

Infrared Spectroscopic Study of the Carbon Dioxide Adsorption on the Surface of Ga₂O₃ Polymorphs

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The adsorption of CO₂ over a set of gallium (III) oxide polymorphs with different crystallographic phases (α , β , and γ) and surface areas (12–105 m² g⁻¹) was studied by in situ infrared spectroscopy. On the bare surface of the activated gallias (i.e., partially dehydroxylated under O₂ and D₂ (H₂) at 723 K), several IR signals of the O–D (O–H) stretching mode were assigned to mono-, di- and tricoordinated OD (OH) groups bonded to gallium cations in tetrahedral and/or octahedral positions. After exposing the surface of the polymorphs to CO₂ at 323 K, a variety of (bi)carbonate species emerged. The more basic hydroxyl groups were able to react with CO₂, to yield two types of bicarbonate species: mono- (m-) and bidentate (b-) [$\nu_{\text{as}}(\text{CO}_3) = 1630 \text{ cm}^{-1}$; $\nu_{\text{s}}(\text{CO}_3) = 1431$ or 1455 cm^{-1} (for m- or b-); $\delta(\text{OH}) = 1225 \text{ cm}^{-1}$]. Together with the bicarbonate groups, IR bands assigned to carboxylate [$\nu_{\text{as}}(\text{CO}_2) = 1750 \text{ cm}^{-1}$; $\nu_{\text{s}}(\text{CO}_2) = 1170 \text{ cm}^{-1}$], bridge carbonate [$\nu_{\text{as}}(\text{CO}_3) = 1680 \text{ cm}^{-1}$; $\nu_{\text{s}}(\text{CO}_3) = 1280 \text{ cm}^{-1}$], bidentate carbonate [$\nu_{\text{as}}(\text{CO}_3) = 1587 \text{ cm}^{-1}$; $\nu_{\text{s}}(\text{CO}_3) = 1325 \text{ cm}^{-1}$], and polydentate carbonate [$\nu_{\text{as}}(\text{CO}_3) = 1460 \text{ cm}^{-1}$; $\nu_{\text{s}}(\text{CO}_3) = 1406 \text{ cm}^{-1}$] species developed, up to approximately 600 Torr of CO₂. However, only the bi- and polydentate carbonate groups still remained on the surface upon outgassing the samples at 323 K. The total amount of adsorbed CO₂, measured by volumetric adsorption (323 K), was $\sim 2.0 \mu\text{mol m}^{-2}$ over any of the polymorphs, congruent with an integrated absorbance of (bi)carbonate species proportional to the surface area of the materials. Upon heating under flowing CO₂ (760 Torr), most of the (bi)carbonate species vanished at $T > 550 \text{ K}$, but polydentate groups remained on the surface up to the highest temperature used (723 K). A thorough discussion of the more probable surface sites involved in the adsorption of CO₂ is made.

1. Introduction

Gallium oxide has recently emerged as a relevant catalytic material (either bulk or supported) for light alkane dehydrogenation and aromatization (Cyclar process),^{1–4} hydrocarbon isomerization,⁵ nitrogen oxides reduction by hydrocarbons,^{6–8} steam reforming of methanol,^{9,10} carbon dioxide hydrogenation to methanol,^{11–13} and carbon dioxide (dry) reforming of methane.¹⁴ However, as compared to aluminas, little is yet known about its surface chemistry.

The existence of five polymorphs of gallium sesquioxide (also named gallia) and their stability relations were studied by Roy et al.¹⁵ in the early fifties. Among these modifications, the β -form is the only stable one, whereas all the other polymorphs (or transition gallias) are metastable and transform into β -Ga₂O₃ at sufficiently high temperatures. The α -, β -, and γ -gallia forms are hexagonal corundum-type (space group $R\bar{3}c$),^{15,16} monoclinic (space group $C2/m$),^{15,17,18} and cubic defect spinel-type (space group $Fd\bar{3}m$)¹⁹ structures, similar to the well-known α -, θ -, and γ -Al₂O₃ structures, respectively.

In regard to the surface properties of the gallia polymorphs, a few studies are focused on the acid–base surface properties of these oxides, using mainly infrared spectroscopy. The Lewis and Brønsted acidities of the α -, β -, and γ forms were investigated by adsorbing carbon monoxide,^{21–23} pyridine,^{21,24} 2,6-dimethylpyridine,²⁴ and acetonitrile.²⁴ The basicity was explored only

on α - and γ -Ga₂O₃, with carbon dioxide, within a reduced range of experimental conditions,^{21,24} despite the remarkably high reactivity of the surface carbonate group with hydrogen.¹³

Along this last guideline, the development of an active Pd/Ga₂O₃ catalyst for methanol synthesis from CO₂ hydrogenation, able to compete with the classical Cu/ZnO formulation, was first reported by Fujitani et al.¹¹ Later on, Bonivardi et al. showed that the addition of gallium oxide to a Pd/SiO₂ catalyst produced a dramatic improvement of the catalytic performance to give oxygenated compounds from carbon dioxide hydrogenation:¹² the turnover rate to methanol increased up to 500-fold (CO₂/H₂ = 1/3, 523 K, and 3 MPa) upon going from clean Pd/silica to Ga–Pd/silica (Ga-to-Pd atomic ratio = 8), and the selectivity to methanol went up, from 17% to 70%, the higher the gallium content on the Pd/SiO₂ was. Bonivardi et al.¹² suggested that the mechanism of methanol synthesis from CO₂ hydrogenation on Ga–Pd/SiO₂ should involve intermediates from adsorbed CO₂ rather than CO, similar to those proposed by Cu/ZnO or over Cu/ZrO₂.^{25–28} Several of these intermediates were detected by temperature-programmed reaction (between 323 and 723 K at 0.1 MPa) under flowing a H₂/CO₂ mixture over pure β -Ga₂O₃ and Pd/ β -Ga₂O₃ (1 wt % Pd), employing in situ Fourier transform infrared (FTIR) spectroscopy.¹³ In particular, carbonate species were hydrogenated over bulk β -Ga₂O₃ to formate and methoxy groups, by hydrogen atoms provided by the dissociative chemisorption of molecular hydrogen on gallia, albeit at temperatures far higher than the usual “methanol synthesis conditions” (523 K).

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Then, a more detailed study on the adsorption of CO₂ on the gallia polymorphs can bring light to a further understanding of their reactivity. This work peruses the interaction of carbon dioxide over different gallium oxide crystal phases by in situ FTIR spectroscopy, between 323 and 723 K, focusing on the characterization of the different surface hydroxyl groups and of the hydrogen–carbonate (bicarbonate) and carbonate species.

2. Experimental Section

2.1. Materials. All the gallia polymorphs were obtained from Ga(NO₃)₃·xH₂O and Ga₂O₃ supplied by Strem Chemicals (99.99% and 99.998% Ga, respectively). We followed the basic preparation methods described in a previous work²⁰ to obtain polymorphs with Brunauer–Emmett–Teller surface areas (*S*_{BET}) between 12 and 105 m² g⁻¹, as briefly outlined below.

Two pure phases of α-Ga₂O₃ were prepared from Ga(NO₃)₃·xH₂O in aqueous NH₄OH (pH = 10), at room temperature (RT).²¹ The precipitated gel was washed several times with doubly distilled water until no residual NO₃⁻ anions were detected in the washing water by UV spectroscopy. One part of this gel was aged at 343 K (3 h) and dried under vacuum at 298 K (4 h), and finally, it was calcined in air at 773 K (1 h) to give α-Ga₂O₃ with an *S*_{BET} = 40 m² g⁻¹ (coded α(40) from now on). The other part of the gel was dried at 343 K (10 h) and calcined at 823 K (6 h) in air; this α-Ga₂O₃ sample (*S*_{BET} = 20 m² g⁻¹) was labeled as α(20).

The γ- and β-Ga₂O₃ phases were synthesized as follows. Hydrated gallium hydroxide gel was obtained by adding an ammonia ethanolic solution (50% v/v) to 7 wt % Ga(NO₃)₃·xH₂O in ethanol at RT. The gel was filtered and washed with ethanol until no NO₃⁻ anions were detected. The resulting material was then dried at 343 K (1 h) and air calcined at 823 K (8 h). A γ-Ga₂O₃ polymorph with an *S*_{BET} equal to 105 m² g⁻¹, coded as γ(105), was obtained. A portion of this last gallium oxide was further calcined in air at 923 K (6 h) to give a β-Ga₂O₃ (*S*_{BET} = 64 m² g⁻¹), labeled as β(64).

