An Infrared Spectroscopic Investigation of the Surface Properties of Magnesium Aluminate Spinel

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Magnesium aluminate (spinel) samples were prepared by decomposition of Mg, Al mixed oxalate and by thermal decomposition of a $Mg(NO_3)_2$-impregnated transition alumina. In the latter preparation, which yields samples more suitable for ir work, transformation to the spinel phase occurs at $\sim 400°C$, as monitored by the XRD spectrum, and by a sudden shift of the surface OH band to $\sim 3740 \text{ cm}^{-1}$. Pyridine (Py), CO, and CO_2 were adsorbed in order to investigate the surface acidity and basicity. Py is most effective in revealing Lewis acidity, which is mostly ascribed to coordinatively unsaturated (cus) Mg^{IV} ions, whereas CO and CO_2 σ-coordinate to only a few such sites. (The Roman numeral in Mg^{IV} symbolizes tetrahedral coordination). CO_2 also adsorbs to give bicarbonates as well as monodentate and bidentate carbonates. Evidence is presented to show the importance of the octahedral coordination (Al^{VI}) and of the degree of surface hydration with respect to surface oxygen basicity. The tetrahedral coordination is shown to be important for the formation of surface bicarbonates, which probably have a bridged structure. The partly inverted cation distribution of some samples was monitored by spectral studies in the surface OH group region and by the adsorption behavior of Py, CO, and CO_2.

INTRODUCTION

In previous papers and communications from our group (*1–6*) the importance of cation coordination in determining the surface behavior of Al-containing systems was already pointed out. Several surface characteristics of transition aluminas are probably better understood if the two possible coordinations for bulk Al ions are considered. These characteristics include the great variety of surface free hydroxyls (*7*), tentatively explained by Peri (*8*) in terms of different numbers of oxide ions surrounding the OH group. In order to check the chemical behavior of surface octahedral Al ions, a thorough investigation of the surface properties of α-Al_2O_3 was undertaken (*3*),

and now Mg spinel is considered. Natural spinel is regarded as a normal spinel (*9*), i.e., a spinel in which the divalent cations are in tetrahedral holes (tetrahedral cations) and the trivalent cations in octahedral holes (octahedral cations), while synthetic spinels, which were also widely regarded as normal (*10*), are now suggested to exhibit a partly inverted distribution (*11–13*), though not exceeding some 10–15%.

If we assume that the surface of a solid reproduces at least the gross features of the bulk, $MgAl_2O_4$ is a suitable system to investigate the properties of tetrahedral Mg (Mg^{IV}) and of octahedral Al (Al^{VI}). As far as the former cations are concerned, refer-

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ence can be also made to the surface characteristics of silica–magnesia gels (*14, 15*), which for pretreatments at temperatures below 800°C were shown to contain some Mg^{2+} substituting for Si^{4+} in the silica network.

EXPERIMENTAL

Instrumentation

Infrared spectra were recorded on a Beckman IR 12 double-beam spectrophotometer, using reference beam screening to obtain suitable 100% baselines in all spectral ranges. N_2 adsorption isotherms at 77°K were determined using a small dead-space BET-like vacuum line. Microgravimetric measurements were carried out with a Sartorius 4102 microbalance.

X-ray diffraction (XRD) spectra were obtained using a high-temperature Guinier-Lenné Enraf-Nonius camera with $CuK\alpha$ radiation. Spectral deconvolution was performed using the IBM 360/67 machine of Turin University by means of a computer program briefly described elsewhere (*3*).

All gases and chemicals were of high purity grade, and the gases were distilled *in vacuo* before use.

Sample Preparation

As the problem of sufficiently high surface areas is a major one in the ir spectroscopic approach to surface chemistry, both to obtain appreciable adsorptive activity and to avoid light scattering, special care was devoted to the preparation. Two main procedures were followed, as briefly described below.

Preparation A. The oxalate complex $H_4Mg[Al(C_2O_4)_3]_2 \cdot 15H_2O$ was decomposed at 600–800°C, either *in vacuo* or in air, to yield a nonporous, well-crystallized spinel (*9*). The XRD lines are only slightly broader than usual due to small crystal size, and the surface area is between 10 and 40 m² g⁻¹ depending on the highest temperature reached and the rate of de-

composition. The ir spectrum is most satisfactory in the 2000- to 4000-cm⁻¹ range, where only a weak symmetrical peak is observed at ∼3740 cm⁻¹ due to surface hydroxyls; the solid is completely opaque in the 1300- to 1700-cm⁻¹ range, probably due to some bulk carbonates produced during the decomposition which cannot be eliminated.

Preparation B. A high external area transition alumina, commercially termed Alon C, was impregnated with the stoichiometric amount of an $Mg(NO_3)_2$ solution to yield $MgAl_2O_4$ and gently heated *in vacuo* to 340°C. At that temperature the nitrate slowly decomposes and its complete destruction can be followed both by pressure reading and ir inspection. After the decomposition, there is no trace of any crystalline phase in the XRD spectrum, and in the ir spectrum surface hydroxyls can be observed absorbing at ∼3690 cm⁻¹.

On increasing the temperature to 400°C, diffraction lines typical of magnesium aluminate spinel appear in the XRD spectrum; at the same time, the surface OH band becomes more symmetrical and shifts abruptly to ∼3740 cm⁻¹, i.e., to the same spectral position as observed in preparation A. The surface behavior of this preparation is therefore considered only after thermal treatment at $T \geqslant 400$°C. The material is macroporous, with an average pore radius of ∼100 Å, and the total surface area ranges between 70 and some 100 m² g⁻¹.

RESULTS

Sample Dehydration

Figure 1 shows the 400–800°C dehydration pattern of a sample coming from preparation B, while the inset shows the relevant water-loss curve. It can be noted that:

(1) There is only one band ascribable to "free" OH groups. The band is slightly asymmetric on the low-frequency side, has a maximum at 3738–3740 cm⁻¹, and posses-

ses $\Delta\bar{\nu}_{\frac{1}{2}}$ = 60–53 cm⁻¹, following the dehydration temperature. It completely disappears by 800°C.

