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Difficulties Concerning the Infrared Identification of Surface Species on Metal Oxides

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INTRODUCTION

The importance of infrared spectroscopy in surface chemistry and catalysis has been underlined recently by the publication of books (*1, 2*) and reviews (*3, 4*) dealing with this subject. Nonetheless sufficient attention has not been given to the influence of impurities on the infrared spectra of adsorbents, especially over the 2500–200 cm^{-1} range of wavenumbers, other than the work of Smith and Eischens on ZnO (*5*).

Two kinds of impurities have to be considered. Some impurities come from the apparatus used and are introduced into the sample during its storage or during the experiments (pollution of the sample), whereas others come from an incomplete decomposition (or purification) of the starting material, including the adsorbed gas remaining after the decomposition of this material.

Lack of knowledge about the impurity content of the adsorbent may not only lead to attributing wrongly some bands to adsorbent properties (*i.e.*, electronic transitions of defects) but may also cause some confusion in the interpretation of the spectrum of the adsorbed phase.

Furthermore, the study of semiconducting oxides results in additional difficulties. Heating *in vacuo* or under oxygen pressure often produces a tremendous variation of the concentration of charge carriers (electrons or holes) in these materials. This results in very important transmission changes and, consequently, in strong modifications of the sensitivity of the band detection.

We want to sum up here some of the results of experiments carried out with alumina, titania (rutile and anatase), gallium oxide, and zinc oxide. With reference to the latter, particular attention is given to the multiphonon absorption that has not been considered previously in the infrared spectrum of oxide catalysts, except for silica.

EXPERIMENTAL METHODS

Materials

γ alumina was supplied by Degussa (Aluminium oxide C), anatase was obtained by oxidation of Ti Cl_4 (*6*) and rutile by heating anatase at 800°C in air. Gallium oxide was prepared by decomposition of the oxalate at 650°C in air and zinc oxide was provided by heating either zinc hydroxide or zinc oxalate in air at specified temperatures. The infrared samples were then prepared by compression of the powders under 2 to 4 $tons/cm^2$.

Apparatus

The infrared cell was an all-glass system onto which the windows (Na Cl) were not waxed (see below) but sealed by using viton o rings. Noncontamination of the samples by the vacuum grease (Apiezon) was ascertained through preliminary experiments performed over a period of one week. The spectrophotometer was the Perkin-Elmer 521 and the spectra were recorded at room temperature (in vacuo unless otherwise specified) after the sample was submitted to the required treatments.

Results and Discussion

Pollution of the Sample and Conditions of Cleaning

Despite their low vapor pressure, many of the adhesives used to attach the windows to the infrared cell body may contaminate the sample. Evidence of such a pollution was given in our laboratory through a series of experiments performed over periods of several days with various cements (waxes numbers 6 and 40 from Edwards, Pliobond from Goodyear, Silicone grease or resins, Araldite from Ciba). The infrared spectra of the samples contaminated by the first three cements show typical absorption bands of saturated hydrocarbons (3000–2800 cm^{-1} and 1480–1370 cm^{-1}), whereas the use of silicone products leads to the formation of the silica OH groups (stretching band at 3740 cm^{-1}). Pollution by Araldite is characterized by more complicated spectra but it may be decreased by using a rather high hardening temperature.

The preceding results lead us to explain the disagreement about the OH stretching bands of rutile (*7*, *8*). The 3740 cm^{-1} value reported in only one paper (*7*) was caused probably by silica impurities evolved from the adhesive used.

This kind of pollution is avoided by using joints or by a direct glass-to-glass sealing. Unfortunately the latter procedure is limited to silica or periclase (*9*) windows.