Another β-gallia sample was prepared by direct calcination in air of the commercial gallium oxide at 1073 K during 6 h. The gallia polymorph obtained, with an *S*_{BET} equal to 12 m² g⁻¹, was coded as β(12).

The crystallographic phase of each gallium oxide type was determined by X-ray diffraction spectrometry (XRD) using a Shimadzu XD-D1 apparatus (Cu Kα radiation). The *S*_{BET} values of the gallium oxides, previously outgassed at 473 K for 3 h under dynamic vacuum (base pressure = 1.33 × 10⁻⁴ Pa), were measured at 77 K employing a Micromeritics Accusorb 2001E apparatus.

Carbon dioxide isotherms were measured at 293 K over a selected set of the polymorphs, using a flow glass reactor connected to one of the ports of the manifold of the Accusorb unit. Before the CO₂ uptakes were measured, each sample was pretreated as described below (activations under O₂ and H₂).

The phase purity and other main features of the samples used in this work are summarized in Figure 1 and Table 1.

2.2. Gallia in-Situ FTIR Studies. Self-supported wafers of each gallia sample (diameter = 13 mm) were made by pressing 30 mg of powder at 5 ton cm⁻². These wafers were placed in turn into a transmission infrared Pyrex cell with water-cooled NaCl windows, which was attached to a conventional manifold system, as previously described.²⁰

Before any adsorption–desorption experiment of CO₂ took place, each wafer was pretreated in-situ: (i) to allow uniform dehydration and dehydroxylation of the surface of the metal oxides and the generation of coordinatively unsaturated (*cus*)

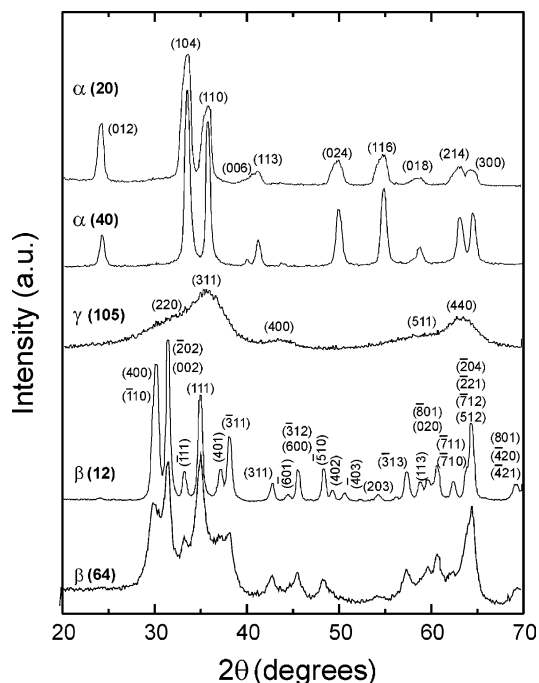


Figure 1. XRD patterns of the gallia polymorphs used in this study.

Ga³⁺ cations²⁰ and (ii) to remove the artificial bands in the 3000–2800 cm⁻¹ region that arise from oil contamination during wafer preparation, which are attributed to the C–H stretching modes.²⁰ This pretreatment procedure was accomplished by the following: (a) an activation step, heating in O₂ (100 cm³ min⁻¹, 5 K min⁻¹) from 298 to 723 K and, next, cooling to 298 K under vacuum (base pressure = 1.33 × 10⁻⁴ Pa), followed by (b) an activation step, heating in H₂ or D₂ (100 cm³ min⁻¹, 5 K min⁻¹) from 298 to 723 K and, then, after 20 min in a vacuum, cooling gradually, to allow reference IR spectra of the pretreated wafers to be taken at different temperatures.

An isothermal CO₂ adsorption–desorption experiment at 323 K was carried out over each pretreated Ga₂O₃ sample, by increasing and decreasing the CO₂ gas pressure inside the cell. Next, a temperature-programmed adsorption (TPA) equilibrium experiment was run, by heating from 323 to 723 K (5 K min⁻¹) while the CO₂ gas flow (100 cm³ min⁻¹) was kept constant through the cell at atmospheric pressure (101.3 kPa = 760 Torr).

No change in the surface area and/or the original XRD pattern of any of the gallia samples was detected after the in-situ FTIR TPA experiments.

The in-situ transmission infrared spectra were registered employing a Shimadzu 8210 FTIR spectrometer with a DLATGS detector (4 cm⁻¹ resolution, 100 scans). When needed, background correction of the spectra was achieved by subtracting the spectra of the pretreated wafers at each temperature; a Lorentzian sum function was used to fit the overlapping bands and to measure peak areas and/or intensities.²⁹

All the gases used in this study were high purity grade and were further purified as follows: H₂ (AGA, 99.999%), N₂ (AGA, 99.998%), and CO₂ (AGA, 99.996%) were passed through MnO/Al₂O₃ and molecular sieve (3 Å, Fisher Co.) traps to eliminate oxygen and water impurities, respectively; O₂ (AGA, 99.999%) was passed through a molecular sieve (3 Å, Fisher Co.) and Ascarite traps to remove water and carbon dioxide, respectively. D₂ (Scott C.P. Grade 99.7%) was introduced into the cell without further purification.

TABLE 1: Polymorphs of Gallium Oxides Used in This Work

sample code	solvent	drying	calcination	crystal phase	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	CO_2 uptake ^a ($\mu\text{mol m}^{-2}$)
$\alpha(20)^b$	H_2O	air, 343 K (10 h)	823 K (6 h)	α	20	
$\alpha(40)^b$	H_2O	vacuum, 298 K (4 h)	823 K (6 h)	α	40	2.0
$\gamma(105)^b$	$\text{C}_2\text{H}_5\text{OH}$	air, 343 K (1 h)	823 K (8 h)	γ	105	1.8
$\beta(64)^b$	$\text{C}_2\text{H}_5\text{OH}$	air, 343 K (1 h)	923 K (6 h)	β	64	2.3
$\beta(12)^c$			1073 K (5 h)	β	12	

^a Measured at 293 K ($p_{\text{CO}_2} = 760$ Torr; see text). ^b $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ as precursor. ^c Commercial Ga_2O_3 as precursor.

3. Results and Discussion

3.1. Surface OH(OD) Groups. The IR spectra of the pretreated gallium oxides, before the adsorption of CO_2 and after environmental background subtraction (rather than pretreated wafer subtraction), showed several overlapping bands between 3800 and 3300 cm^{-1} , due to the stretching modes of different hydroxyl groups. It is important to note that the activation under H_2 of the gallium oxides only reduces the band intensity of the OH species; it does not change the general features of the spectra.²⁰ Since the total surface area and the crystal phase of the oxides were preserved after all the in-situ FTIR experiments, the decrease in the intensity of the OH bands is clearly caused by a partial dehydroxylation of the oxides after the activation by heating in hydrogen.²⁰

Still, as the spectra in the hydroxyl IR region were obscured by the interference of gaseous water from the environment (outside the IR cell), we decided to employ deuterium instead of hydrogen during the activation process to study the stretching infrared bands of surface OH (or OD) groups in more detail. The use of D_2 in the pretreatment protocol afforded excellent spectra in the 2800–2400 cm^{-1} region, with a higher signal-to-noise ratio and better resolved signals than the activation under H_2 . Therefore, we will discuss here the spectra of the gallia polymorphs activated under oxygen and then under D_2 , i.e., oxides where all the OH groups were exchanged to OD species.

Figure 2 presents the IR signals in the 2800–2400 cm^{-1} region at 323 and 723 K for three of the pretreated polymorphs. Despite the complex features of these spectra, both the intensity and the position of the bands assigned to the stretching mode of the OD groups— $\nu(\text{OD})$ —remained almost unchanged along the full range of temperature, i.e., during the last cooling step performed at the end of the pretreatment protocol (and after 20 min in a vacuum at 723 K), except for the α - Ga_2O_3 polymorph.