(2) A small amount of H-bonded hydroxyls is observed, absorbing below 3650 cm⁻¹, and this is eliminated by 500–600°C.

(3) In the 400–800°C range, 1.8 water molecules are desorbed per 100 Å², corresponding to the last 3.6 surface OH groups. If this figure is compared with the water amount corresponding to the complete dehydration of a spinel surface, for which a close-packed oxygen lattice is normally assumed, we see that after the preparation, i.e., after thermal treatment at 400°C, the sample is over 80% dehydrated. This figure is even larger for preparation A, during which higher temperatures are reached.

The Chemisorption of Carbon Monoxide

In a previous paper (*2*) concerning the interaction of CO with several aluminas (α, η, θ, γ, δ), this molecule provided evidence for very strong Lewis acidic sites;

FIG. 1. Infrared spectra in the OH stretching region of MgAl₂O₄ dehydrated at (°C): 1, 400; 2, 500; 3, 600; 4, 700; 5, 800. The dotted part of curve 5 is relative to a partly inverted sample (see text). Inset: water loss curve of MgAl₂O₄ in the 400–800°C temperature range. The percentage water loss was calculated on the basis of the theoretical amount of water on a close-packed oxygen plane.

their concentration was fairly small on transition aluminas and entirely missing on α-Al₂O₃. These sites were therefore ascribed to a small fraction of the tetrahedrally coordinated Al ions (Al^{IV}).

CO adsorbs at room temperature on Mg spinel in small amounts, comparable to those observed on transition aluminas. The amounts depend on dehydration temperature. After a dehydration at 800°C, when the surface is fully dehydrated, the CO uptake reaches its maximum value of ∼0.40 molecules/100 Å², indicating that only a minor fraction of the coordinatively unsaturated cations is strong enough as Lewis centers to σ-coordinate CO.

CO chemisorption produces an ir band at 2195–2200 cm⁻¹, i.e., some 60 cm⁻¹ above the frequency of the gas (Fig. 2A). The chemisorbed phase is quickly eliminated by pumping off at room temperature.

The Chemisorption of Pyridine

The adsorption of pyridine (Py) is widely used to monitor strong surface acidity of both Lewis and Brønsted types [see, for example, Ref. (*16*)]. Spectroscopically, its behavior is conveniently followed, in the case of a Lewis coordination, by checking the shifts of A₁ ring modes (mainly modes 8a and 19b), i.e., the modes belonging to the same symmetry class of the *N*-acidic center bond coordinate, while the Brønsted type adsorption is monitored by the appearance of bands at ∼1630 and ∼1540 cm⁻¹ as well as by a reversed intensity ratio of the modes at ∼1440 and ∼1490 cm⁻¹ compared to the Lewis coordinated species.

Py H-bonded to surface OH groups through the nitrogen lone pair is characterized by the 8a ring mode at 1590–1600 cm⁻¹, i.e., some 10 wave numbers above the frequency of the liquid, and by a fast desorbability below 150°C (*16*). Under a high Py pressure, a physical adsorption can also take place, characterized by the 8a and
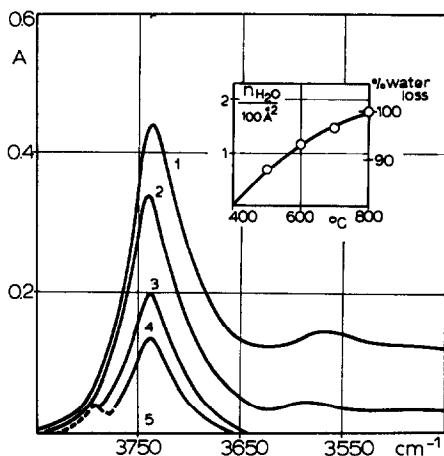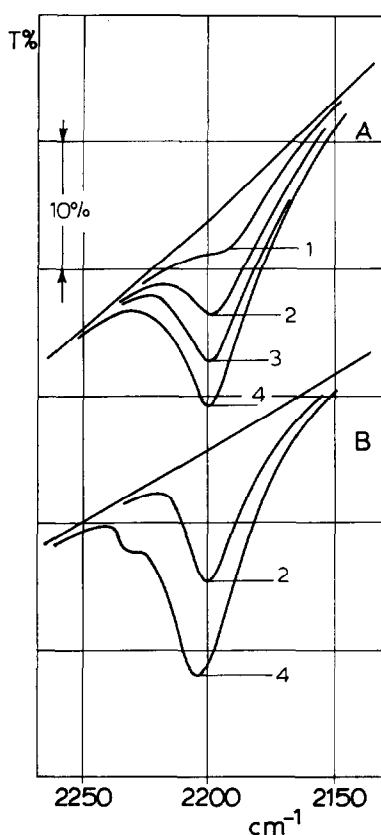
FIG. 2. The spectra due to the adsorption of CO (40 Torr) onto a regular spinel sample (A) and onto a partly inverted one (B). Dehydration temperatures (°C) are: 1, 400; 2, 500; 3, 600; 4, 700.

8b modes very close together in the 1570- to 1580-cm^{-1} range, i.e., in the range typical of the liquid phase. This species is quickly evacuated at room temperature.

Figure 3A shows the spectra in the 8a–8b mode range due to Py adsorption at various coverages on a spinel sample dehydrated at 700°C, and the inset reports the amounts remaining chemisorbed after Py evacuation at various temperatures. It can be noted that:

(1) A Py species nonreversible at room temperature is easily evidenced, characterized by a fairly constant 8b mode at 1577 cm^{-1} and by a 8a mode broad and asymmetric on the low-frequency side, whose band maximum shifts upward, upon

Py evacuation at increasing temperatures, from ~1605 to ~1615 cm^{-1}. Part of this species is already desorbed at room temperature, as shown by curves 2 and 3, and is completely desorbed by 300°C. The behavior and spectral features indicate a Py species coordinated to Lewis acidic sites (LPy), i.e., to coordinatively unsaturated (cus) surface cations.

