$ = ±0.5 cm^{-1}; $s(\bar{v}_{HPY}^{19b})$ = ±1.0 cm^{-1}.

given in Table 2, the abscissae and ordinates were calculated by Eq. (9). The deviations of those values were determined from the empirical errors by the Gaussian error propagation law applied to Eq. (9). Because of the inhomogeneity of the error variances weighted least squares had to be used, and the following sum of squares about regression was minimized:

$$Q = \sum_{i=1}^{n} \omega_i \, (Y_i - B \cdot X_i^2 \overset{!}{=} \text{Min}, \quad (12)$$

with ω_i being the weights. Therefore, parameter B and its error variance are given by

$$B = \sum_{i=1}^{n} \omega_i \, X_i Y_i \Big/ \sum_{i=1}^{n} \omega_i X_i^2,$$

$$s(B) = \left(Q \Big/ \sum_{i=1}^{n} \omega_i X_i^2/(n-1) \right)^{1/2}. \quad (13)$$

The true value of B, called β, is placed in the confidence interval

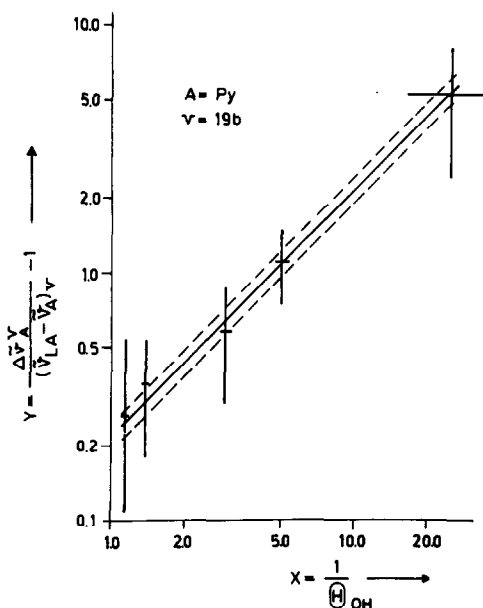$$B - t(p,f)s(B) < \beta < B + t(p,f)s(B) \quad (14)$$

FIG. 5. Double-logarithmic plot of the implicit function $Y = B \cdot X$ (cf. Eq. (9)) for obtaining slope B. The points are given together with their error variances $s(X)$ and $s(Y)$; the broken lines limit the confidence interval defined by $f = 4$ and $p = 5\%$.

in which $t(p,f)$ is the coefficient of the t distribution for $f = n - 1$ degrees of freedom of the equalized straight line, and a probability level of $p = 5\%$, respectively. The real equalized straight line $Y = B \cdot X$ has a confidence interval as follows:

$$X[B - t(p,f)s(B)] < Y$$
$$< X[B + t(p,f)s(B)].$$

The transformed data X_i and Y_i including their single errors $s(X_i)$ and $s(Y_i)$ and the equalized straight line $Y = B \cdot X$ together with its confidence interval are shown in Fig. 5. For B and its error variance we obtained $B = 0.2184$ and $s(B) = 0.0090$; this results in $c_{Lac} = 0.371 \pm 0.043$ nm^{-2} with a 5% probability level of error $(t(p,f) = 2.78)$. The error of c_{OH} was not taken into account; i.e., the indicated error refers to the demonstrated method, exclusively. In any case, c_{Lac} can be only as exact as c_{OH}.

DISCUSSION

The finding of a smooth straight line in Fig. 5 confirms the validity of the proposed method according to Eq. (9); the calculated error indicates a fairly good precision of the Lac determination. The results showing that one active Lac exists per 2.4–3 nm^2 will not be discussed here in detail, the more so as they are very plausible values (cf., for instance, the data in Refs. (22–24)).

The Lac concentration obtained in this way also agrees very well with the respective data of Table 1 determined via the θ_{OH}^* values. θ_{OH}^* may be found not only from the point of intersection as shown in Fig. 3, but also from the hyperbolic $\bar{\nu}_A^v$ vs θ_{OH} plot (Fig. 4) by use of $(\bar{\nu}_{LPY}^{19b} - \tfrac{1}{2}\Delta\bar{\nu}_{PY}^{19b})$ as an ordinate for θ_{OH}^*. Both procedures yield nearly identical θ_{OH}^* of about 0.21 for the SiO$_2$–GeO$_2$/PY system.

In the following, the assumptions necessary for the application of the proposed methods will be briefly summarized and discussed.