Figure 3 plots the functional relationship between the total integrated absorbance of the whole $\nu(\text{OD})$ band after the pretreatment procedure and the surface areas of the full set of gallia polymorphs. The linear relationship obtained suggests that these OD species are located on the surface of the oxides; that is, the surface concentration of these groups is approximately the same over each polymorph. It follows then that the chosen pretreatment protocol was effective to produce uniform dehydration—or partial dehydroxylation—of the oxides.

Several peaks can be easily distinguished in Figure 2, which are usually assigned to mono-, di-, and/or tricoordinated OD groups bounded to Ga^{3+} surface cations.^{22,23,30} Nevertheless, we can go further in the assignment of these OD surface groups on the gallias by considering the approaches used to identify the OH surface species on one of the closer neighbor oxides, i.e., aluminas, due to their structural similarities.

Yet, different models have been developed to assign the hydroxyls infrared spectrum of aluminas, viz., Knözinger's,³¹ Peri's,³² Tsynganenko's,³³ and Busca's models,³⁴ and it is worth mentioning that, after decades of work devoted to the study of the OH groups on the surface of aluminas, some controversy

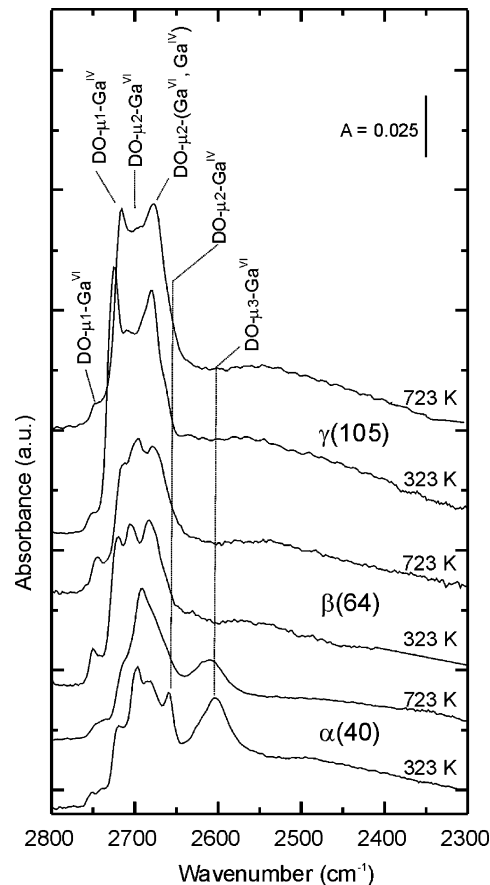


Figure 2. Infrared spectra measured at 723 and 323 K of the stretching mode of surface OD groups of selected gallia polymorphs after their thermal activation at 723 K, first under O_2 (760 Torr) and then under D_2 (760 Torr). No background subtraction was made.

still remains about the assignment of the $\nu(\text{OH})$ signals.^{35,36} However, in general terms, all these models have a point in common: the lower wavenumbers for the alumina hydroxyls can be readily explained in terms of increasing covalency of the Al–O bond in the Al–OH entity, which weakens the O–H bond strength. In other words, the isolated, monocoordinated OH groups are assigned to higher wavenumber signals, and the multicoordinated OH species are systematically assigned to the bands located at the lowest wavenumbers.

Probably, the most successful model to describe the surface OH groups of aluminas is the one developed by Knözinger and Ratnasamy.³¹ Briefly, this model considers the following: (i) the termination of γ - and η -alumina occurs along a limited number of low-index crystal planes, namely, the (111), (110), and (100) planes; (ii) neither reconstruction nor ion migration occurs during the dehydration process at high temperatures; and (iii) the stretching wavenumber of the OH species is determined by the net electrical charge (NC) of the OH group, where the NC is determined by the coordination of the OH group and of the cation(s) involved in the bonding. The NC is calculated as the sum of the negative charge of the anion (OH) and the sum

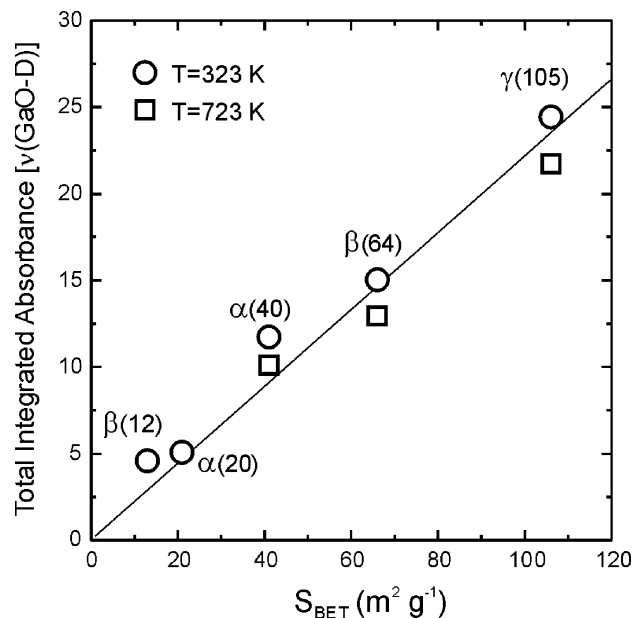


Figure 3. Relationship between the total integrated absorbance of the surface OD bands and the Brunauer–Emmett–Teller surface area (S_{BET}) of the gallia polymorphs.

of the strengths of the electrostatic bonds (i.e., the cation charge divided by its coordination number) between the anion and the adjacent cations.³¹ On the basis of these assumptions, Knözinger and Ratnasamy selected nine possible OH configurations, which were reduced to five configurations after dismissing possible differences of relative orientation of the OH species related to the Al³⁺ cations.³¹ The highest wavenumber bands were assigned to the configurations with the lowest NC values and vice versa.

So, the use of Knözinger's model to assign the different $\nu(\text{OD})$ bands on our Ga₂O₃ samples requires previous considerations from a structural standpoint. In the case of α -Ga₂O₃, which has a corundum structure like α -Al₂O₃, all Ga³⁺ ions are in a 6-fold coordination.^{16,21} Then, assuming that neither reconstruction nor relaxation of the surface atoms occurs, we can only expect Ga^{VI} on the surface for any cleavage plane of this polymorph. The monoclinic β -Ga₂O₃ has two kinds of coordinated Ga³⁺ ions, each one in the same bulk proportion, namely, octahedral and tetrahedral—hereafter referred to as Ga^{VI} and Ga^{IV}, respectively.^{17,37} The species β -Ga₂O₃ shows two cleavage planes; the far more frequent and stable is the (100), the second being the (001).^{38,39} The first plane is mainly formed by oxygen bonded to Ga^{VI} and Ga^{IV} in identical surface proportions.^{40,41} Finally, for γ -Ga₂O₃, which features a spinel structure with predominance of Ga³⁺ in octahedral coordination,^{21,42} there is no preponderance reported, to the best of our knowledge, of any cleavage plane.

Furthermore, some of us have recently identified and characterized by IR spectroscopy two kinds of Ga–H surface bonds, as endorsed by the comparison of the measured IR spectra of the surface of different well-defined Ga₂O₃ polymorphs (α -, β -, and γ -Ga₂O₃) with the spectra of known gallium hydrides molecules²⁰ and with the properties forecast by quantum chemical calculations on the β -Ga₂O₃ (100) crystal plane.⁴⁰ An excellent correlation between the gallium site coordination in the bulk of the gallia polymorphs and the assigned $\nu(\text{Ga}^{\text{VI}}\text{–H})$ or $\nu(\text{Ga}^{\text{IV}}\text{–H})$ surface signal was observed on the pretreated oxides. As small deviations of the surface Ga coordination from the ideal or theoretical bulk composition are to be expected after relaxation or reconstruction due to surface

reordering, we concluded that (i) almost 90% of the surface Ga³⁺ cations are Ga^{VI} species on α -Ga₂O₃, while the remaining 10% are in tetrahedral position, (ii) approximately half of the surface gallium sites are Ga^{VI} or Ga^{IV} species over the β -Ga₂O₃ polymorph, and (iii) an enrichment of 73% of Ga^{VI} is observed in the case of γ -Ga₂O₃.²⁰ In all these cases, the samples went through the same pretreatment protocol as the one described in the Experimental Section.

