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**Dissecting the steps of CO<sub>2</sub> reduction: 1. The interaction of CO and CO<sub>2</sub> with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>: an *in situ* FTIR study**

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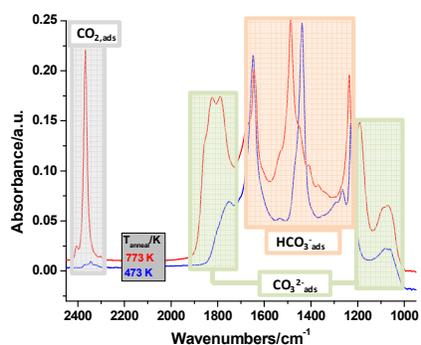
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The adsorption of CO<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> produces calcinations temperature-dependent surface species.

**Dissecting the steps of CO<sub>2</sub> reduction: 1. The interaction of CO and CO<sub>2</sub> with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>: an *in situ* FTIR study**

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**Abstract**

The adsorption of CO<sub>2</sub> and CO was investigated on a pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support material that has been used in Pd and Ru catalysts for the reduction of CO<sub>2</sub>. The adsorption of CO<sub>2</sub> resulted in the formation of carbonates, bicarbonates and linearly adsorbed CO<sub>2</sub> species. The amount and the nature of the adsorbed species were dependent on the annealing temperature of the alumina support. On  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> annealed at 473 K mostly bicarbonates formed, while no adsorbed CO<sub>2</sub> was seen on this highly hydroxylated surface. With increasing calcinations temperature the amounts of both surface carbonates and linear adsorbed CO<sub>2</sub> increased, but still the most abundant surface species were bicarbonates. Surface carbonates and adsorbed CO<sub>2</sub> can readily be removed from the alumina surface, while bicarbonates are stable to elevated temperatures. The interaction of CO with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is much weaker than that of CO<sub>2</sub>. At room temperatures CO adsorbs only on Lewis acid sites, and can be readily removed by evacuation. At 100 K CO can probe different

defect sites on the alumina surface. Under no conditions we have observed the formation of any carbonates or bicarbonates upon the interaction of CO with the pure alumina support. In co-adsorption experiments CO competes for adsorption sites with the linearly adsorbed CO<sub>2</sub> on the 773 K-annealed  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface; but it does not result in the desorption of CO<sub>2</sub>, rather in the increased weakly-held carbonate production. After the removal of adsorbed CO, CO<sub>2</sub> moves back to its original adsorption sites, i.e., Lewis acidic Al<sup>3+</sup> centers. The exposure of a CO<sub>2</sub>-saturated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to H<sub>2</sub>O did not affect any of the adsorbed surface species. The findings of this study will be used to rationalize the results of our ongoing *in situ* and *in operando* studies on the reduction of CO<sub>2</sub> on supported Pd and Ru catalysts.

**Keywords:** IR spectroscopy;  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; CO and CO<sub>2</sub> adsorption; Lewis sites; surface hydroxyls

**Introduction:** The critical role of the nature of the support material in determining the product selectivity of CO<sub>2</sub> reduction over supported metal catalysts has long been realized and studied extensively [1,2]. In our own studies of CO<sub>2</sub> reduction over alumina-supported Pd and Ru catalysts we have observed that Al<sub>2</sub>O<sub>3</sub> was not merely a support for the active metal particles, but an active participant in the CO<sub>2</sub> reduction process [3,4]. When Pd was present in atomic dispersion on the alumina support CO was produced with very high selectivity. In contrast, when Pd was dispersed on a carbon-based support (multiwall carbon nanotubes (MWCNTs)) no catalytic activity was detected over the atomically dispersed metal. However, adding La<sub>2</sub>O<sub>3</sub> to this latter system resulted in a catalyst that exhibited very similar activity and selectivity to the atomically dispersed Pd on alumina. The support material can exert two major effects on the catalyst system: it can influence the electronic properties of the active metal centers (in particular when the metal is present in very high (atomic) dispersion), and it can also participate in the

reaction itself by interacting with some of the reactants, or/and products. The modification of the electronic state of the active metal centers may influence the interaction between the reactants and the catalyst, the stabilities of adsorption complexes, and reaction intermediates. On the other hand, participation of the support material in the catalytic process by adsorbing one (or more) reactant can enhance the rate of the catalytic reaction by supplying activated species for the reaction. In this study we have examined the interaction of CO<sub>2</sub> with the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support itself (Part 1), and also with Pd/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts we have tested before in the reduction of CO<sub>2</sub> with H<sub>2</sub> (Part 2).

The interaction of CO<sub>2</sub> with oxide surfaces have extensively been studied previously for the characterization of the basicity of these materials [5-8]. Since  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is one of the most widely used support materials in industrial catalytic processes, its interaction with CO<sub>2</sub> has attracted a lot of attention and has been investigated since the early days of the application of IR spectroscopy in catalysis. In general, the interaction of CO<sub>2</sub> with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is rather weak. The exposure of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to CO<sub>2</sub> results in a number of adsorbed species: weakly held, adsorbed CO<sub>2</sub> and carbonates and bicarbonates, and all of these species can conveniently be characterized by IR spectroscopy [9,10]. The amount of surface carbonates formed as well as the structure of the bicarbonate species have been shown to strongly depend on the extent of dehydration and dehydroxylation which are proportional to the calcinations temperature. Calcination at low sample temperature, i.e. the removal of adsorbed H<sub>2</sub>O primarily, resulted in the formation of B1 type of bicarbonates, very small amount of carbonates, and no adsorbed CO<sub>2</sub> [7]. With increasing calcination temperature, i.e. with increasing extent of dehydration and subsequent dehydroxylation, B2 type of bicarbonates formed, and the amounts of both weakly held carbonates and adsorbed CO<sub>2</sub> increased significantly. Bicarbonates form via the reaction

between surface  $-OH$  groups and  $CO_2$ , while carbonates are produced by the interaction of basic surface  $O^{2-}$  ions and  $CO_2$ .  $CO_2$  can also adsorb on surface defect sites, consisting of, primarily, sites which were formed by dehydroxylation (Lewis acid sites). The interaction of  $CO$  with  $\gamma-Al_2O_3$  has also been investigated in details, however there are still unanswered questions regarding primarily the possible direct formation of carbonates from  $CO$ . The work of Padley et al., [11] suggested that the exposure of both calcined and reduced  $\gamma-Al_2O_3$  to  $CO$  resulted in the formation of bicarbonates (and possibly a very small amount of carbonates), while no Lewis acid site-bound  $CO$  was observed. These findings were contrasted by those of Morterra and Magnacca who claimed that “no carbonates were ever observed” on pure, laboratory prepared transition aluminas even in the presence of gas phase oxygen [12]. In recent studies Föttinger and co-workers have proposed a “water gas shift” mechanism for the formation of carbonates from  $CO$  on both pure alumina support and on alumina-supported Pd catalysts, utilizing isotopically labeled  $CO$ . In their mechanism an oxygen down  $CO$  molecule (adsorbed on a surface oxygen vacancy or other defect) would react with an adjacent hydroxyl group to form a surface carbonate and an adsorbed water molecule [13,14].