Atmospheric impurities retained by the solid during its preparation and storage are more difficult to eliminate. Special care must be taken regarding the action of hydrocarbons. These compounds may reduce the oxide surface on heating, hence contribute to the non-stoichiometry of highly divided metal oxides (*10*) and give rise to various absorption bands. Apart from the expected OH stretching and bending vibrations, the spectra of the most divided oxides used here, i.e., alumina (100 m^2/g BET), anatase (91 m^2/g), and gallia (70 m^2/g) show a number of bands located in the 3000–2800 and 1600–1300 cm^{-1} ranges. The bands observed in the latter interval cannot be ascribed exclusively to the C-H bending vibrations of saturated hydrocarbons because they frequently appear alone. The contribution of weakened $C=C$ stretching vibrations (1550–1600 cm^{-1}) and of carbon-oxygen linkages is then to be implicated, these species arising from cracking and oxidation processes occuring during the outgassing of the samples.

Therefore the bands observed on "bare" alumina samples near 1580 and 1480 cm^{-1} (*11*, *12*) must be ascribed to this kind of impurities and not to "lattice vibrations" or "lattice defects". Inasmuch as a recent work (*12*) has left some uncertainty on this subject, we must emphasize that the removal of hydrocarboned impurities requires drastic treatments. The degassing of alumina and anatase samples at temperatures even greater than 400°C often seems to remove these impurities but, in fact, it gives rise to products whose absorption bands may be very weak or sometimes undetected. However, subsequent treatment in gaseous atmospheres in some cases produce new impurities showing absorption bands which may wrongly be ascribed to the reaction between the adsorbate and the pure adsorbent.

The behavior of alumina is illustrated by Figs. 1 and 2. After outgassing at 600°C, an apparently bare sample then was heated in dry oxygen at the same temperature. The spectrum recorded after cooling to room temperature and evacuation shows (Fig. 1) an increase of the surface OH concentration (3800–3500 cm^{-1}) and the formation of carbonate and bicarbonate species (bands located at 3640, 1655, and 1230 cm^{-1}). Detailed analysis of these species does not come within the scope of this paper and will be made in a more general one dealing with the adsorption and the oxidation of olefins over alumina (*13*). We do want to stress that the complete removal of such species requires an outgassing up to 600°C. If the cleaning procedure is less drastic, a single band at 1370 cm^{-1} is observed. Such a band had been noticed in the spectrum of chromia-alumina (*14*), and the defect structure of the oxide was then invoked. However, in the present case, this band may be removed completely and does not appear again through drastic reduction treatments.

FIG. 1. Oxidation of an apparently bare alumina sample: —— initial sample – – – after oxidation at 600°C (100 torr O_2, 6 hr).

Therefore, the responsible species must be a carbonaceous impurity (probably carbonate ion). Similar results were obtained with titania and gallia but the cleaning procedure required was less drastic (500°C).

Figure 2 shows the results obtained by hydrogenation of an impure alumina sample at 300°C and evacuation at 100°C. The bands may be ascribed not only to C-H deformation vibrations (1445 cm^{-1}) but also to several carbonate species (1650, 1595, 1445, 1370, 1230 cm^{-1}). Furthermore, the sample cannot be cleaned up unless it is oxidized and then outgassed at 600°C.

On the other hand, the presence of carbon

FIG. 2. Hydrogenation of an impure alumina sample: —— initial sample – – – after hydrogenation at 300°C (80 torr H_2, 3 hr).

monoxide on "bare" alumina- and silica-supported platinum has been reported (absorption band near 2100 cm^{-1}) (*15*). We also observed this phenomenon with alumina-supported iridium. The results presented suggest that the oxidation of hydrocarbons retained by the support is to be incriminated.

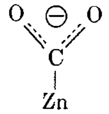
Impurities Arising from the Starting Materials

The metal oxide samples prepared by decomposition of organic salts are often much more divided than those provided by dehydrating crystallized hydroxides and, consequently, more suitable as catalysts. However, the complete removal of organic residues and adsorbed gases arising from the decomposition (mainly CO and CO_2) is rarely checked and the influence of such impurities on the catalytic properties has to be cleared up. In this connection, the infrared spectroscopy seems to be a sensitive tool. The material studied here is the zinc oxide which is especially convenient because the properties of the pure crystal have been investigated extensively and can be compared with the behavior of polycrystalline samples. Similar results were obtained with other oxides arising from oxalate or carbonate decomposition.