We can now take a closer look at the IR spectra in the OD region (Figure 2). Surely, the detailed features of the IR adsorption spectrum on α -Ga₂O₃ have to be mainly ascribed to OD groups bonded to Ga^{VI} cations, but the inclusion of surface Ga^{IV} in some species must also be considered (see below). Keeping in mind Knözinger's rule—the higher the stretching wavenumber the lower the group coordination—the OD infrared bands on this gallia polymorph at 723 K are assigned as follows: the very weak peak at 2746 cm⁻¹ to monocoordinated OD on one Ga^{VI} cation (DO– μ_1 -Ga^{VI}, NC = –0.50), the strong band at 2699 cm⁻¹ to OD dicoordinated to two Ga^{VI} cations (DO– μ_2 -Ga^{VI}, NC = 0), and the medium and broad signal at 2604 cm⁻¹ to triple bonded OD over three Ga^{VI} cations (DO– μ_3 -Ga^{VI}, NC = 0.50). The first two peaks can be neatly appreciated in the β - and γ -Ga₂O₃ polymorphs too. However, the last band at 2604 cm⁻¹ can hardly be distinguished on the gallium oxides with monoclinic and cubic spinel crystalline structures, that is, where the probability of finding a surface ensemble of three adjacent Ga^{VI} cations should be almost zero owing to the increasing presence of Ga^{IV} cations on the surface of the β and γ phases. With respect to the shoulders at 2720, 2682, and 2659 cm⁻¹, it is possible to ascribe these signals to the presence of Ga³⁺ in a 4-fold coordination, which will be discussed later.

Figure 2 also shows two additional, intense, and sharp peaks at 2719 and 2680 cm⁻¹ (at any temperature) on both the β and γ gallia samples, between which the strong band at 2699 cm⁻¹, related to OD dicoordinated to two Ga^{VI} cations, was located in the α polymorph. Among the possible configurations, the most plausible assignments for these two bands are the following: OD groups monocoordinated to one Ga³⁺ cation in tetrahedral position (DO– μ_1 -Ga^{IV}, NC = –0.25) and OD dicoordinated to Ga^{IV} and Ga^{VI} cations [DO– μ_2 -(Ga^{IV}, Ga^{VI}), NC = 0.25], respectively.

Together with the above-mentioned surface ODs, there is also, however, a dicoordinated configuration that is difficult to disregard a priori: DO– μ_2 -Ga^{IV} (NC = 0.50) on the β - and γ -polymorphs. Unfortunately, the broad band below 2650 cm⁻¹ clearly interferes in the detection and/or assignment of the signals to one or more surface species. This very broad $\nu(\text{OD})$ band, clearly observed on the β - and γ -polymorphs, is usually attributed to hydrogen-bonding interactions between adjacent OD (or OH) groups that downshift and broaden the $\nu(\text{OD})$ bands.

Table 2 summarizes the $\nu(\text{OD})$ or $\nu(\text{OH})$ wavenumbers measured in this work at 323 K on the Ga₂O₃ polymorphs, which were thermally activated first under O₂ and then under D₂ or H₂, at 723 K each. The experimental ratios of the $\nu(\text{OH})/\nu(\text{OD})$ frequencies were in the range of 1.35–1.36, in agreement with the expected theoretical ratio of 1.37 for the H–D isotopic exchange of OH species [$\nu(\text{OH})/\nu(\text{OD}) = (\mu_{\text{OD}}/\mu_{\text{OH}})^{1/2}$, where μ_{OD} and μ_{OH} are the reduced masses of OD and OH, respectively].

The relative intensity and location of the OH IR peaks at 323 K on our pretreated gallias are congruent with those reported by Otero Areán's group^{22–24,30} on their activated (outgassed at

TABLE 2: Stretching Wavenumbers of OD and OH Species on Activated Gallia Polymorphs

NC ^a	OD (or OH) config	This Work ^{b,k}						Other Works ^{c,k} (refs 21, 23, and 30)		
		$\nu(\text{OD})$ (cm ⁻¹)			$\nu(\text{OH})$ (cm ⁻¹)			$\nu(\text{OH})$ (cm ⁻¹)		
		$\alpha(40)$	$\beta(64)$	$\gamma(105)$	$\alpha(40)$	$\beta(64)$	$\gamma(105)$	$\alpha\text{-Ga}_2\text{O}_3^d$	$\beta\text{-Ga}_2\text{O}_3^e$	$\gamma\text{-Ga}_2\text{O}_3^f$
-0.50	DO- $\mu_1\text{-Ga}^{\text{VI}}$	2746 w	2750 w	2750 w	3735 w	3720 w	n.d.	g		
-0.25	DO- $\mu_1\text{-Ga}^{\text{IV}}$	2720 sh	2719 s	2715 s	n.d.	3683 s	3680 s	3693 sh	3695 s	3692 s
0	DO- $\mu_2\text{-Ga}^{\text{VI}}$	2699 s	2702 s	2695 s	3647 s	3660 s	3655 s	3656 s	3672 s	3665 s ^h
0.25	DO- $\mu_2\text{-(Ga}^{\text{VI}}, \text{Ga}^{\text{IV}})$	2682 sh	2680 s	2675 s	n.d.	3634 s	3629 s		3650 s	3637 s ⁱ
0.50	DO- $\mu_2\text{-Ga}^{\text{IV}}$	2659 s			n.d.			3604 sh		
0.50	DO- $\mu_3\text{-(Ga}^{\text{VI}})$	2604 m			3543 m			j		

^a Net charge. ^b Values measured at 323 K in a vacuum over the gallium oxides, which were thermally activated at 723 K, first under O₂ (101.3 kPa) and then under D₂ or H₂ (101.3 kPa). See text. ^c Values measured at 77 K in a vacuum, on oxides thermally activated in a vacuum at 673 K, except for Vimont et al.²⁴ ^d $S_{\text{BET}} = 77 \text{ m}^2 \text{ g}^{-1}$. ^e $S_{\text{BET}} = 40 \text{ m}^2 \text{ g}^{-1}$. ^f $S_{\text{BET}} = 120\text{--}160 \text{ m}^2 \text{ g}^{-1}$. ^{h,i} These bands were reported as a broad one at 3660–3330 cm⁻¹ in the work of Vimont et al.²⁴ ^j A very weak band at $\sim 3750 \text{ cm}^{-1}$ and a broad band at $\sim 3550 \text{ cm}^{-1}$ can be distinguished in Figure 3b of the work of Lavalley et al.²¹ ^k These letters have the following meaning: s = strong, m = medium, w = weak, v = very, b = broad, and sh = shoulder.

673 K) gallia polymorphs (Table 2). In the case of the α -polymorph, two (not reported) signals in the work of Lavalley et al.,²¹ a very weak one at $\sim 3750 \text{ cm}^{-1}$ and a broad band at $\sim 3550 \text{ cm}^{-1}$, can clearly be discerned on the spectrum of their $\alpha\text{-Ga}_2\text{O}_3$ sample, which are coincident with the OH stretching wavenumbers assigned here to the HO- $\mu_1\text{-Ga}^{\text{VI}}$ and HO- $\mu_3\text{-Ga}^{\text{VI}}$ configurations, respectively. Their shoulder at 3693 cm⁻¹ could be an indication of surface reconstruction on the activated $\alpha\text{-Ga}_2\text{O}_3$ leading to the appearance of Ga^{IV} species over their sample, as suggested by the authors from their IR results using CO and pyridine as probe molecules.²¹ In the same direction, the bands at 2720, 2682, and 2659 cm⁻¹ in our $\alpha\text{-Ga}_2\text{O}_3$ sample (clearly visible at 323 K) are indeed an indication of the surface reconstruction or relaxation of the surface of this crystal phase, since these wavenumbers are assigned to deuterioxylys involving at least one bond to 4-fold coordinated Ga³⁺ cations. As we mentioned above, approximately 10% of the total surface Ga³⁺ ions were in a tetrahedral position, that is, Ga^{IV} species, over the surface of the pretreated α -gallia after hydrogen chemisorption at RT.²⁰ Moreover, said surface reconstruction seems to be temperature-dependent: the higher the temperature is set, the lower the amount of dicoordinated OD on Ga^{IV} sites becomes, by conversion to DO- $\mu_2\text{-(Ga}^{\text{VI}})$ surface species (the total integrated absorbance remains constant with temperature variations, and the phenomenon is fully reversible).