Here we report the results of our  $CO$  and  $CO_2$  adsorption studies over a  $\gamma-Al_2O_3$  support (Part 1) and three Pd/ $\gamma-Al_2O_3$  catalysts (0.5, 2.5 and 10 wt% Pd loadings) (Part 2) studied in the reduction of  $CO_2$  with  $H_2$ . The aim of this work was to identify the species that formed on the surfaces of these materials and might be relevant mechanistically in the  $CO_2$  reduction process. We conducted these adsorption experiments as a function of either the calcination temperature ( $\gamma-Al_2O_3$ ), or the pretreatment environment (calcinations, reduction and oxidation) over the Pd/ $\gamma-Al_2O_3$  catalysts. Our results show that upon exposure of all the materials investigated in this study (i.e.,  $Al_2O_3$  and Pd/ $\gamma-Al_2O_3$ ) to  $CO_2$  at ambient temperature bicarbonates on the alumina

support are the dominant surface species formed. Exposing  $\text{Al}_2\text{O}_3$  to CO at 300 K, in complete agreement with Morterra et al.[12], resulted in the formation of neither carbonate nor bicarbonate species. However, both carbonate and bicarbonate formations were observed on Pd/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalysts after annealing and oxidation. No carbonate/bicarbonate species formed over the Pd/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalysts after reduction in  $\text{H}_2$ . These results seem to suggest that oxygen bound to either the Pd particles, or, more probably, to the Pd/alumina interface can readily react with CO and responsible for the formation of  $\text{CO}_2$  that, in turn, produces surface carbonates/bicarbonates on the alumina support material.

**Experimental:** The  $\gamma$ - $\text{Al}_2\text{O}_3$  used throughout these studies was a commercial SBA-200 Puralox material from Condea with a BET surface area of  $\sim 200 \text{ m}^2/\text{g}$ . Prior to IR measurements the alumina sample was annealed in vacuum at 773 K for 2 h (in the low temperature CO adsorption study the alumina support was annealed at different temperatures).

The IR measurements were carried out on a Bruker Vertex 80 spectrometer equipped with a liquid nitrogen-cooled MCT detector, operated at  $4 \text{ cm}^{-1}$  resolution. Each spectrum reported was the average of 256 scans, and referenced to the spectrum of the clean sample. The IR cell is a modified 2  $\frac{3}{4}$ " stainless steel cube equipped with KBr windows and connections to pumping stations and a gas handling system. The sample holder rod has ceramic feedthrough for heating and thermocouple connections. The powder samples ( $\gamma$ - $\text{Al}_2\text{O}_3$  support and Pd/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalysts) were pressed onto a tungsten mesh which was attached to copper heating legs allowing resistive heating of the samples (temperature range: 100 – 1000 K). The temperature of the sample was monitored by a thermocouple spot welded to the top center of the tungsten mesh. The pressure in the IR cell could be controlled between  $2 \times 10^{-8}$  and 760 Torr. Oxygen and hydrogen gas used

for cleaning and reduction of the samples were used as received (both gases were research purity). The CO and CO<sub>2</sub> used in the adsorption measurements were purified: CO was kept under liquid nitrogen in order to eliminate any metal-carbonyl impurities might be present in metal cylinder-stored CO, while CO<sub>2</sub> was cleaned by cycles of freeze/pump/thaw. A typical experiment was conducted by first pre-treating the sample in vacuum at the indicated temperature and then carrying out the adsorption experiments. The adsorbate (CO<sub>2</sub> or CO) was added (usually in a step-wise manner) to the cell in a desired amount and after equilibration an IR spectrum was collected. The stepwise addition of the adsorbate was continued until the equilibrium pressure in the IR cell was ~0.3 Torr. Then the cell was evacuated and the removal of adsorbed species was monitored by IR as a function of evacuation time or annealing temperature.

**Results and Discussion: 1. CO<sub>2</sub> adsorption at 295 K:** The interaction of CO<sub>2</sub> with the alumina support used for the catalyst preparation was investigated first to gain insight into the adsorptive properties of the support material itself without the presence of active catalytic component (i.e, Pd metal). All the CO<sub>2</sub> adsorption measurements were carried out at 295 K sample temperature. The alumina was first annealed at the desired temperature in vacuum ( $\sim 2 \times 10^{-8}$  Torr) for two hours, then cooled to room temperature and exposed to CO<sub>2</sub> in a step-wise manner, i.e., CO<sub>2</sub> was introduced into the IR cell in increasing amounts, and an IR spectrum was collected after each aliquot. (The resulting series of IR spectra for each of the four annealed sample are shown in Fig. S1 in the Supplementary Information. The assignments of IR peaks observed after exposure of the alumina sample to CO<sub>2</sub> are summarized in Table S1 in the Supplementary Information.) IR spectra collected at the highest CO<sub>2</sub> pressure (0.034-0.039 Torr equilibrium gas pressure) from the four alumina supports calcined at 473, 573, 673 and 773 K

are displayed in Fig. 1. The series of IR spectra reveals systematic variations with the calcination temperature, and these changes were consistent with those discussed in prior studies of CO<sub>2</sub> adsorption on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [15] and on  $\eta$ -Al<sub>2</sub>O<sub>3</sub> [7]. The IR spectrum collected after annealing the sample at 473 K showed primarily the formation of B1 type bicarbonates with absorption features at 1230, 1438 and 1650 cm<sup>-1</sup> [7;8]. This low temperature annealing resulted in the removal of mostly adsorbed water from the alumina surface, while all the surface hydroxyl groups remained intact. There is also some weak IR features in the spectrum suggesting the presence of weakly held carbonates (1798, 1532, 1267 and 1206 cm<sup>-1</sup>) [7, 15], and “free” carbonates (1409 cm<sup>-1</sup>) [5]. Note the almost complete absence of IR signatures in 2350-2380 cm<sup>-1</sup> spectral region that is characteristic of ends-on CO<sub>2</sub> complexes adsorbed onto Lewis acid sites (Al<sup>3+</sup> ions) [16]. It is also worth mentioning that only an extremely weak IR band is seen in the  $\nu_{\text{O-H}}$  spectral region where the O-H stretching vibration of the bicarbonate species should appear (3620 cm<sup>-1</sup>). The very intense  $\delta_{\text{OH}}$  IR feature of bicarbonates at 1230 cm<sup>-1</sup> clearly evidences the formation of a large amount of bicarbonates, but the O-H stretching vibration of this species is very weak due, most probably, to the interaction of the OH group in the bicarbonate with the surface OH groups of the fully hydroxylated alumina support. Calcination of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 573 K brings about significant changes in the IR spectrum after CO<sub>2</sub> exposure. Most notable are the large decrease in the intensity of the 1438 cm<sup>-1</sup> feature, and the appearances of the IR features at 1469, 2360 and 3610 cm<sup>-1</sup>. In addition, the bands of surface carbonates became more intense, as the weak shoulder on the high frequency side of the 1798 cm<sup>-1</sup> band became much more intense, and developed into a new feature at around 1751 cm<sup>-1</sup>. All these changes can be attributed to small, but definitely noticeable dehydroxylation of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface. The increasing extent of dehydroxylation with increasing calcination temperature can clearly be seen in the IR spectra