The analysis of the desorption products of ZnO ex-oxalate, performed by mass spectrometry, showed that carbon dioxide is not fully eliminated by outgassing at 500°C (*16*). Consequently the absorption bands remaining on the infrared spectrum of "bare" ZnO samples after outgassing at moderate temperatures should not be ascribed to "lattice defects" (*17*) without further investigation.

Figure 3 presents the results obtained with a ZnO sample prepared by decomposition of zinc oxalate at 400°C in air for 4 hr and then pelleted. The spectrum (*a*) was recorded in air and the others were obtained after various treatments including a final heating in oxygen at 400°C to restore the transmittance by trapping the free electrons. The transmittance of the sample (10 mg/cm^2) amounted to 40% at 2000 cm^{-1} and 25% at 800 cm^{-1}. No hydrocarbons were detected on the solid.

The spectrum *a* exhibits strong absorption bands in the 1600–1200 cm^{-1} and the 1100–800 cm^{-1} ranges. The former, which are too wide to be fruitfully discussed, are much affected by subsequent thermal treatments. After outgassing at 400°C (12 hr), absorption maxima are observed at 1540 cm^{-1} and 1330 cm^{-1} which may be ascribed to a carboxylate species:



Heating at 700°C in oxygen (160 Torr, 2 hr) followed by degassing at 400°C (4 hr) causes an absorption shift towards the lower frequencies with maxima at 1350 cm^{-1} and 1190 cm^{-1} (spectrum *c*). Attribution of such bands is more difficult and probably involves the bonding of carbon atoms with lattice anions. Finally, a prolonged heating at 700°C in oxygen and a subsequent outgassing at 400°C remove all bands above 1100 cm^{-1} (spectrum *d*).

The origin of the absorption bands observed below 1100 cm^{-1} must then be discussed taking into account the results obtained with various polycrystalline ZnO samples (Table 1) and presented on Fig. 4 (spectra *e* to *h*). The chemical and spectral analyses which were performed with samples ex-hydroxide revealed the presence of only ppm of Cu and Pb and did not detect carbon or nitrogen. The carbon and nitrogen content of the sample ex-oxalate is not known but must be rather low because of the high preparation temperature. All the spectra show bands located at 1020–980 and 910–870 cm^{-1}, all but one (sample of low density) a shoulder near 1080 cm^{-1}. The bending vibrations of residual OH groups cannot be invoked because the corresponding stretching vibrations are not observed on spectra *e* and *h* which have a sufficient transmittance (30%) above 3000 cm^{-1}. As the concentration of other foreign impurities is too low to be reasonably incriminated, the following factors must be taken into account:

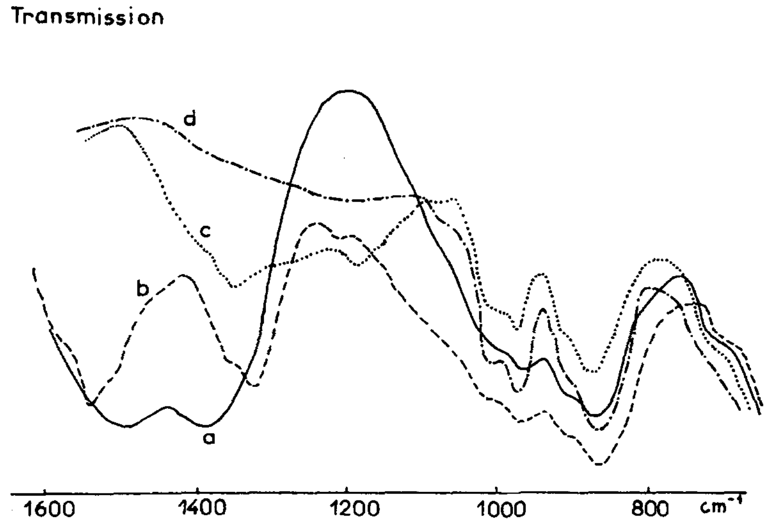


FIG. 3. Infrared spectra of Zn O ex-oxalate after various treatments (see text).