Finally, bands at frequencies lower than 3600 cm⁻¹ on β - and γ -gallia polymorphs can also become visible in the works of Otero Areán's group at about 3450 cm⁻¹.^{21,23,24} That is, the presence multiple-coordinated hydroxyls on the Ga³⁺ sites of their own oxides is evident.

The approach used in this work, i.e., the use of different gallia polymorphs of varying surface area together with a D₂ pretreatment, allowed us to explain the most important features of the IR region of OH stretching for gallium (III) oxides.

3.2. Formation of (Bi)carbonate Species on Gallia after CO₂ Adsorption. Upon exposure of the activated α -, β -, and γ -gallia polymorphs to CO₂ at 323 K, several signals readily evolved in the 2000–1000 cm⁻¹ region, which further grew after increasing the superimposed pressure (Figures 4a, 5a, and 6a). The total integrated absorbance of these bands as a function of the CO₂ pressure, for all the studied samples, is shown in Figure 7. It is clear that in every case a plateau is reached over approximately 600 Torr of CO₂.

After the evacuation of the IR cell at 323 K (base pressure = $1.33 \times 10^{-4} \text{ Pa}$), the intensity of most of these bands decreased, and finally, after 15 min of evacuation, about 32–38% of the total integrated signal remained. This fact suggests a moderate interaction between the CO₂ molecule and the

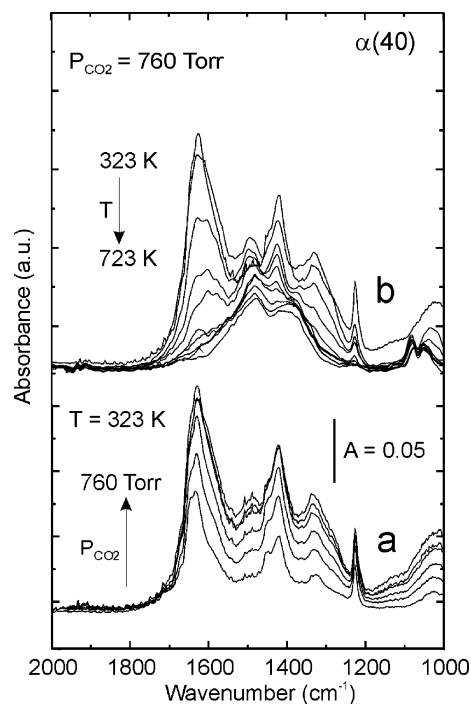


Figure 4. Evolution of the infrared signals of surface (bi)carbonate species on the $\alpha(40)$ sample: (a) isothermal adsorption of CO₂ at 323 K, by increasing the pressure up to 760 Torr; (b) temperature-programmed adsorption of CO₂ from 323 to 723 K, at 5 K min⁻¹, under flowing CO₂ (100 cm³ min⁻¹) at 760 Torr.

surface of the gallium oxides or, in other words, the presence of mild O₂⁻ and OH basic centers on the surface of these materials.

A typical resolved spectrum of the region is shown in Figure 8. For the correct assignment of the IR signals of the surface species chemisorbed onto Ga₂O₃ (usually assigned to bicarbonate and carbonate species), it is appropriate to examine the following features: (i) the wavenumber of the IR signals of carbonates adsorbed over other metal oxides, (ii) the width of the ν_3 -band splitting of the CO₃⁼ anion (that is, the $\Delta\nu_3 = \nu_{\text{as}} - \nu_{\text{s}}$ CO₃ stretching modes) due to the loss of its D_{3h} symmetry by chemisorption,^{43,44} and (iii) the thermal evolution of the intensity of each signal (thermal stability).

Accordingly, after isothermal sorption at 323 K, TPA experiments of CO₂ between 323 and 723 K ($\beta = 5 \text{ K min}^{-1}$) were performed, by flowing carbon dioxide (100 cm³ min⁻¹) at atmospheric pressure. The resulting infrared spectra are shown in Figures 4b, 5b, and 6b. As an example, the thermal evolution of each of the typical bands of the (bi)carbonate species formed

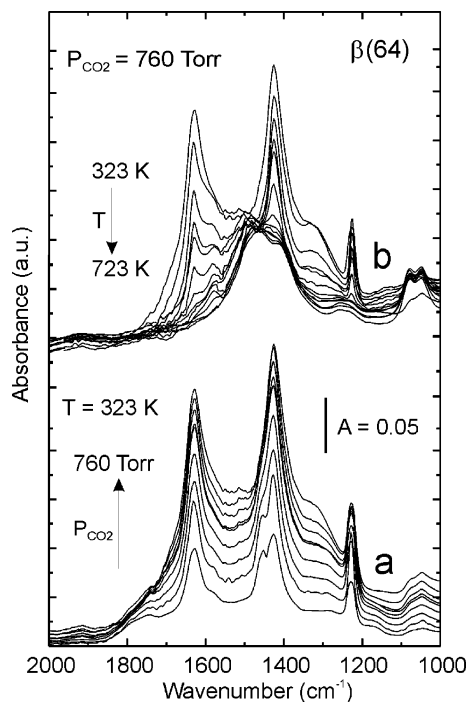


Figure 5. Evolution of the infrared signals of surface (bi)carbonate species on the $\beta(64)$ sample using the same experimental conditions as in Figure 4.

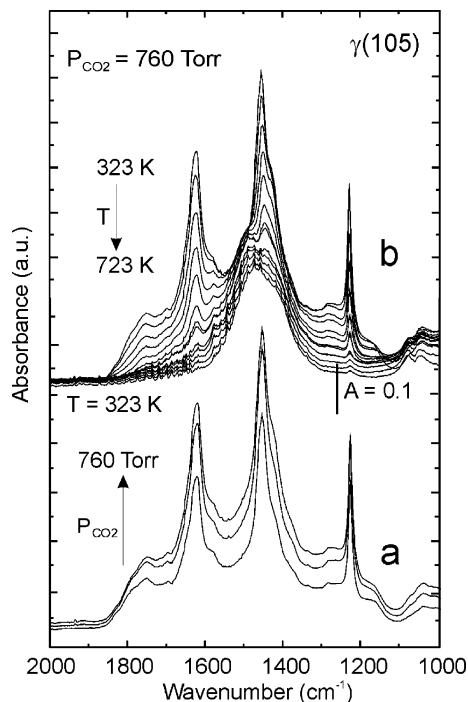


Figure 6. Evolution of the infrared signals of surface (bi)carbonate species on the $\gamma(105)$ sample using the same experimental conditions as in Figure 4.

onto the surface of γ -Ga₂O₃, together with their total integrated absorbance, is shown in Figure 9, to aid in the signal assignment.

The bands at 1750 and 1170 cm⁻¹ ($\Delta\nu_3 = 580$ cm⁻¹) and at 1680 and 1280 cm⁻¹ ($\Delta\nu_3 = 400$ cm⁻¹) rapidly vanished upon increasing the adsorption temperature above 450 K (see Figures 8 and 9). In principle, both pairs of bands can be assigned either to bridged (or organicle) carbonates or to strongly perturbed CO₂ adsorbed species (carboxylate), because the splitting and position of these surface groups are usually similar.⁴⁴

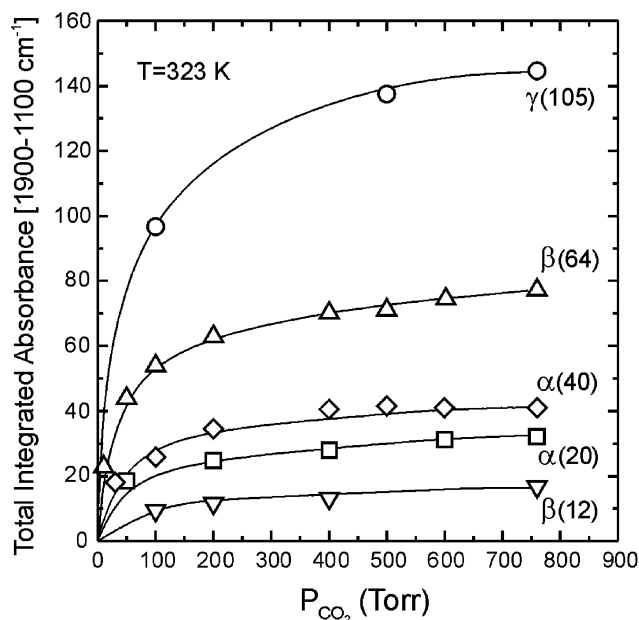


Figure 7. Isothermal carbon dioxide uptake on the whole set of gallia polymorphs measured by infrared absorption in the 1900–1100 cm⁻¹ region as a function of the equilibrium pressure of CO₂ gas.