collected after calcination at 673 and finally 773 K. After the 773 K calcination pretreatment, the  $\nu_{\text{O-H}}$  feature of the surface bicarbonates observed at  $3620\text{ cm}^{-1}$  after 473 and 573 K annealing becomes very sharp, intense and red shifts to  $\sim 3609\text{ cm}^{-1}$ . The increased sharpness of this feature suggests that the OH group of the bicarbonate species is free from interaction with surface hydroxyls of the alumina. The extensive dehydroxylation at 773 K is also supported by the development of a high intensity IR band centered at  $2366\text{ cm}^{-1}$ , characteristic of weakly held, Lewis acid site-bound  $\text{CO}_2$ , interacting with coordinatively unsaturated, tetrahedral  $\text{Al}^{3+}$  ions (the weak band centered at  $\sim 2406\text{ cm}^{-1}$  can also be assigned to a similar undercoordinated tetrahedral  $\text{Al}^{3+}$  site in a different crystallographic location on the alumina surface) [12 and references therein]. Another significant consequence of the extensive dehydroxylation is the large intensity gain of a series of IR bands in the  $1700\text{-}1900\text{ cm}^{-1}$  spectral region, paralleled by the intensity increase of the IR feature at  $1206\text{ cm}^{-1}$ . These IR bands represent weakly held surface carbonates (bridging carbonates [12], bridging  $\text{CO}_2$  surface species [17]), and they can be readily removed by evacuation at 295 K. It is also worth mentioning that after the highest temperature calcinations (773 K) most of the B1 type bicarbonates convert to B2 type ones, as evidenced by the interconversion of the  $1438\text{ cm}^{-1}$  band to the one centered at  $1486\text{ cm}^{-1}$ , exactly the same fashion as it has been shown by Morterra et al., for  $\eta\text{-Al}_2\text{O}_3$  [7]. It is also interesting to note that the development of the B2 type bicarbonate species coincides with a large intensity decrease of one of the  $\nu_{\text{O-H}}$  vibrational features of  $\gamma\text{-Al}_2\text{O}_3$ , specifically the least acidic one positioned at  $3779\text{ cm}^{-1}$ . Interestingly, not much is known about the difference between the two types of bicarbonate species (i.e., B1 and B2). What we found was that when the gamma-alumina was calcined at temperatures lower than 473 K mostly B1 bicarbonates form, while above 673 K almost exclusively B2 forms. The key difference, we believe, is not really in the nature of the

bicarbonate species, but the effect of the alumina surface on these bicarbonate species. At  $T < 473$  K the surface is practically fully hydroxylated, so the bicarbonates formed are most probably interact with large number of surface hydroxyls present (this is supported by the absence, or very low intensity of the O-H vibrational feature of the bicarbonate species at  $\sim 3610$   $\text{cm}^{-1}$ ). When the concentration of surface hydroxyls were significantly reduced ( $T > 673$  K) only B2 type of bicarbonates formed. On this dehydrated, and partially dehydroxylated alumina surface the bicarbonates seem to interact in a much lesser extent with OH groups than on the fully hydroxylated surface.

All the IR bands observed after the exposure of the alumina sample to  $\text{CO}_2$  loose, with varying extent, their intensities upon evacuation at 300 K, and subsequent annealing. A series of IR spectra obtained during the stepwise annealing (from 300 to 600 K) of the 773 K-annealed,  $\text{CO}_2$ -saturated  $\gamma\text{-Al}_2\text{O}_3$  samples is shown in Fig. S2. All the IR spectra were collected at 300 K sample temperature. The intensities of IR features representing weakly adsorbed carbonates (IR bands in the  $1700\text{-}1900$   $\text{cm}^{-1}$  range) and Lewis acid site-adsorbed  $\text{CO}_2$  molecules ( $\sim 2365$  and  $2407$   $\text{cm}^{-1}$ ) decrease rapidly as the sample is heated from 300 to 400 K. The intensities of the bicarbonates species are rather stable, and retain some of their intensities even after annealing to 600 K (bottom spectrum). Concomitant with the intensity decrease of all the bicarbonate-related IR features is the intensity increase of the Al-O-H band at  $3779$   $\text{cm}^{-1}$ : as the bicarbonates thermally decompose, the surface hydroxyls, occupied by these bicarbonates, re-form. Besides the very low intensity bicarbonate bands after the 600 K annealing the features still visible in the  $1300\text{-}1600$   $\text{cm}^{-1}$  spectral region are most probably represent bidentate (“organic”) carbonates [9].

**2. CO adsorption at 100 K:** Parallel with the  $\text{CO}_2$  adsorption measurements, we have also investigated the adsorption of CO on the same annealed (at different temperatures) alumina

surfaces, in order to further characterize and understand the different surface sites on the specific alumina we have used for the preparation of supported metal (Pd and Ru) catalysts. Adsorption of CO at cryogenic temperatures ( $<100$  K) has been widely used to characterize the adsorption/defect sites on alumina surfaces [see 12 and references therein]]. At these low temperatures CO can interact with hydroxyl groups (weakly) and also with different types of coordinatively unsaturated  $\text{Al}^{3+}$  ions [12] formed during dehydration/dehydroxylation. IR spectra collected at the conclusion of CO adsorption ( $P_{\text{CO equilibrium}}=0.035$  Torr) on the annealed (473 – 973 K) alumina samples at low temperature (100 K) are summarized in Fig. 2. The samples were annealed at the indicated temperature for 2 hrs and then exposed to CO at 100 K sample temperature to increasing amounts of CO, and IR spectra were collected after the introduction of each CO aliquot (series of spectra collected during these experiments are presented in Fig. S3). (The assignments of IR features observed after exposure of the alumina sample to CO are summarized in Table S2 in the Supplementary Information.) Three spectral regions of  $\nu_{\text{OH}}$  ( $3250\text{-}3850\text{ cm}^{-1}$ ),  $\nu_{\text{CO}}$  ( $2050\text{-}2300\text{ cm}^{-1}$ ) and  $\nu_{\text{AlO}}$  ( $950\text{-}1150\text{ cm}^{-1}$ ) can easily be distinguished. The IR spectra obtained from the 473 K-annealed  $\gamma\text{-Al}_2\text{O}_3$  sample show only very weak features in the  $\nu_{\text{OH}}$  and  $\nu_{\text{AlO}}$  regions, due to the presence of an almost fully hydroxylated surface under the mild calcination applied prior to CO adsorption. In the  $\nu_{\text{CO}}$  region there are only two, albeit high intensity, bands assigned to CO adsorbed on surface hydroxyls ( $2158\text{-}2155\text{ cm}^{-1}$ ) via weak hydrogen bonding and CO adsorbed on Lewis acid sites ( $2194\text{-}2186\text{ cm}^{-1}$ ) located on low index crystal planes of the alumina support [12]. The intensity of surface hydroxyl-bound CO feature is higher than that of the Lewis site-bound CO in concert with the low extent of dehydroxylation of the alumina surface at this low annealing temperature. (Also note that the hydroxyl-bound CO feature is rather broad on this low temperature annealed sample due to the