(1) lattice vibrations, (2) electronic transitions associated with lattice defects, and (3) absorption due to free carriers.

The absorption of free electrons in ZnO single crystals was shown to increase continuously with wavelength (*18*). In a recent work (*3*), a very wide absorption maximum was ascribed to the same factor. However, according to our results, such an extremum may arise from the combination of two variables, that is, the increase of the absorption coefficient with wavelength (free carriers) and the decrease of the scattering losses with increasing wavelength. Such a band indeed was not observed if the scattering losses were minimized.

The excitation of electrons out of bound states as interstitial zinc atoms and/or oxygen vacancies may also be envisaged. However the density of these states (i.e., of lattice defects) must be sharply decreased by the treatment in oxygen and cannot be invoked, at least in the case of the strongest bands. Finally, it is suggested that these bands arise from lattice vibrations, that is, multiphonon absorption (the

TABLE 1

Spectrum	Origin of the zinc oxide	Nature of the sample:	Thermal treatment	Sample transmittance at 800 cm^{-1}
e	oxalate dec. 1000°C in air	pellet, 12 mg/cm^2	500°C first in vacuo, then in oxygen	30%
f	hydroxide dec. 850°C in air	pellet, 20 mg/cm^2	—	25%
g	hydroxide dec. 850°C in air	powder just clamped between NaCl windows, 2 mg/cm^2	—	35%
h	hydroxide dec. 450°C in air	pellet, 10 mg/cm^2	400°C first in vacuo, then in oxygen	35%

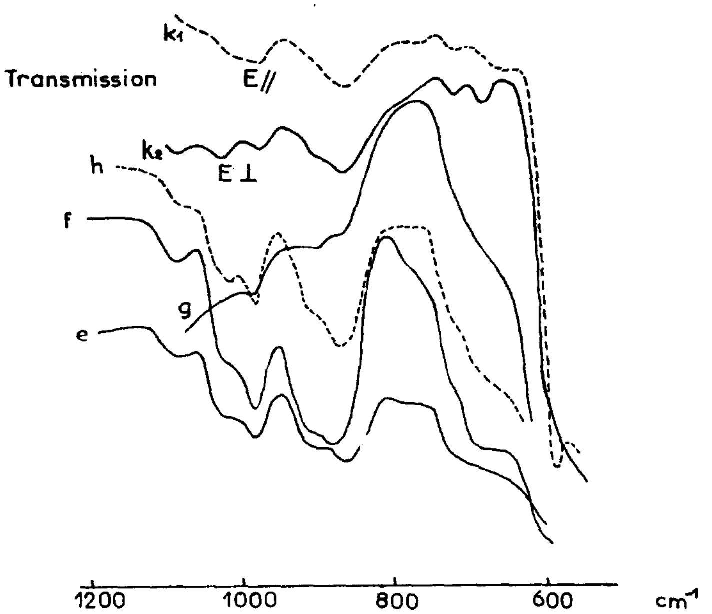


FIG. 4. Infrared spectra of various Zn O samples (see text).

fundamental vibrations, relevant to the zone-center[1] phonons, are located below 600 cm^{-1}). In fact, absorption bands of a ZnO powder in this region were already ascribed to multiphonons (*19*) but the absence of hydroxyl groups was not checked. This view is better supported by the examination of the spectra k_1 and k_2 of Fig. 4 (polarized light), relative to a pure ZnO single crystal (20 μ thickness) (*20*) which may be considered as multiphonon spectra.[1]

In short, an infrared study of surface species pertaining to metal oxides cannot be undertaken before an efficient cleaning procedure has been achieved. In many cases this procedure must include the oxidation of the sample before outgassing, and blank experiments (i.e., without adsorbate) have to be systematically performed. In addition, the multiphonon spectrum of the solid must not be neglected. Typical semiconducting oxides offer a particular difficulty because this absorption may be obscured by the free carriers absorption which itself depends strongly upon the surrounding atmosphere.

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[1] An accurate calculation of the multiphonon spectrum requires data concerning zone-boundary phonons which are not available at the present time.

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