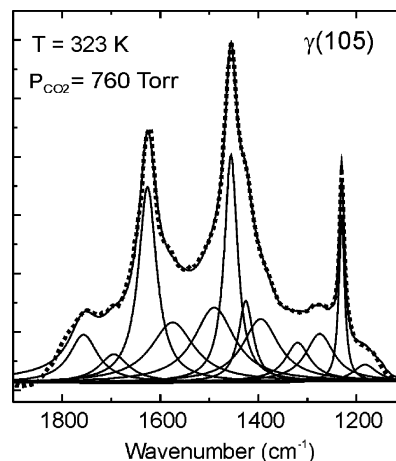


Figure 8. Resolved infrared spectrum in the 1900–1100 cm⁻¹ region corresponding to the absorption bands of the carboxylate, carbonate, and bicarbonate groups on the surface of the γ -Ga₂O₃ polymorph: (dots) experimental data.

Although some authors have proposed that bridged carbonates adsorbed on metal oxides exhibit a $\Delta\nu_3$ splitting of 400 cm⁻¹ or more,^{43,45,46} Busca and Lorenzelli⁴⁴ have shown some concern about such assignment. Theoretical and experimental data seem to indicate that a $\Delta\nu_3$ splitting higher than 400 cm⁻¹ cannot be induced by carbonate ions bridged over two cations.^{44,47} Certainly, CO₂ has proved to be a very versatile ligand in metal complexes, which can coordinate in several conformations—as a result of charge transfer—giving CO₂^{δ-} radical anions with structures that encompass simple monocoordinated species as well as complex polycordinated ones.⁴⁸ Nevertheless, it is expected that CO₂^{δ-} adducts have lower thermal stability than bridged carbonates, as was recently pointed out by Gibson.⁴⁸ Said lower thermal stability is revealed in Figure 9, which shows that the integrated IR absorbance of the pair of bands at 1750 and 1170 cm⁻¹ promptly decays to about half the intensity of the other pair, located at 1680 and 1280 cm⁻¹, whereas both pairs had about the same intensity at 323 K. Therefore, on the basis of the above considerations, the bands at 1750 and 1170

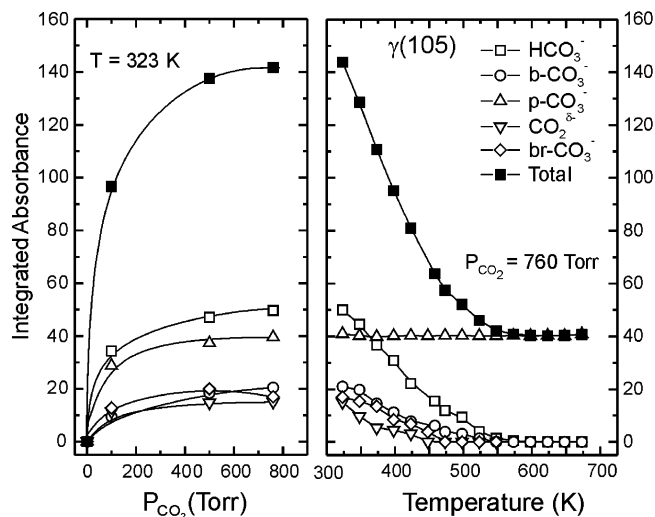


Figure 9. Evolution of the integrated absorbance signals of the carboxylate, carbonate, and bicarbonate groups on $\gamma(105)$: (a) isothermal adsorption of CO_2 at 323 K as a function of the CO_2 pressure; (b) temperature-programmed adsorption of CO_2 (5 K min^{-1}), under flowing CO_2 ($100 \text{ cm}^3 \text{ min}^{-1}$) at 760 Torr.

cm^{-1} are ascribed to the ν_{as} and ν_{s} modes of surface carboxylate, while the bands at 1680 and 1280 cm^{-1} are assigned to similar modes of bridged carbonates, respectively.

The most intense bands, located at 1630 , 1431 (and 1455), and 1225 cm^{-1} (Figure 8) are assigned to bicarbonate, or hydrogen carbonate (HCO_3^-) species on the gallia polymorphs, whose IR modes are $\nu_{\text{as}}(\text{CO}_3)$, $\nu_{\text{s}}(\text{CO}_3)$, and $\delta(\text{HO})$, respectively. The ν_3 -band splitting of the species, 199 cm^{-1} (and 175 cm^{-1}), is in agreement with that of adsorbed bicarbonates ($<200 \text{ cm}^{-1}$) on different metal oxides.^{44,49,50–52}

Now, two IR band for the $\nu_{\text{s}}(\text{CO}_3)$ mode were observed at 1431 and 1455 cm^{-1} . Figures 4a, 5a, and 6a show the differential growth of these overlapping peaks under increasing CO_2 pressure (they are resolved for the $\gamma\text{-Ga}_2\text{O}_3$ sample in Figure 8). Then, it can be postulated that two types of bicarbonate species are formed over the surface of gallium oxides. The measured $\Delta\nu_3$'s (199 and 175 cm^{-1}) are certainly lower than 400 cm^{-1} , which allow us to dismiss bicarbonate groups on bridged coordination, but they can be attributed to bidentate and monodentate species, the $\Delta\nu_3$ of the former bicarbonate being smaller than the one of the monodentate group.⁴⁴ Hence, the band with $\nu_{\text{s}}(\text{CO}_3)$ at 1431 cm^{-1} is assigned to monodentate bicarbonate (m-HCO_3^-) and the band $\nu_{\text{s}}(\text{CO}_3) = 1455 \text{ cm}^{-1}$ is assigned to bidentate bicarbonate (b-HCO_3^-).

On transition aluminas (e.g., γ and η), two kinds of bicarbonates, named B1 and B2, were identified by Morterra et al.⁵³ The $\nu_{\text{s}}(\text{CO}_3)$ modes of these species appeared at 1450 and 1480 cm^{-1} for the B1 and B2 types, respectively. These workers suggested that B1 bicarbonates were formed on Al^{IV} surface sites, where surface hydroxyls were abundant in monodentate coordination, while B2 bicarbonates were formed on a “more dehydroxylated” surface (dehydrated in a vacuum at temperatures higher than 500 K), by reaction with the basic OH (3775 cm^{-1}) and, partially, with the more acidic OH at 3690 cm^{-1} bridge-coordinated to two Al^{IV} cations. However, the induced splitting between the asymmetric and symmetric CO_3 modes in bridged (carbonate) species on metal oxides has been usually reported to be larger than 400 cm^{-1} ,⁴⁴ whereas the $\Delta\nu_3$ of B1 and B2 groups observed by Morterra et al. were 210 and 170 cm^{-1} ,⁵³ that is, rather lower than the one expected for

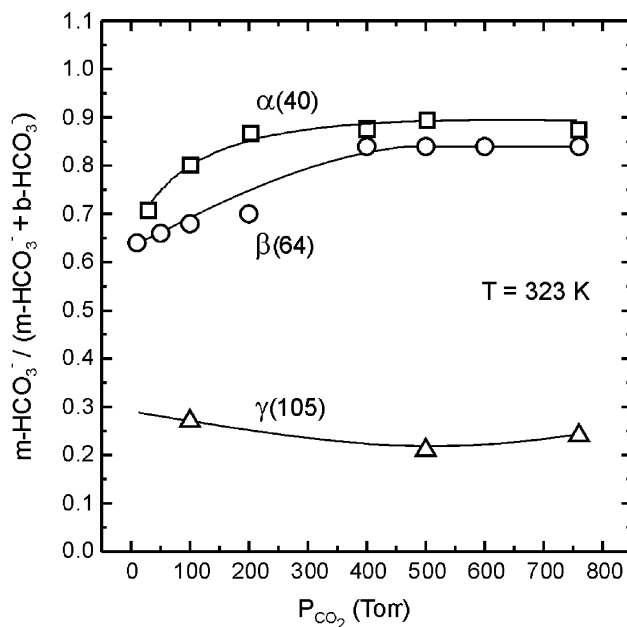


Figure 10. Fraction of surface monodentate bicarbonate (m-HCO_3^-) on the gallia polymorphs, as a function of the CO_2 pressure, at 323 K.

bridged species. We believe, as pointed out above, that bidentate bicarbonate is a more plausible assignment for their B2 species.