(2) Spectrum 1 reveals that the fraction reversible at room temperature is made up of several components. There is a liquid-like physically adsorbed phase, monitored by the broadness of the 8b band, on which two weak shoulders are just observable on either side. In addition there is a shoulder on the low-frequency side of band 8a at ~1595 cm^{-1}, which is assigned to the 8a mode of another Py species whose 8b mode is not resolved in the broad 1597-cm^{-1} band. It is ascribed to nitrogen H-bonded Py and/or to Py coordinated to weak Lewis acidic sites. In fact, a sample dehydrated at 800°C, which no longer possesses OH groups and is thus unable to H-bond Py, still exhibits a shoulder at ~1595 cm^{-1}.

(3) There is a weak band at 1637 cm^{-1} that might be thought of as the 8a mode of some PyH$^+$, although the partner band at 1540 cm^{-1} was not resolved and the intensity inversion previously mentioned could never be observed owing to the much higher amount of Lewis-coordinated Py (LPy). Therefore, the existence of a few Brønsted acidic sites on the MgAl$_2$O$_4$ surface cannot be ruled out, but it remains extremely doubtful, also in view of the occurrence around the above reported frequency of a combination mode often observed on Py complexes (*25*).

Parallel to the above reported spectral changes, Py adsorption brings about a severe perturbation of the OH band at 3740 cm^{-1} and the creation of a broad absorption centered at ~3400 cm^{-1} clearly due to H-bonded hydroxyls. Py evacuation
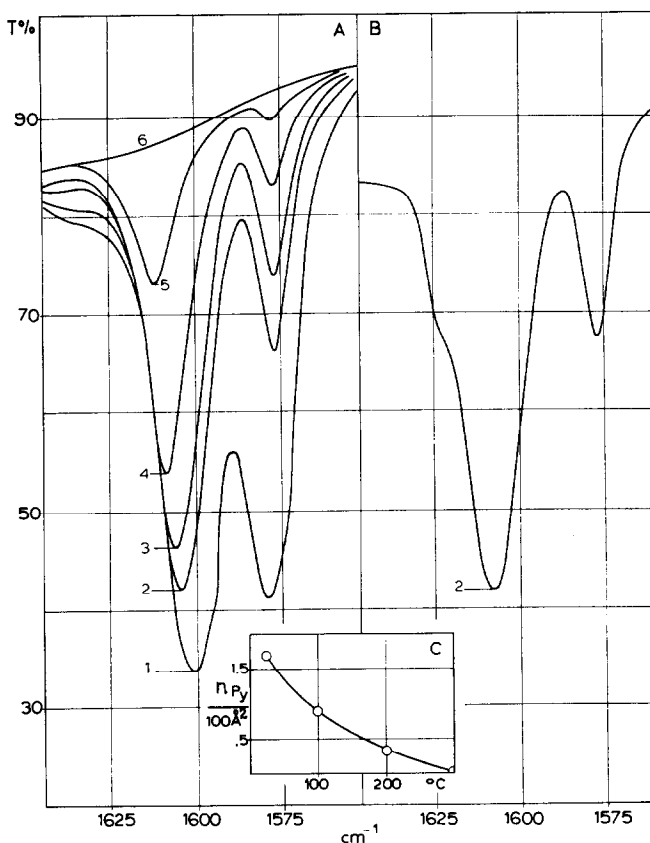
FIG. 3. The adsorption of pyridine (Py) onto $MgAl_2O_4$ dehydrated at 700°C. (A) The ir spectrum in the 8a–8b mode region of a regular sample. Curve 1, under a pressure of 5 Torr; Curves 2–6: after Py desorption at (°C): 25, 10 min; 25, 60 min; 100, 30 min; 200, 30 min; 300, 30 min. (B) The same as (A), for a partly inverted sample. (C) Number of molecules still adsorbed, as a function of Py evacuation temperature.

at room temperature does not restore the original OH spectrum entirely, but desorption at 200°C will do so. This means that some OH groups are also perturbed through a π-cloud H-bonding from Lewis-coordinated Py molecules. Moreover, this double interaction is found to give the LPy not a higher but rather a lower strength, as shown by the easier removal and the lower frequency of the 8a mode.

Finally, the carbon monoxide which could be adsorbed on this sample before Py adsorption is no longer adsorbable after Py adsorption. Only after Py evacuation at 200°C does the activity toward CO start to be recovered, and it becomes complete after the total elimination of LPy at 300°C.

It is therefore concluded that, out of the (at least) 1.7 Lewis sites per 100 Å² evidenced by the strong Py coordination, the 0.6 strongest ones are also responsible for the CO band at 2195 cm⁻¹.

The Adsorption of Carbon Dioxide

The chemisorption of CO_2 reveals acidic sites when the molecule preserves its linear shape upon adsorption, and basic sites as well as acid–base couples when carbonate-like species are formed (5, 6, 17). Figure 4C shows the adsorption of CO_2 onto $MgAl_2O_4$ in its quantitative aspects. It is seen that:

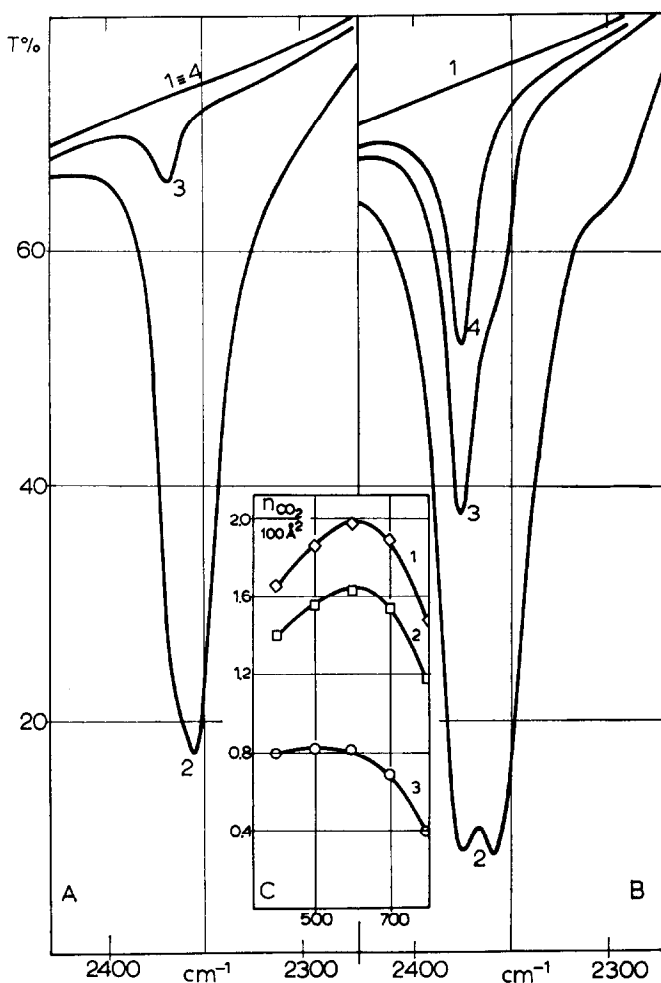(1) The uptake is pressure dependent and

FIG. 4. (A) Spectral modifications caused by the adsorption of CO_2 (40 Torr) in the 2230- to 2430-cm^{-1} range on a spinel sample dehydrated at 400°C. Curve 1, background; curve 2, 40 Torr of CO_2 added; curve 3, pumped off at room temperature, 30 sec; curve 4, pumped off at room temperature, 2 min. (B) The same as (A), for a sample dehydrated at 700°C. (C) Amounts of CO_2 adsorbed as a function of dehydration temperature at various CO_2 pressures: ($\Diamond \Diamond \Diamond$) 150 Torr; ($\Box \Box \Box$) 40 Torr; ($\bigcirc \bigcirc \bigcirc$) after evacuation at room temperature.

depends on dehydration temperature between 400 and 600°C only as far as the species reversible at room temperature are concerned, the nonreversible amount being nearly constant in the whole range.

(2) Quite a few of the coordination vacancies created upon water desorption are saturated by CO_2 at any dehydration stage. In particular, in the 400–600°C activation interval, 1.1 water molecules are desorbed per 100 $Å^2$, i.e., 2.2 OH groups,

to which only an increment of 0.25 CO_2 adsorbed molecules corresponds.

(3) In the 600–800°C dehydration interval, in which some 0.7 water molecules are further desorbed, there is a sharp decrease of both reversible and nonreversible CO_2 adsorption. As after each thermal treatment the surface area was checked by N_2 adsorption at 77°K and the adsorbed amounts were related to the actual area, this decreased activity is real and must be ascribed to some surface modifications.

In spite of the small coverage, CO_2 adsorption causes strong spectral changes of severe complexity, and these are now considered range by range.

The 2250- to 2450-cm⁻¹ Range

Absorption in this range is typical of the Σ_u^+ mode of linear CO_2 and is shown in Fig. 4 for spinel samples dehydrated at 400 and 700°C (sections A and B, respectively). At least two components are visible, centered at 2360 and 2375 cm⁻¹, respectively, whose intensities are nearly equal on the 700°C sample, while the low-frequency component is definitely predominant on the 400°C one. The low-frequency band is quickly removed on evacuation at room temperature, while the high-frequency one is also reversible at room temperature but requires prolonged pumping. Similar bands were also observed on transition aluminas (6, 18–20), although both position and reversibility were not quite the same, the higher-absorbing one, in particular, being much more resistant on aluminas.

Computer deconvolution of the spectra shows that the intensity of the low-frequency band grows in the 400–500°C dehydration interval and remains fairly constant for higher activation temperatures, while the high-frequency component grows in the whole 400–800°C interval. This suggests that neither of them is ascribable to physically adsorbed CO_2, because at the pressures used here P/P_0 is of the order of 10⁻⁵. An interaction with surface OH groups must also be ruled out, in view of the trend with activation temperature and the complete dehydroxylation achieved at 800°C. Both components are therefore assigned to CO_2 linearly coordinated to coordinatively unsaturated surface cations of somewhat different polarizing strength.

Preadsorption of Py at high coverages (a few Torr of Py) completely inhibits the formation of both linear CO_2 species, while the band at 2360 cm⁻¹ is formed again

when CO_2 contacts a surface from which Py has been desorbed at room temperature. This confirms that at least part of the Py exhibiting the lowest frequency 8a mode (shoulder at ∼1595 cm⁻¹) is due to a weak Lewis acidic site. The band at 2375 cm⁻¹ is gradually formed again after Py desorption at temperatures above room temperature.

Finally it is noted that the decreased activity toward CO_2 exhibited after activation above 600°C cannot be ascribed to these linear forms, so that the surface modifications previously postulated should probably be attributed to a lower basicity of oxide ions on a highly dehydrated surface.

The 3500- to 3800-cm⁻¹ Range

The main effect produced in this range by CO_2 adsorption is a perturbation of the high-frequency portion of the free OH band and the production of a sharp band at ∼3618 cm⁻¹, as shown in the inset to Fig. 5. This band is easily assigned on the basis of previous observations (6, 18, 19) to the ν_{OH} mode of surface bicarbonates formed through a specific interaction between CO_2 and surface OH groups.

A minor effect, partly responsible for the spectral modifications observed, is the formation of two medium-weak bands at 3725 and 3610 cm⁻¹, not resolved in Fig. 5 but clearly observed on fully dehydrated samples, which are not observed when CO_2 is allowed, at the same pressure, into the empty cell. They are thus assigned to a Fermi resonant couple of combination modes of CO_2 adsorbed in the linear form [these bands are normally observed at 3716 and 3609 cm⁻¹ in gaseous CO_2 (21)].