(i) Besides Lacs also OH groups must be present on the surface. Furthermore, an unambiguous correlation between the inten-

sity enhancement of the characteristic HA band at increasing A coverage and the simultaneous "consumption" of hydroxyls has to exist; if this is so, the number of OH species may also be larger than one for as long as each OH type is indicated by a distinct ir band and all these types form only one HA in the spectroscopic sense. On the other hand, this procedure does not work in the present form for adsorbents which bear several types of OH groups forming a complex ir absorption in the ν_{OH} region, such as alumina or silica–alumina. At present, there may also be some difficulties in determining c_{OH} very precisely for oxides other than SiO_2 or related mixed oxides (such as those used here).

(ii) Reasonable conceptions about the stoichiometry of interaction within the surface complexes are needed. Larger adsorbates with one or one predominant electron donor site (such as PY (11)) seem to be especially suitable for forming 1 : 1 complexes.

(iii) There may also be only one type of Lewis site on the surface under investigation, or two hardly different and spectroscopically not distinguishable types forming one LA; in the latter case, both types of Lacs will be covered.

(iv) The OH groups must not be so acidic as to transfer protons; in the present systems formation of pyridinium ions can be excluded (11).

(v) The spectroscopic parameters also have to satisfy certain prerequisites:

(1) For use of Eq. (3), i.e., Lac determination from separated bands of HA and LA, the relation between the extinction coefficients $(\epsilon_{HA}/\epsilon_{LA})_v$ must be known.

(2) For use of Eq. (9), i.e., Lac determination from overlapped single bands of HA and LA, it is necessary for the half-band widths of the single bands to be nearly the same. Furthermore, the magnitude of $\Delta\bar{\nu}_A{}^v$ has to be within a certain range. If $\Delta\bar{\nu}_A{}^v$ is too large in relation to $\Delta\bar{\nu}_{1/2}$ of the single bands, the formation of shoulders as in Fig. 2b is observed. If it is too low, the uncer-

tainty of the procedure will become too high.

(3) The constancy of the wavenumbers of the HA and LA bands must be ensured (cf. points (i) and (iii)). Moreover, $\bar{\nu}_{HA}{}^v$ is to be taken from a model system including an adsorbent with proton donor sites only.

Summarizing, this multitude of restrictions may oppose widespread applicability of the method. After all, this depends on the actual conditions in relevant systems, and on the spectroscopic aptitude of the adsorbate used (in the sense of Fig. 1). In principle, also probe molecules other than PY with strong electron donor sites should fit the assumptions listed above (amines, nitriles, ketones, and other molecules).

Knowledge of the Lac concentration is a prerequisite in order to arrange surface models of the oxides and mixed oxides in question. This may be helpful in obtaining more insight into the fundamental nature of the adsorption process as well as when dealing with more practical questions. Detailed information about the Lac concentration is, above all, important for problems of catalysis. Correlations between these data and those from catalytic processes, for instance, concentrations of cracking products, may contribute to the formulation of relevant reaction mechanisms.

In the silica mixed oxides prepared by chemical modifying (19, 20), some idea of the distribution of the "foreign" oxides in the SiO_2 matrix can be obtained if the number of Lacs spectroscopically measured is correlated with the total number of the "foreign" atoms determined by chemical-analytical methods (25). Depending on the geometrical parameters of those foreign oxides compared to SiO_2, they are arranged in clusters instead of layers in the mixed oxides (26).

CONCLUSIONS

A new method for the quantitative determination of Lewis sites on oxide surfaces by an infrared technique has been described, and the limits and possibilities of

its application have been discussed. This method has the following advantages:

(i) It is a fast and gentle procedure. Data can be obtained routinely.

(ii) The proposed method does not influence the state of the samples in any way, which means that comparing measurements with other, for instance, catalytic and chemical-analytical procedures, can be undertaken following the infrared investigation.

(iii) Only the active, accessible Lewis sites are covered. This means at the same time that the measured c_{Lac} can vary with the type (the size) of the adsorbate molecules.

(iv) It should be emphasized that concerning the Lac determination from overlapped HA and LA bands no idea of the quantity of the quotient of extinction coefficients, $(\epsilon_{HA}/\epsilon_{LA})_v$, is needed, because that is involved in the slope of the Y vs X plot (cf. Fig. 5). In the reverse case (with known c_{Lac}), one can calculate this quotient from the experimental data.

Application of the method to the $SiO_2-B_2O_3$ and SiO_2-GeO_2 systems results in reasonable values of the Lac concentration (B and Ge centers) in these surfaces.

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