presence of a number of different types of hydroxyls present. In the IR spectra of adsorbed CO on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> annealed at higher temperatures (mainly at 673 and 773 K) this IR feature is much sharper, since the variation in the acidity of the hydroxyl groups in these samples is much smaller.) The interaction of CO with these Lewis acid sites results in the development of a low intensity negative IR band at around 1050 cm<sup>-1</sup> as the strained Al-O vibration on the surface relaxes due to the adsorption of CO [12]. The most significant change in the IR spectra as the annealing temperature of the alumina sample is raised to 573 K is the large intensity gain of the Lewis site-adsorbed CO feature (2197-2188 cm<sup>-1</sup>). With increasing annealing temperature the number of surface Lewis acid sites increases, therefore, more CO can adsorb. The intensity of the OH-bound CO feature (2163-2159 cm<sup>-1</sup>) does not drop significantly, although this feature becomes sharper. As the number of Lewis site-adsorbed CO increases, the intensity of the negative peak at ~1050 cm<sup>-1</sup> increases as well. Note also the increase in the intensities of the negative IR features at 3794 and 3787 cm<sup>-1</sup> of surface  $\nu_{\text{OH}}$  vibrations, and the appearance of a broad, weak feature at ~3340 cm<sup>-1</sup> which is the result of the shift in the  $\nu_{\text{OH}}$  vibrational feature of surface hydroxyls as they interact with CO via hydrogen bonding. As the surface becomes less hydroxylated the interaction between surface OH groups decreases, and the  $\nu_{\text{OH}}$  vibration of the remaining (mostly individual) OH groups becomes more sensitive to the adsorption of CO. These trends continue for the sample annealed at 673 K: the OH-bound CO feature becomes even sharper, while its intensity somewhat decreases, the intensity of the  $\nu_{\text{AlO}}$  vibrational band (negative feature) further increases with the increase in the number of surface Lewis acid sites with the increasing extent of dehydroxylation. There is also a large increase in the intensity of the  $\nu_{\text{OH}}$  feature red shifted by the interaction with CO. Beside the two intense  $\nu_{\text{CO}}$  features we have discussed so far, two new, low intensity bands appear on the 673 K-annealed sample at

$\sim 2220$  and  $2240\text{ cm}^{-1}$ . These IR features have been assigned to the most Lewis acidic sites on the alumina surface, located, most probably, on step edges and corners of the alumina crystallites [12]. The intensities of these high frequency  $\nu_{\text{CO}}$  vibrational features increase as the sample is heated to 773 K. At this temperature the surface is extensively dehydroxylated as evidence by the large intensity of the  $2194\text{-}2186\text{ cm}^{-1}$  band, and the decrease in the intensity of the IR feature at  $\sim 2155\text{ cm}^{-1}$ . As the intensity of this latter feature decreases, it becomes sharper, suggesting that the adsorption sites these CO molecules bind to become more homogeneous (non-interacting, individual OH groups). It is also interesting to note that although the number of hydroxyl-bound CO molecules decrease (large intensity drop of the  $2155\text{ cm}^{-1}$  band), the intensity of the shifted  $\nu_{\text{OH}}$  vibrational feature ( $\sim 3555\text{ cm}^{-1}$ ) reaches its maximum. The Lewis site-bound CO band also reaches its maximum intensity on this 773 K annealed alumina sample, in concert with the largest negative  $\nu_{\text{AlO}}$  feature at  $\sim 1050\text{ cm}^{-1}$ . The almost fully dehydroxylated alumina surface (obtained after annealing at 973 K) adsorbs CO only on Lewis acid sites, as the intensity of the OH-bound CO feature is only present as a weak shoulder at the highest CO pressure on this sample, and no negative peak or shifted OH signal can be seen in the  $\nu_{\text{OH}}$  spectral region. Adsorption of CO on the Lewis sites of this almost completely dehydroxylated surface results in an intense double negative feature in the  $1050\text{-}1090\text{ cm}^{-1}$  range, blue shifted in comparison with the feature observed for the hydroxylated samples. This large shift and intensity gain may be due to the absence of OH groups on the alumina surface (change in the relaxation in the absence of OH groups), or/and the possible initiation of phase transformation on the surface of the  $\gamma\text{-Al}_2\text{O}_3$  particles at this highest annealing temperature.

As we have mentioned it earlier the stabilities of these adsorbed CO species on the alumina surface were rather low. Figure 3 displays two series of IR spectra collected from the CO

saturated, 473 (panel a) and 773 K (panel b) annealed alumina samples during stepwise annealing from 100 to 200 K (473 K-annealed) and 300 K (773 K-annealed), in 25 K steps. (After each annealing step the sample was always cooled back to 100 K for spectrum acquisition.) The intensity of the IR feature ( $\sim 2155\text{ cm}^{-1}$ ) representing the most weakly adsorbed CO species drops significantly even during evacuation at 100 K, and it almost completely disappears after annealing at 125 K (the shifted  $\nu_{\text{OH}}$  vibrational feature at around  $3555\text{ cm}^{-1}$  loses most of its intensity after flashing the sample to 125 K). Beside the large intensity drops of the  $2155$  and  $3555\text{ cm}^{-1}$  bands, the IR feature of the Lewis acid site bound CO feature also loses some of its intensity, together with the decrease in the intensity of the negative IR band of Al-O vibrations around  $1030\text{ cm}^{-1}$ . The Lewis site bound CO feature of the 473 K-annealed sample loses its intensity very fast, and after annealing to 200 K it completely disappears. Due to the large number of Lewis site-bound CO on the 773 K annealed alumina surface the decrease in the intensity of this feature ( $2189\text{-}2208\text{ cm}^{-1}$ ) is much slower than over the 473 K annealed sample. It disappears only after annealing the sample to 250 K. The low intensity IR feature at  $\sim 2220\text{ cm}^{-1}$  gradually loses its intensity above 225 K, and after 300 K annealing the only remaining low intensity IR feature at  $2240\text{ cm}^{-1}$ , representing  $\nu_{\text{CO}}$  vibrations of CO molecules bound to the most Lewis acidic surface defects remains. The intensity of this feature does not change during annealing the sample at 300 K. The inset in Fig. 3b shows the variation of the  $\nu_{\text{CO}}$  vibrational features at low CO coverage (from 175 K to 300 K). These spectra seem to indicate that even the IR feature in the  $2230\text{-}2245\text{ cm}^{-1}$  spectral region consists of two bands, showing that there is slight acid strength difference in the Lewis acid sites these CO molecules adsorb to.