The 1200- to 1800-cm⁻¹ Range

Figures 5 and 6 show the carbonate-like species formed on a sample treated at 400 and 700°C, respectively. The spectra are quite complex and at least three families of surface compounds can be adduced on the basis of the resistance to evacuation
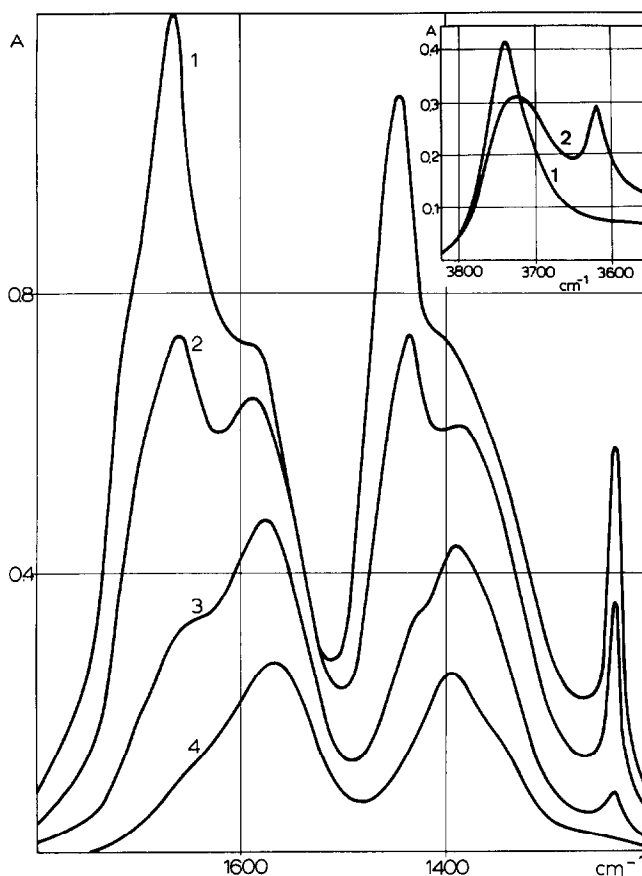
FIG. 5. The ir spectra in the carbonate region of $MgAl_2O_4$ dehydrated at 400°C. Curve 1, 40 Torr of CO_2; curve 2, evacuated at room temperature; curve 3, evacuated at 100°C; curve 4, evacuated at 200°C. Inset: Perturbation produced by CO_2 adsorption on the surface hydroxyls. Curve 1, sample dehydrated at 400°C; curve 2, 40 Torr of CO_2 added.

and the dependence on dehydration temperature.

(A) First there are the surface bicarbonates, whose ν_{OH} has been already mentioned and whose ν_{CO_2} modes are at 1660–1665 and 1430–1448 cm^{-1}, respectively (asymmetric and symmetric stretch), following the dehydration temperature, and whose δ_{OH} mode is at 1225–1240 cm^{-1}. Their amounts obviously depend on surface OH population and can be inhibited by the preadsorption of Py. This either means that H-bonded Py involves the reactive OH groups too strongly or that the bicarbonate formation proceeds through the preliminary coordination of CO_2 onto a coordinatively unsaturated cation of those

that also chemisorb Py, followed by the ligand displacement of a nearby hydroxyl. Bicarbonate formation is still inhibited after Py evacuation at room temperature, i.e., after the removal of nitrogen H-bonded Py, if any, and of weak LPy, whereas Py desorption at higher temperatures gradually allows bicarbonates to be formed upon CO_2 adsorption. This indicates that LPy molecules which are also H-bonded to surface OH groups through the π-cloud are responsible for bicarbonate inhibition, no matter which of the two effects is ultimately responsible. The answer to the above question probably lies in Parkyns' $C^{18}O_2$ experiments on γ-Al_2O_3 (19), in which it was shown that bicarbonates
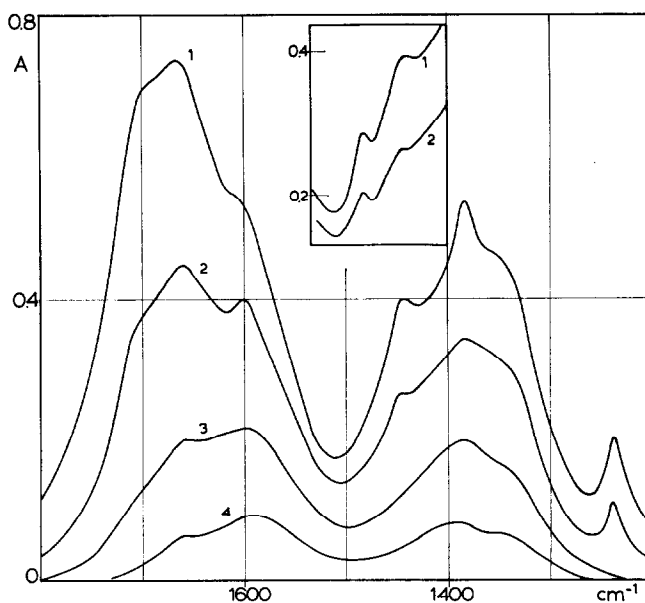
FIG. 6. The ir spectra in the carbonate region of $MgAl_2O_4$ dehydrated at 700°C. Curve 1, 40 Torr of CO_2; curve 2, evacuated at room temperature; curve 3, evacuated at 100°C: curve 4, evacuated at 200°C. Inset: Curves 1 and 2 obtained, in the 1400- to 1530-cm^{-1} range, on a partly inverted spinel sample.

form through the preliminary coordination of CO_2 to a coordinatively unsaturated cation.

(B) A second family of carbonates, definitely prevaling after high-temperature activations, has the high-frequency mode within 1660 and 1710 cm^{-1} (at least two main components are apparent at 1670 and 1710 cm^{-1}, respectively) and the low-frequency mode, broad and not resolved, at 1335–1355 cm^{-1}. Although the higher $\bar{\nu}$ mode slightly exceeds the frequency range previously indicated for bidentate species (17), this is the suggested assignment, as it is also consistent with its being favored by high degrees of dehydration. In fact bidentate formation requires a coordination vacancy to be available in the same coordination sphere of a basic oxygen.