During the isothermal adsorption of CO_2 at 323 K on the gallium oxides, some differences between the predominance of each type of surface bicarbonate on the polymorphs were observed. So, the fraction of m-HCO_3^- species was calculated, from the integrated absorbance of the $\nu_{\text{s}}(\text{CO}_3)$ modes, as the ratio between m-HCO_3^- and total HCO_3^- groups (that is, $\text{m-HCO}_3^- + \text{b-HCO}_3^-$), assuming identical IR absorption coefficients. Figure 10 displays the variation of said m-HCO_3^- fraction as a function of the CO_2 pressure for each polymorph. The monodentate coordination prevails on α - and β -gallia: over 400 Torr of CO_2 , the fraction of m-HCO_3^- was approximately 0.85 for each polymorph. Meanwhile, the b-HCO_3^- species predominates over the surface of γ -gallia (the m-HCO_3^- fraction was always ca. 0.27).

Surely, bicarbonate species are formed by chemisorption of CO_2 on OH basic groups so that, in principle, CO_2 chemisorption might well serve as a surface probe to help in unraveling the final surface “topology” of the activated gallia polymorphs. Yet, because the IR combination bands/overtone of the gas-phase CO_2 (centered at 3612 and 3715 cm^{-1}) interfere in the detection of the $\nu(\text{OH})$ signal, we run experiments of CO_2 adsorption over predeuterated gallia polymorphs.

Figure 11 nicely shows a direct correlation between the integrated absorbance of the vibration modes of the bicarbonate species and the integrated absorbance of the stretching mode of surface ODs attached to gallium cations of the different predeuterated gallia polymorphs, at 323 K. This fact is an obvious indication that the amount of HCO_3^- groups is proportional to the surface of the oxides (see also Figure 3).

Unfortunately, though, no correlation between the bicarbonate type and the crystal phase of gallia was made evident. As an example, Figure 12 shows the $\nu(\text{OD})$ and $\delta(\text{OD})$ regions of the spectrum before and after the CO_2 adsorption at 323 K over a $\gamma\text{-Ga}_2\text{O}_3$ sample prerduced with D_2 instead of H_2 . After adsorption of CO_2 , a band at 2665 cm^{-1} and another one at 973 cm^{-1} emerged. These bands are assigned to the $\nu(\text{OD})$ and $\delta(\text{OD})$ modes of DCO_3^- groups, in agreement with the expected isotopic shift of the $\nu(\text{OH})$ and $\delta(\text{OH})$ modes of HCO_3^- , which

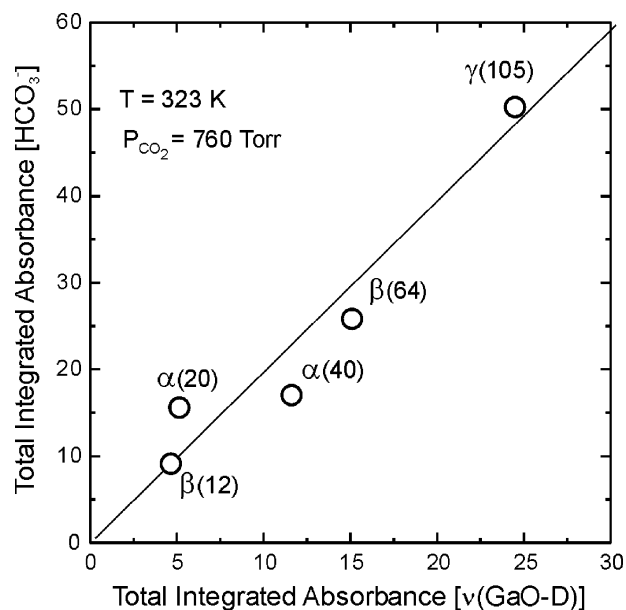


Figure 11. Total integrated absorbance of the bicarbonate species over the complete set of gallia polymorphs ($p_{\text{CO}_2} = 760$ Torr) versus the total integrated absorbance of OD groups bonded to surface gallium cations prior to CO₂ adsorption.

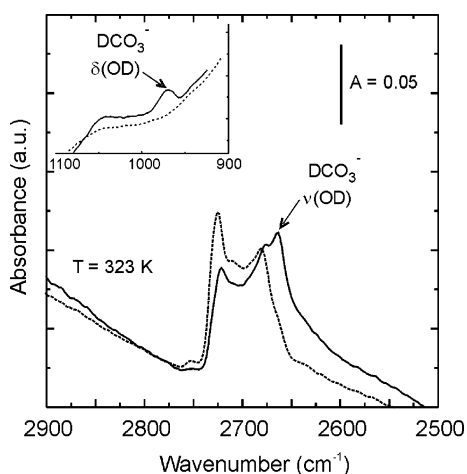


Figure 12. Infrared spectra of the stretching and bending OD modes before (dashed line) and after (full line) CO₂ adsorption at 760 Torr (323 K), on the surface of $\gamma(105)$ previously activated under flowing D₂ at 723 K.

are located around 3600 and 1225 cm⁻¹, respectively.^{44,49,50,53} The evolution of the $\nu(\text{OD})$ and $\delta(\text{OD})$ modes of deuterated bicarbonate species was accompanied by the decreasing intensity, mainly, of the IR bands at 2750 and 2715 cm⁻¹ (they correspond to DO- μ_1 -Ga^{VI} and DO- μ_1 -Ga^{IV}, respectively), which indicated the consumption of the more basic surface OD groups, rather than multiple-bonded DO species. However, no connection between the surface Ga³⁺ coordination and the bicarbonate species (mono- or bidentate) was found.

Nevertheless, even though it is not clear at the moment how to correlate the type and/or extent of the formation of each surface bicarbonate species on the different gallia polymorphs, we will suggest a possible explanation in what follows.

Two groups of IR signals still remain unidentified, but fortunately, there is enough background data about them. So, the bands located at 1587 and 1325 cm⁻¹ are ascribed to the $\nu_{\text{as}}(\text{CO}_3)$ and $\nu_{\text{s}}(\text{CO}_3)$ modes of bidentate carbonate species (b-CO₃²⁻), because the band splitting for this pair of bands ($\Delta\nu_3 =$

TABLE 3: Wavenumbers of Infrared Bands of (Bi)carbonate Species on the Surface of Gallium Oxide Polymorphs

surface species	$\nu_{\text{as}}(\text{CO}_3)$ (cm ⁻¹)	$\nu_{\text{s}}(\text{CO}_3)$ (cm ⁻¹)	$\delta(\text{OH})$ (cm ⁻¹)
CO ₂ ^{δ-} (carboxylate)	1750 ^a	1170 ^b	
br-CO ₃ ⁼ (bridged carbonate)	1680	1280	
b-CO ₃ ⁼ (bidentate carbonate)	1587	1325	
p-CO ₃ ⁼ (polydentate carbonate)	1460	1406	
m-HCO ₃ ⁼ (monodentate bicarbonate)	1630	1431	1225 (973 ^c)
b-HCO ₃ ⁼ (bidentate bicarbonate)	1630	1455	1225 (973 ^c)

^a $\nu_{\text{as}}(\text{CO}_2)$. ^b $\nu_{\text{s}}(\text{CO}_2)$. ^c Corresponding to the $\delta(\text{OD})$ mode [$\nu(\text{OD}) = 2665$ cm⁻¹].

262 cm⁻¹) is in close agreement to the 300 cm⁻¹ splitting found for such species over other metal oxides.^{35,44,49–52,54,55}

Last, two bands at ca. 1460 and 1406 cm⁻¹ can also be distinguished. They were highly overlapped at 323 K but became clearly visible when the other carbonate signals faded out at about 473 K (see Figures 4b, 5b, and 6b). These bands could account for the presence of either monodentate (m-CO₃⁼) or polydentate carbonate (p-CO₃⁼) species, which have similar ν_3 -band positions and $\Delta\nu_3 \leq 100$ cm⁻¹.^{44–46,49,50} Yet, in regard to the thermal stability of the different carbonate species, the surface m-CO₃⁼ should be much less stable than the p-CO₃⁼.^{44,49} Upon increasing the temperature along the thermal adsorption experiment of CO₂, no decrease of the intensity of the peaks at 1460 and 1406 cm⁻¹ was noticed although, on heating, the CO₂^{δ-}, br-CO₃⁼, b-CO₃⁼, and HCO₃⁼ species decomposed (see also Figure 9). Therefore, the strong thermal resistance and the rather low separation between the two C–O stretching modes of this species should be ascribed to multiple-bonded CO₂ over the gallium oxide surface, that is, polydentate carbonate species [$\nu_{\text{as}}(\text{CO}_3) = 1460$ cm⁻¹ and $\nu_{\text{s}}(\text{CO}_3) = 1406$ cm⁻¹].