**3. CO adsorption at 295 K:** Since the results of the 100 K adsorption experiments showed that CO can only adsorb, with appreciable strength, to Lewis acid sites on the  $\gamma\text{-Al}_2\text{O}_3$  surface, we

carried out CO adsorption experiments at an ambient temperature of 295 K only on the 773 K annealed sample. Panels **a** and **b** of Fig. 4 display two series of IR spectra obtained during CO adsorption at 295 K (panel a) and during the subsequent evacuation (panel b), respectively. As the series of IR spectra in Fig. 4a shows CO adsorbs to the most Lewis acidic defect sites first, and the second absorption feature ( $2223\text{-}2220\text{ cm}^{-1}$ ) appear, together with the low frequency Lewis site bound CO ( $2211\text{-}2207\text{ cm}^{-1}$ ), only after the saturation of the  $2242\text{-}2236\text{ cm}^{-1}$  IR band. The intensities of these latter two IR features do not saturate under the experimental conditions applied, even in the presence of gas phase CO (see the inset in panel b of Fig 4). At room temperature the stabilities of the two lower frequency IR features are very low, and short evacuation completely eliminates them. Even the IR feature of the most strongly bound CO decreases significantly during evacuation, although even after 10 min evacuation at 295 K it is present with appreciable intensity. These results are in complete agreement with those of Morterra et al. [12] who examined the interaction of CO and CO<sub>2</sub> with aluminas treated under different conditions. The results presented here for the adsorption of CO at both 295 and 100 K sample temperature are somewhat different from those recently reported by Föttinger et al. [13,14], who claimed that surface carbonates (actually bicarbonates) can readily form on clean alumina surfaces in the absence of any transition metals. Studying the interaction of CO with  $\gamma\text{-Al}_2\text{O}_3$  and Pd/ $\gamma\text{-Al}_2\text{O}_3$  systems they found that regardless of the presence or absence of Pd, significant amount of bicarbonates were produced on the alumina surface [13]. These contradicting finding are even more puzzling in light of the similarities of the  $\gamma\text{-Al}_2\text{O}_3$  samples studied in reference 13 and by us: both are Puralox SBA 200 samples. Their results were in concert with those of an earlier study by Padley et al. [11] who reported on the formation of surface carbonates on alumina at ambient temperatures. On the other hand, Morterra et al. [12]

have pointed out that they have never observed the formation of surface carbonates “on pure laboratory transition aluminas ... not even in the presence of oxygen or air”. Their conclusion seems to be completely supported by our data as we have never seen the formation of any carbonates (bicarbonates) on pure alumina surfaces (The inset in panel b of Fig. 4 clearly reveal the complete absence of bicarbonates even in the presence of gas phase CO.). (We will show in part 2 of this study that bicarbonates on Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surfaces can form on annealed or oxidized samples, but not on the fully reduced ones [17].) Our observations (and those of Morterra et al. [12]) suggest that the mechanism proposed by Föttinger et al. [13] for the formation of carbonates on undoped, pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> may need to be re-evaluated.

**Co-Adsorption of CO<sub>2</sub> with CO and H<sub>2</sub>O at 295 K:** Since the reaction we are interested to investigate on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported metal catalysts (CO<sub>2</sub> reduction with H<sub>2</sub>) produces water and CO we also studied the co-adsorption of CO and CO<sub>2</sub>, and H<sub>2</sub>O and CO<sub>2</sub> on the 773 K-annealed clean support material at 295 K. First the 773 K-annealed alumina was saturated with CO<sub>2</sub> at 295 K, and the excess CO<sub>2</sub> (gas phase CO<sub>2</sub>) was removed by evacuation. Next stepwise CO adsorption was carried out, and the variations in the IR spectra were monitored as a function of time (i.e., CO exposure). The series of IR spectra recorded in this experiment is shown Fig. 5 (panel a: 1050-2000 cm<sup>-1</sup>, and panel b: 2100-3850 cm<sup>-1</sup> spectral ranges). In the spectral range of carbonates/bicarbonates very minor variations in the IR spectra can be seen: slight intensity increase in the weakly held carbonates at ~1195 and 1725-1900 cm<sup>-1</sup>. The intensities of the bicarbonate features do not seem to vary at all. The most significant change in the IR spectrum as a results of CO exposure of the CO<sub>2</sub>-saturated alumina is the fast intensity drop of the chemisorbed linear CO<sub>2</sub> feature at ~2365 cm<sup>-1</sup>, and the appearance of the Lewis acid site bound CO feature at ~2240 cm<sup>-1</sup>. At higher CO amounts (when the presence of gas phase CO can

clearly be seen) the intensity of almost all chemisorbed  $\text{CO}_2$  signal disappears, and the lower frequency adsorbed CO feature at  $\sim 2220 \text{ cm}^{-1}$  appears. These results unambiguously substantiate that CO and  $\text{CO}_2$  are competing for the same adsorption sites. Although  $\text{CO}_2$  adsorbs stronger to these  $\text{Al}^{3+}$  sites, in the presence of CO in excess most of the adsorption sites are occupied by weakly held CO. Even more interesting are the results obtained in the evacuation step following the CO adsorption on the  $\text{CO}_2$ -saturated alumina. The IR spectra displayed in panels **a** and **b** of Fig. 6 clearly show that as weakly held CO is removed from the alumina the chemisorbed  $\text{CO}_2$  feature completely regains its original intensity. Furthermore, as it is clear from panel a, the intensities of the IR features of weakly held carbonates decrease during the evacuation process (but not the bicarbonates). These results clearly indicate that during CO exposure as CO replaces  $\text{CO}_2$  on  $\text{Al}^{3+}$  sites  $\text{CO}_2$  does not desorb, rather converts to weakly held carbonates. Then, when adsorbed CO is removed by evacuation  $\text{CO}_2$  moves back to its original adsorption sites. These observations are in full agreement with those of Morterra et al. on the CO/ $\text{CO}_2$  co-adsorption on  $\eta\text{-Al}_2\text{O}_3$  [7].

The effect of water on the adsorption of  $\text{CO}_2$  on a 773 K-annealed  $\gamma\text{-Al}_2\text{O}_3$  was investigated in two different experiments: in one of the experiments the sample was first saturated with  $\text{CO}_2$  at 295 K followed by evacuation to remove the excess  $\text{CO}_2$  from the IR cell, and then the sample was exposed to  $\text{H}_2\text{O}$  in a stepwise manner. In the second experiment the alumina was first exposed to  $\text{H}_2\text{O}$  at 295 K and then to a large dose of  $\text{CO}_2$ , and the variations in the IR spectra were followed as a function exposure time. The series of IR spectra obtained during the exposure of a  $\text{CO}_2$ -saturated  $\gamma\text{-Al}_2\text{O}_3$  sample to  $\text{H}_2\text{O}$  is displayed in Fig. S4. The most striking observation is the invariance of the IR features associated with adsorbed  $\text{CO}_2$ , as well as with carbonates/bicarbonates to the introduction of water onto the  $\text{CO}_2$ -saturated sample. The only