(C) A third group of carbonates is also observed, whose high-frequency mode is centered between 1575 and 1660 cm^{-1}, depending on the dehydration temperature, and whose low-frequency mode is consist-

ently at 1390–1400 cm^{-1}.[1] This group prevails on the low-temperature-activated samples and is the carbonate species which is by far the most resistant to desportion (see, e.g., spectrum 4 of Figs. 5 and 6).

The assignment of this species is even less straightforward than the previous one, as the range is not really typical of any $(CO_3)^{2-}$ species but rather of $(CO_2)^-$ or carboxylate groups. Nevertheless, this assignment must, in our opinion, be discarded, as it is difficult to admit the existence on this system of cationic electron donor centers, especially at low dehydration stages. On the other hand, anionic electron donor centers would yield what is commonly called a monodentate carbonate rather than a carboxylate. This is in fact our assignment, even though both observed CO stretching modes are at some-

[1] On the top of the 1390- to 1400-cm^{-1} band, a sharp peak is often observed (see, e.g., spectrum 1 of Fig. 6) due to the Σ_g^+ mode of linearly bound CO_2, in which the adsorption produced enough asymmetry to make this mode weakly active.
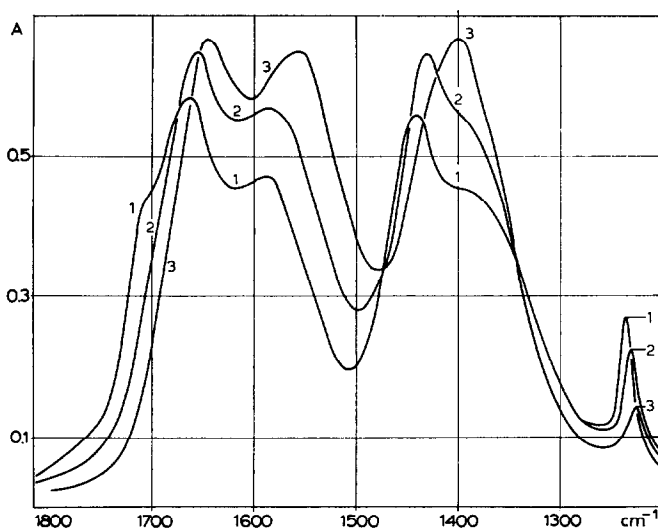
FIG. 7. Spectral modifications in the carbonate region due to the adsorption of small amounts of water onto preadsorbed CO_2. Curve 1, sample dehydrated at 600°C, contacted with CO_2 (40 Torr), and evacuated at 25°C; curve 2, 0.1 Torr of water added; curve 3, 0.3 Torr of water added.

what higher frequencies than normally found (*17*, *22*).

To check the assignment, small amounts of water vapor were allowed onto a sample that was previously dehydrated at 600°C, contacted with CO_2, and evacuated at room temperature (Fig. 7). We see that bicarbonates and the bidentates with ν_{CO} at 1710 cm^{-1} are quickly eliminated, while the other bidentates initially have their ν_{CO} mode shifted downward. For higher water amounts, they will be decreased in intensity. The bands tentatively assigned to monodentates are intensified, with the appearance of one more component whose high frequency mode is at 1550 cm^{-1}.

The reactions schematized below, which were also postulated on other systems (*22*),
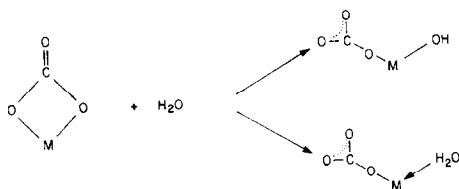
are probably caused by water adsorption and support the proposed assignment.

Samples with Anomalous Spectral Features

Some samples were found, mostly coming from a fast decomposition during preparation B, which exhibited to a variable extent some anomalous spectral features that can be summarized as follows:

(1) The OH spectrum exhibits, at the highest dehydration stages, a weak band at $\sim$3800 cm^{-1}, as shown by the dotted part of curve 4 in Fig. 1.

(2) After dehydration at $T > 500$°C, in the spectrum of chemisorbed CO there is a resolved shoulder at $\sim$2232 cm^{-1}, while the main band is a little broader and centered at $\sim$2205 cm^{-1} (see Fig. 2B) suggesting that it is made up of two components, the higher one being located at some 2210 cm^{-1}.

(3) Mode 8a of Py adsorbed and evacuated at room temperature (Fig. 3B) is definitely broader and centered at 1608 cm^{-1}, i.e., some five wave numbers above the position of regular samples, and possesses a resolved shoulder at 1623 cm^{-1}.

(4) CO_2 adsorption leads to the formation of small amounts of a bicarbonate

species, which only differs from the "regular" one with respect to the asymmetric ν_{CO_2} mode at 1480 cm^{-1} (see the inset to Fig. 6).

All of these features are typical of transition aluminas (1–4, 6–8, 23, 24) and were all shown to be connected with the existence on such systems of Al^{IV} ions (2–4, 6, 24). These data are thus assumed as the spectroscopic evidence for a partly inverted cationic distribution within fast decomposed samples.

DISCUSSION

Surface Hydroxyls

It is impossible to decide whether the 3740-cm^{-1} band is due to OH groups in the coordination sphere of Mg^{IV} or Al^{VI} or shared by both. We would only remark that the last two possibilities are consistent with the previous observation (1, 3, 4) that when the OH group involves Al ions and these are only Al^{VI}, the OH frequency is in the 3730- to 3750-cm^{-1} range. OH bands at higher frequencies are, on the contrary, characteristic of Al^{IV} ions (3, 36) and such an assignment yields one of the criteria for the identification of inverted samples.

Lewis Acidity

Lewis acidity is evidenced by the adsorption of LPy, CO, CO₂ in the linear form, and by the interaction between Py and the other two molecules. Py reveals two types of Lewis sites of different strengths. The concentration of the stronger one (8a mode at 1605–1615 cm^{-1}) is, after complete dehydration, over 2.0 molecules/100 Å^2.[2] The weaker LPy (8a mode at ~1595 cm^{-1}) is difficult to evaluate in

quantitative terms, but if the extinction coefficients of similar chemical structures can be assumed not to vary too much in a narrow spectral range, this species is expected to be rather scarce.