In addition, these last two, b-CO₃⁼ and p-CO₃⁼, species were the only ones that (partially) remained over the surfaces of the gallias after outgassing these materials at 323 K (as indicated above, only ~35% of the total integrated absorbance in the 2000–1100 cm⁻¹ region prevailed after 15 min of evacuation), which confirm their higher stability as compared to the other (bi)carbonate groups.

To summarize the analysis on the many IR bands assigned to (bi)carbonate species on the gallia polymorphs, Table 3 sketches the various surface groups identified and the location of their vibration modes, as discussed in this study.

One final observation, that expands the reach and scope of the previous examination, comes to light from Figure 13. This figure presents the total integrated absorbance of (i) the whole set of IR signals between 1900 and 1100 cm⁻¹, (ii) the dicoordinated carbonates plus carboxylate groups, and (iii) the

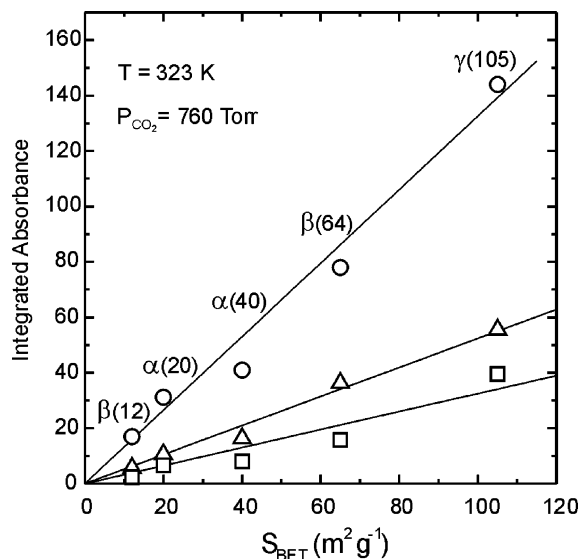


Figure 13. Integrated absorbance of (i) the whole set of surface (bi)carbonate infrared bands (open circles), (ii) the dicoordinated carbonates ($\text{b-CO}_3^- + \text{br-CO}_3^-$) plus carboxylate groups (open triangles), and (iii) the polycarbonate species (open squares) versus the BET surface area of the gallia polymorphs.

multiple-coordinated carbonates, at 323 K, versus the specific surface of each gallia polymorph. Remarkably, the direct proportionality between the surface concentration of the (bi)carbonates and the Ga_2O_3 surface area indicates that there is no substantial difference among the surface basicity of these polymorphs. Moreover, isothermal volumetric CO_2 adsorption at room temperature (293 K) performed over α (40), β (64), and γ (105) samples yielded uptakes of 2.0, 2.3, and 1.8 $\mu\text{mol CO}_2 \text{ m}^{-2}$ (760 Torr of CO_2), respectively, i.e., almost similar values for each gallium oxide (see Table 1).

Thus, we can suggest similar mechanisms of (bi)carbonate formation upon CO_2 adsorption on the different gallia polymorphs activated sequentially in O_2 , H_2 , and vacuum at 723 K, as follows:

It seems reasonable, first, to postulate that bridged and bidentate carbonates reflect the presence of acid–base pair sites or *cus* $\text{Ga}^{3+}-\text{O}^{2-}$ centers, while polydentate species involves a Lewis acid site, i.e., a *cus* Ga^{3+} center, close to the *cus* $\text{Ga}^{3+}-\text{O}^{2-}$ pairs. Analogous mechanisms have been proposed by Bachiller-Baeza et al.⁴⁹ for the formation of di- and polycoordinate carbonate groups on zirconium oxides.

In the case of the monodentate bicarbonate species, the CO_2 molecule interacts over Brønsted basic sites still present after the activation of the metal oxides, that is, OH groups coordinated to only one Ga^{3+} cation. On the other hand, the bidentate bicarbonate species reveals the presence of a *cus* $\text{Ga}^{3+}-\text{OH}$ pair, i.e., an oxygen vacancy by the Ga^{3+} bonded to the OH group. In this way, we could explain the much higher fraction of b-HCO_3^- found on γ - Ga_2O_3 than on the α - or β -phases, upon considering the poor crystallinity of the first oxide ($S_{\text{BET}} = 105 \text{ m}^2 \text{ g}^{-1}$), which would favor the amount of said *cus* $\text{Ga}^{3+}-\text{OH}$ centers via the presence of a larger amount of surface defects.

In regard to the formation of the $\text{CO}_2^{\delta-}$, or carboxylate groups, Busca and Lorenzelli⁴⁴ suggested that pairs of bands exhibiting large $\Delta\nu_3$ splittings should be assigned to species with a $\eta^2\text{-C,O}$ structure like the one showed in Table 3, rather than a complex of the $\eta^1\text{-C}$ type, at least for transition metal oxides. In our case, the $\eta^2\text{-CO}_2$ complex can be stabilized by (i) back-bonding between d orbitals of the Ga^{3+} ion ($3d^{10}$) and the π^* orbitals of a $\text{C}=\text{O}$ bond of CO_2 or (ii) interaction between

electron donor sites (e.g., partially reduced gallium cations, $\text{Ga}^{\delta+}$, with $\delta < 2$), which were generated by the activation procedure of the oxides,^{22,56} and the CO_2 molecule. A multiple coordinated $\text{CO}_2^{\delta-}$ adduct should be dismissed, since it requires a high concentration of closely spaced *cus* Ga^{3+} centers.⁴⁸

Hence, we can conclude that the low thermal stabilities of the (bi)carbonate species and the easy removal of most of these groups by simple evacuation at low temperature (323 K) indicate that gallium oxide has a weak basicity, which appears to be rather insensitive to the crystal bulk structure. This last result contrasts with the surface acid–base properties of other metal oxides, such as ZrO_2 ^{49,50} or Al_2O_3 ,³⁵ which are strongly dependent on the bulk crystal phase. The reason for such unusual behavior of gallia polymorphs can rest partially on surface restructuring, a fact that was unveiled by the OH infrared spectrum modification with temperature (viz., Figure 2) and has also been put forward in previous studies.^{20,21}

4. Conclusions

This study concerns the interaction of carbon dioxide over the surface of three activated gallium (III) oxides, i.e., α , β , and γ modifications, with widely different BET surface areas. The surface of these D_2 pretreated oxides revealed the presence of five types of OD surface species, which were mono-, di-, and tricoordinated to octahedral (Ga^{VI}) and/or tetrahedral (Ga^{IV}) surface gallium cations. In particular, the surface reconstruction of α - Ga_2O_3 was put forth to explain the detection of OD groups bonded to Ga^{IV} cations.

When the gallia polymorphs were exposed to increasing CO_2 pressure, at 323 K, several IR bands developed in the 2000–1000 cm^{-1} region. They were assigned to different (bi)carbonate-type species, and some of them (namely, the carboxylate, bicarbonate, and bridge-carbonate groups) were easily removed by outgassing the samples at said temperature. Upon heating the polymorphs in flowing CO_2 (760 Torr), most of the carbonaceous species disappeared at $T > 550 \text{ K}$, except for polydentate carbonates, which remained on the surface even at 723 K. The integrated absorbance of these bands was always proportional to the BET surface area of the polymorphs, while no correlation between the carbonate type and the coordination of surface gallium cations was found. Only the high surface area sample, γ - Ga_2O_3 , was able to form a sizable amount of bidentate bicarbonate, b-HCO_3^- (rather than m-HCO_3^-), which was attributed to a larger amount of surface defects on this polymorph.

Summarizing, these gallia polymorphs have shown almost identical, weak surface basicity.

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