new IR features appearing as a result of H<sub>2</sub>O exposure are the ones associated with adsorbed H<sub>2</sub>O at >3000 cm<sup>-1</sup>. These broad bands arise from the strong hydrogen bonding among adsorbed water molecules. The intensity of the 3608 cm<sup>-1</sup> O-H vibrational feature of the bicarbonate species decrease significantly as these hydroxyl groups interact with adsorbed water. This interaction results in the appearance of a new IR band at around 3532 cm<sup>-1</sup>. The intensity of the IR feature of linearly adsorbed CO<sub>2</sub> (at 2367 cm<sup>-1</sup>) decrease somewhat with water addition, and concomitantly there is a small intensity increase in some of the IR features of weakly held (“organic”) carbonates (bands at ~1190 and 1800-1860 cm<sup>-1</sup>). This is caused by the competition between H<sub>2</sub>O and CO<sub>2</sub> for the same adsorption sites (i.e., surface Al<sup>3+</sup>). Similarly to the case of CO/CO<sub>2</sub> co-adsorption discussed above, water exposure of the CO<sub>2</sub>-saturated alumina does not result in CO<sub>2</sub> desorption, rather the “conversion” of chemisorbed CO<sub>2</sub> into some type of carbonates (“organic”), most probably in bidentate bridging binding configuration. In the second experiment of H<sub>2</sub>O/CO<sub>2</sub> co-adsorption first we exposed the 773 K-annealed sample to H<sub>2</sub>O and then added a large aliquot of CO<sub>2</sub> to the system, and followed the development of IR features as a function of time (Fig. S5). The IR features observed on this hydrated sample after CO<sub>2</sub> exposure are identical to those seen on the alumina annealed at 773 K prior to H<sub>2</sub>O exposure. One might have expected to obtain IR spectra from this water-exposed alumina similar to the ones we recorded from samples annealed to low temperatures (bottom black spectrum in Fig. 1). On that fully hydroxylated sample no chemisorbed CO<sub>2</sub> was observed (absence of the IR feature at 2365 cm<sup>-1</sup>), and also B1 bicarbonates formed (characteristic IR band at 1438 cm<sup>-1</sup>). Furthermore, the intensities of the bidentate carbonate (weakly held carbonate) features (~1190 and 1750-1880 cm<sup>-1</sup>) were very low on the 473 K-annealed alumina. On the water-exposed alumina, however, all of these IR features are present with high intensities. These results clearly

indicate that the re-hydroxylation of the dehydroxylated (elevated temperature-calcined)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is not a simple, straightforward process. Exposure of the dehydroxylated alumina surface to water does not eliminate the Lewis acidic Al<sup>3+</sup> sites from the surface by water dissociation, rather, water is present in a molecularly adsorbed state. (When we heated the sample to elevated temperatures (maximum 773 K) in the presence of H<sub>2</sub>O and then carried out CO<sub>2</sub> adsorption at 295 K we always observed the same phenomenon, i.e., no re-hydroxylation of the alumina surface.) These results are in agreement with findings of our prior study where we have shown that the rate of dehydration of ethanol at 473 K were much faster on the 773 K-annealed alumina (Lewis acidic sites were present), than on the one that was annealed only at 473 K (only Brönsted acidic sites were present) [18]. Even more relevant to our discussion here is the observation that the ethanol conversion rates over these two samples (annealed at 473 and 773 K) remained different (and constant) over the course of the experiment (about 90 min time-on-stream). Although a lot of water was produced in the ethanol dehydration reaction, the Lewis acidic sites created prior to the reaction studies during annealing at 773 K were not converted back to Brönsted acidic OH groups.

**Conclusions:** The interactions of CO and CO<sub>2</sub> with annealed (from 473 to 973 K)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, used for the preparation of supported Pd and Ru catalysts for the catalytic reduction of CO<sub>2</sub>, were investigated by *in situ* FTIR spectroscopy. The goal of this study was to understand how  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> interacts with the reactant CO<sub>2</sub>, and the possible intermediate and product CO. These findings will aid our *in situ* and *in operando* studies on identifying adsorbates and intermediates present on the support surface under catalytic conditions. The adsorption of CO<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> resulted in the formation of bicarbonates and weakly held surface carbonates, together with linearly adsorbed CO<sub>2</sub>. The amount and the nature of carbonates and bicarbonates

strongly depended on the calcination temperature of the alumina support. Linear adsorbed CO<sub>2</sub> was observed only on samples that were annealed at temperatures higher than 473 K. The amount of surface carbonates increased proportionally with the annealing temperature. The most stable surface species on the alumina after CO<sub>2</sub> exposure were bicarbonates, present even at elevated temperatures following CO<sub>2</sub> adsorption at 295 K. At 295 K CO can only adsorb on Lewis acid sites, and the strength of adsorption is proportional to the acidity of the adsorption center. At 100 K CO can adsorb on surface hydroxyls and on Lewis acid sites. The interaction of CO with surface hydroxyls is weak, as they can be removed by evacuation at around 150 K. At room temperature CO is only present on the most Lewis acidic surface defect sites on the alumina support material. Under no conditions we have observed the formation of surface carbonates or bicarbonates upon the exposure of the pure alumina sample to CO. These findings further support the conclusions of other studies that on pure alumina no carbonates can form from CO [12], and contradicts the findings of some earlier [11] and more recent studies [13,14]. Co-adsorption of either CO or H<sub>2</sub>O with CO<sub>2</sub> resulted in competition for the Lewis acidic Al<sup>3+</sup> sites. Neither CO nor H<sub>2</sub>O exposure of the CO<sub>2</sub>-saturated alumina resulted in CO<sub>2</sub> desorption, rather the adsorbed linear CO<sub>2</sub> was reversibly converted to weakly held bidentate carbonates.