Lewis coordination of Py to Mg^{IV} sites on silica–magnesia gels is characterized by the 8a mode at 1610 cm^{-1} and by a high thermal resistance (15), while Py on MgO (Mg^{VI}) exhibits the 8a mode just below 1600 cm^{-1} and a low resistance to evacuation (26). On transition aluminas, two LPy of high and very high thermal resistance are observed, with 8a modes at ~1615 and ~1625 cm^{-1}, respectively (23), and both species are shown to be connected with Al^{IV} ions (4, 27), while on α-Al₂O₃ LPy at Al^{VI} centers is weakly held and absorbs at 1596 cm^{-1} (4, 24). These data allow the assignment of the strong LPy species observed on MgAl₂O₄ to sites involving Mg^{IV} ions and of the weak species to sites involving Al^{VI} ions. Data reported on the partly inverted samples also agree with this assignment. It is thus observed that the frequency of A₁ modes and the thermal resistance of LPy species are higher for tetrahedral than for octahedral ions, and that for a given coordination both frequencies and thermal resistance are higher the higher the polarizing power of the cation (Al^{IV} > Mg^{IV}) (28).

If a cross-sectional area of 6.74 Å^2 is assumed for an oxygen ion in the close-packed lattice (29), 100 Å^2 of the "averaged" (111) plane,[3] orderly dehydrated (6), are found to possess 7.0 octahedral ions and 3.5 tetrahedral ions which give rise to 1.75 tetrahedral coordinative vacancies, 5.25 octahedral coordinative vacancies, and 1.75 bridging coordinative vacancies. In the absence of any indication of the crystal plane most favorably exposed by MgAl₂O₄,

[2] The figure of 1.7 Py molecules/100 Å^2 of Fig. 3C slightly increases on a sample fully dehydrated at 800°C. Moreover, this is not the total amount of strong LPy, as Py evacuation at ambient temperature is shown in Fig. 3A to eliminate some of these species.

[3] There are two possible terminations for the (111) face of the spinel structure, in view of the existence of two layers with such an index of different cationic composition. By an "averaged" (111) face we mean a surface containing 50% of each termination.

a tentative simplified calculation can be also done as follows. The complete dehydration of 100 Å^2, containing 14.8 oxygen ions, brings about the elimination of 7.4 water molecules and leaves 7.4 cus oxygen ions and 7.4 cationic coordinative vacancies. The crude application of the stoichiometric ratio assigns 2.47 such coordinative vacancies to tetrahedral ions and 4.94 to octahedral ions. From either approach it is seen that Lewis coordination of Py approaches complete coverage of Mg^{IV} cus ions, while the saturation of Al^{VI} cus ions is fairly minimal, unless the extinction coefficient of the 1595-cm^{-1} 8a mode is very low. Data concerning CO adsorption and CO/Py interaction indicate that the band at $\sim$2200 cm^{-1} is ascribable to a few Mg^{IV} ions, whose concentration does not exceed some 15–20% of the total tetrahedral occupation. It is to be noted that the assignment of the $\sim$2200-cm^{-1} band can be made also in the absence of any datum on the adsorption of CO on silica–magnesia and without the information coming from CO/Py interaction, in that the behavior of CO on Al^{IV} of transition aluminas is quite different (*2*); the behavior of CO on MgO (Mg^{VI}) is also very different, leading to polymeric and ketenic structures rather than to σ-coordinated species, (*30–33*) and no CO chemisorbs on α-Al$_2$O$_3$ (*2*).

The adsorption of CO$_2$ in the linear form occurs at two types of Lewis acidic centers, the low-frequency band (2360 cm^{-1}) involving Al^{VI} cus ions and the high-frequency one (2375 cm^{-1}) involving Mg^{IV} cus ions. This assignment, which agrees with the trend of ion polarizing strength and with previous findings on η- and α-Al$_2$O$_3$ (*5, 6*), is definitely proved by the Py/CO$_2$ interaction previously reported. As for the amounts involved, there is no direct information from microgravimetric measurements in view of the simultaneous adsorption of CO$_2$ in other forms. However, it is believed that linear CO$_2$ also reveals a minor fraction of Lewis acidic centers. In

fact (i) the amount of Al^{VI} ions active in Lewis coordination is suggested by Py to be quite small, and the relevant Py species inhibits the 2360-cm^{-1} band entirely; (ii) considerable amounts of LPy coordinated at Mg^{IV} centers, whose amounts are known from Fig. 3a, must be desorbed at $T \geqslant 100$°C before the 2375-cm^{-1} band starts being restored. Besides, the difference between curves 3 and 2 of Fig. 4C is $\sim$0.8 CO$_2$ molecules/100 Å^2. This figure represents the amount of CO$_2$ reversibly adsorbed at room temperature, which was shown to include all of the linearly held species and a certain amount of carbonate-like species, so that the total amount of σ-coordinated CO$_2$ at either Lewis center is indirectly evaluated to be quite small and, in the case of Mg^{IV} ions, of the same order of σ-coordinated CO.

The small uptake of CO and linear CO$_2$ compared to the uptake of LPy suggests that the tetrahedral Lewis acidic sites are actually made up of a collection of ions, whose adsorbing center is the tetrahedral ion and whose strengths are influenced by the nature and number of coordinatively unsaturated ions surrounding it. A "hard" base like Py is able to chemisorb at each of such acidic centers, though with variable strength and frequency shift, while "soft" bases like CO and CO$_2$ can only chemisorb at those sites that are made very strong by the particular coordinative situation around them.

The present data, together with all data so far collected on Lewis acidity, allow us to conclude that at the surface of oxides of metals with no d electrons only the tetrahedral configuration allows the σ or Lewis coordination of (i) CO, with ν_{CO} well above that of the gas, (ii) of Py, with the 8a mode above 1600 cm^{-1},[4] and (iii) of CO$_2$

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[4] In this respect it is noteworthy that on highly dehydrated SiO$_2$, on which the creation of defects able to chemisorb H$_2$ at room temperature was previously demonstrated (*34*), some Py strongly

in a linear form, with the Σ_μ^+ mode above ~ 2360 cm^{-1}. The actual frequencies exhibited by such species, as well as their resistance to evacuation, strictly depend on the polarizing field produced by the tetrahedral ion, i.e., on the formal charge and ionic radius (28).

Surface Basicity

Surface basicity is revealed by the formation of carbonate-like structures upon CO_2 adsorption. In the case of bicarbonates, the basicity involves part of the surface OH groups, while the formation of monodentates and bidentates concerns the basicity of surface oxygen ions.

The quantitative data of Fig. 4C indicate that the overall coverage of CO_2 is quite small. In particular, the nonreversible fraction of the carbonate-like structures, which on the basis of the integrated absorbances approximately represents two-thirds of the total amount, is 0.8 groups/100 Å^2 after dehydration at 600°C and is halved at 800°C. In the first case, the data of Fig. 1 and the rough calculations reported above indicate that in 100 Å^2 of surface there are ~ 1.3 residual OH groups and ~ 6.7 cus oxygen ions, while in the second case there are 7.4 cus oxygen ions. The total coverages of carbonate-like structures under a high CO_2 pressure are, therefore, $\sim 15\%$ on the 600°C sample and $\sim 8\%$ on the fully dehydrated sample, while the nonreversible fractions are ~ 10 and $\sim 5.5\%$, respectively. These rough figures indicate that the surface basicity of Mg spinel is low, as on all Al-containing oxides (5, 6, 19), and that it is higher than on transition aluminas (6) and lower than on α-Al$_2$O$_3$ (5).

Moreover, these figures and the spectra indicate that the decrease of activity for carbonate formation with increasing dehydration temperature cannot be solely as-

cribed to the decreased population of sites for bicarbonates, but is also due to a decreased activity of surface oxygens, whose basicity is deduced to be promoted by surface hydration. A similar conclusion was drawn in the case of α-Al$_2$O$_3$ (5). Also the transformation of monodentate carbonates into bidentates at high dehydration stages is the monitor of a decreased oxygen basicity and of the need of a cus cation to cooperate in the stabilization of the surface group. In fact after a dehydration at 400°C the surface is already $\sim 80\%$ dehydrated, and at each stage there are as many cationic as anionic vacancies, so that bidentates could form at each stage. Nevertheless, when the surface hydration is still high enough, there are some oxygens basic enough to stabilize carbonates in the monodentate configuration. Also other systems exhibit the formation of bridging structures on a highly dehydrated surface. On α-Al$_2$O$_3$ (4, 5) and on MgO (22), where the only cationic coordination is the octahedral one, bidentates are by far the most prevailing structures, so that on this group of oxides this behavior seems peculiar to the octahedral coordination rather than to the chemical nature of the cation. On the contrary, on all transition aluminas only organic carbonates, i.e., structures bridging a basic oxygen and an anionic vacancy in two adjoining coordination spheres, are formed to an appreciable extent after dehydration at high temperature (6, 19). This is due, we believe, to the higher polarizing power of Al^{IV} compared to Al^{VI}: The carbonate group formed at the basic oxygen carried by an Al^{VI} is better stabilized by bridging onto an adjoining Al$_{cus}^{IV}$ rather than on a coordinative vacancy carried by the same Al^{VI}, even though a higher strain of the O–C–O angle is likely to be produced. In fact the distance between two lattice oxygens in a spinel structure is somewhat higher than normally observed in organic carbonates. On MgAl$_2$O$_4$, the introduction of a new element into the same spinel struc-

chemisorbs exhibiting the 8a mode at ~ 1625 cm^{-1} (35). Also Py on AlPO$_4$ exhibits the 8a mode above 1610 cm^{-1} (36).

ture, as is typical of some transition aluminas, causes bidentates to become again the most abundant species on a highly dehydrated surface, as on systems with the only octahedral coordination. This is explained in view of the lower polarizing power of Mg^{IV} compared to Al^{IV}, so that the bridging carbonate preferably forms onto the same Al^{VI} cation carrying the cus oxygen rather than on two adjoining cations.

The conversion of bidentates into monodentates after admission of some water indicates that the oxygen center responsible for the two structures is the same and that only its basicity varies as a consequence of the varied surface hydration. As far as bicarbonates are concerned, Py/CO_2 interaction is again fairly useful for the assignment. In fact it shows that LPy held at Mg^{IV} cus ions must be evacuated for bicarbonates to form again upon contact with CO_2. This interaction does not answer the question concerning the mechanism of bicarbonate formation previously considered, in that LPy at Mg^{IV} could inhibit the formation of bicarbonates either because a preliminary σ-coordination of CO_2 at such sites is needed, or because the basic OH groups are next to an Mg^{IV} center from which LPy strongly involves them in a π-cloud H-bonding. It is also possible that the difference between the two inhibition mechanisms is merely formal, and that the acid–base double center is actually needed to form a bridging bicarbonate, as also suggested in the case of η-Al_2O_3. This hypothesis is confirmed by the experiment of Fig. 7. The admission of small amounts of water, which either coordinate at cus cationic sites or dissociatively chemisorb at anion–cation cus double centers (7), quickly eliminates the bicarbonates, indicating that the need of a cus cation for bicarbonate formation is not merely a kinetic requirement but rather a structural one. The need of the tetrahedral coordination for the formation of bicarbonates at

the surface of this Al-containing oxide is thus evidenced, and is consistent with previous findings concerning the presence of bicarbonates at the surface of all transition aluminas (6, 18, 19) and their absence at the surface of well-crystallized α-Al_2O_3 (5). Finally, the low CO_2 coverage and the continuous frequency shift of the bands of carbonate-like structures with both coverage and surface hydration suggest that, as in the case of Lewis acidity, surface basicity is also promoted by a certain number of surface ions surrounding the adsorbing center, which can participate in the charge release mechanism from the surface to the adsorbed group. This hypothesis was also proposed for the η-$Al_2O_3/$ CO_2 interaction (6), where the definitely lower CO_2 coverage indicated that an even larger number of surface ions were involved in the chemisorption process.

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