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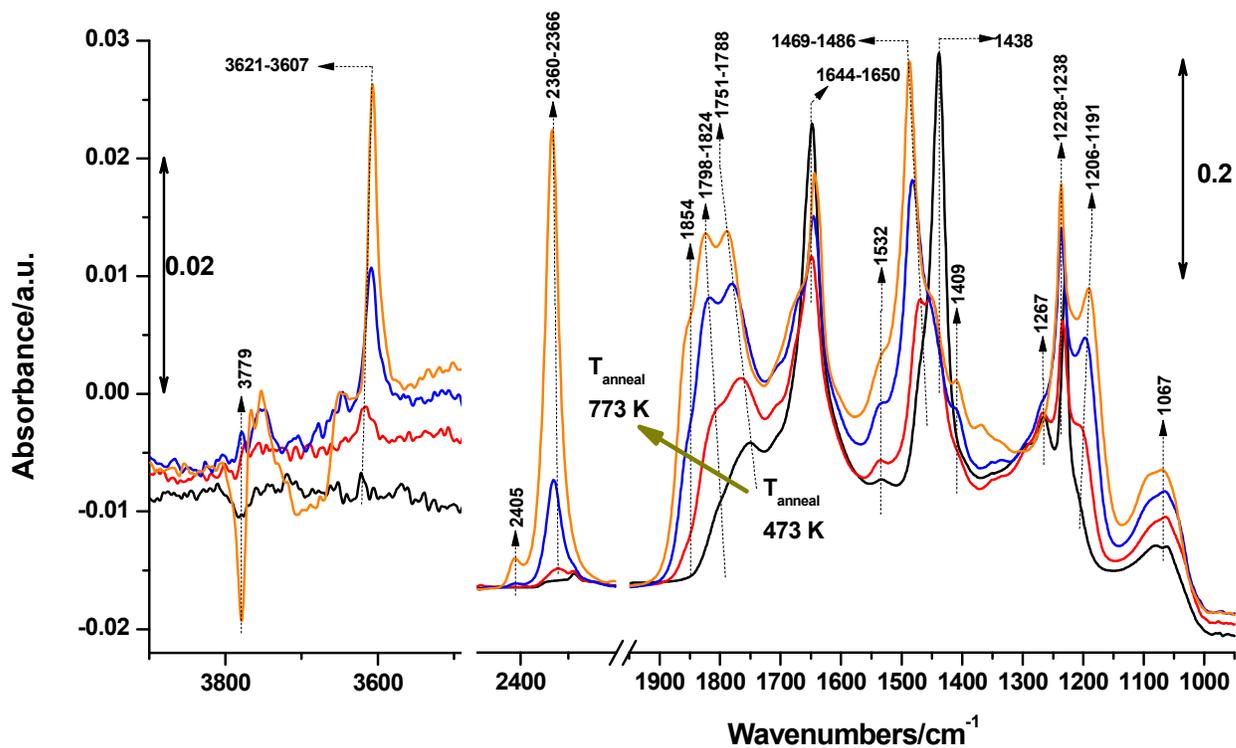
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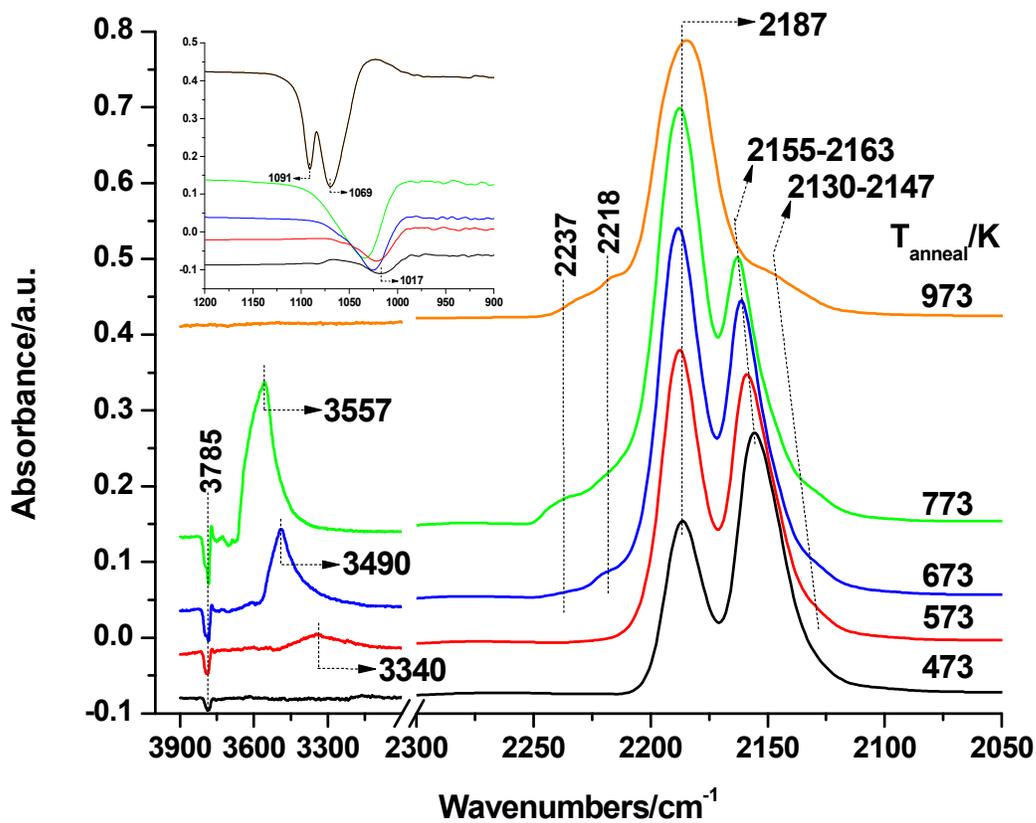
**Acknowledgements:** We gratefully acknowledge the US Department of Energy Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences for the support of this work. The synthesis and catalyst pre-treatment portion of the work described in this manuscript was supported by a Laboratory Directed Research and Development (LDRD) project at the

Pacific Northwest National Laboratory (PNNL). PNNL is operated for the US DOE by Battelle Memorial Institute. J.H.K. also acknowledges the support of this work by the 2013 Research Fund of UNIST (Ulsan National Institute of Science and Technology, Ulsan, Korea).

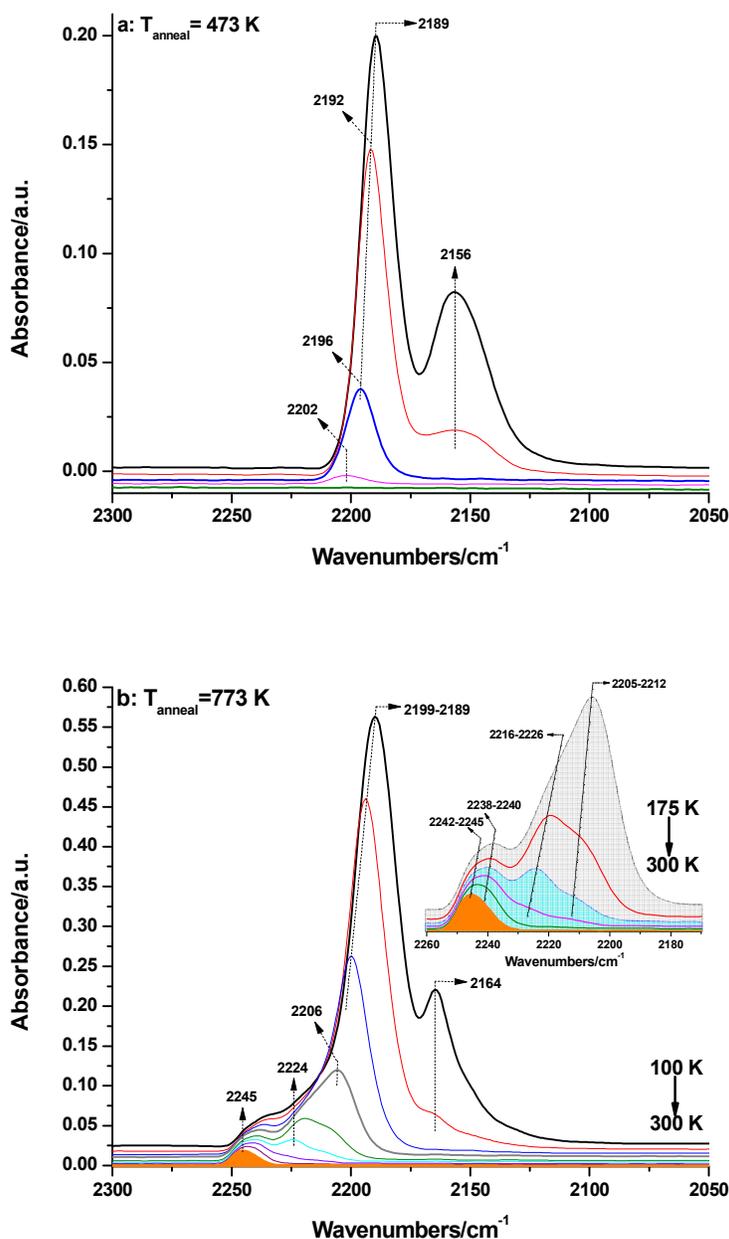
**Figure 1.** IR spectra collected from a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample after CO<sub>2</sub> exposure at 295 K. Prior to CO<sub>2</sub> adsorption the sample was annealed from 473 K (bottom, black spectrum) to 773 K (top, orange spectrum).



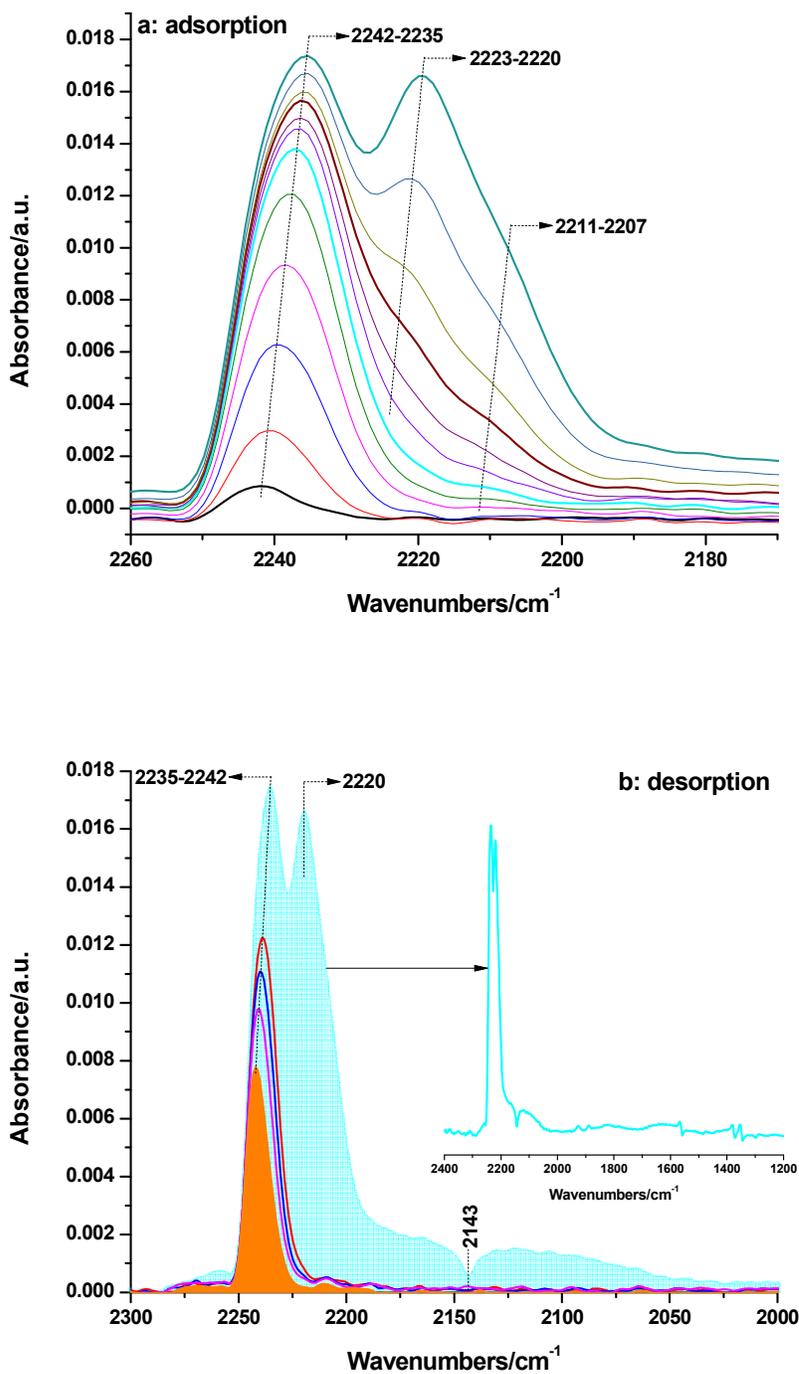
**Figure 2.** IR spectra collected from annealed (from 473 to 973 K)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples after the conclusion of CO adsorption at 100 K. ( $P_{\text{CO, equilibrium}}=0.035$  Torr)



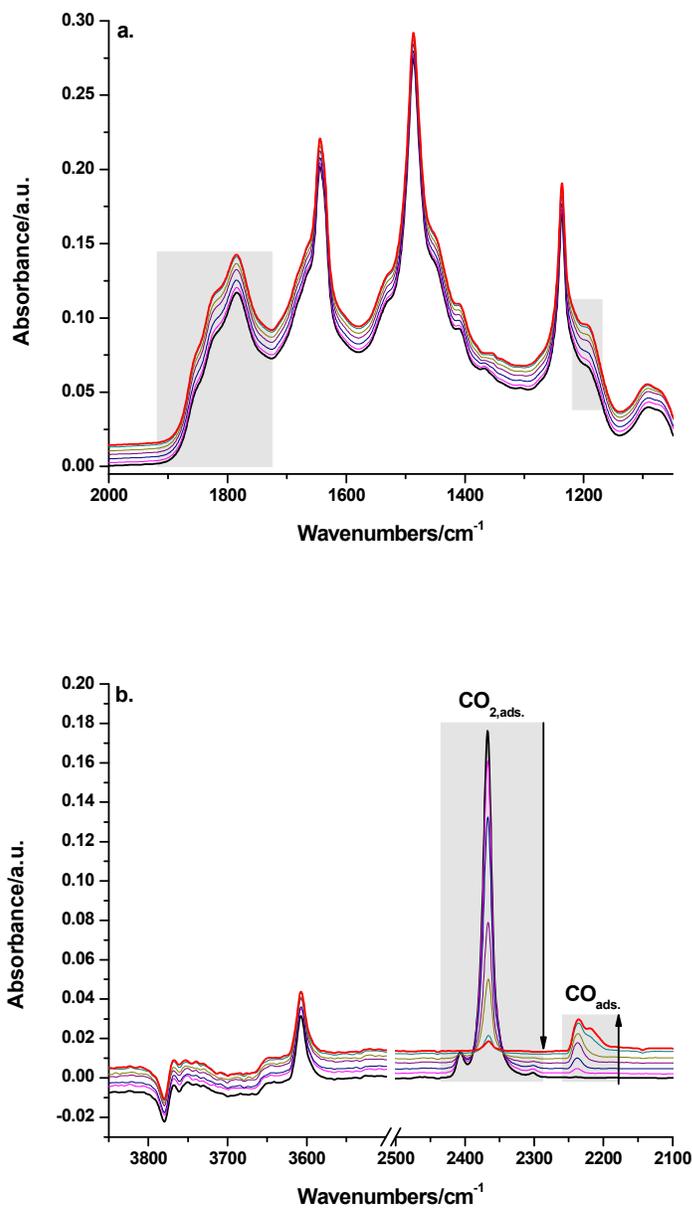
**Figure 3.** IR spectra collected during the stepwise annealing following CO adsorption at 100 K on the 473 K (panel a) and 773 K (panel b) annealed  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples. The temperature interval between two consecutive IR spectra is 25 K. All the spectra were collected at 100 K sample temperature. The inset in panel b shows the IR spectra collected from 175 to 300 K.



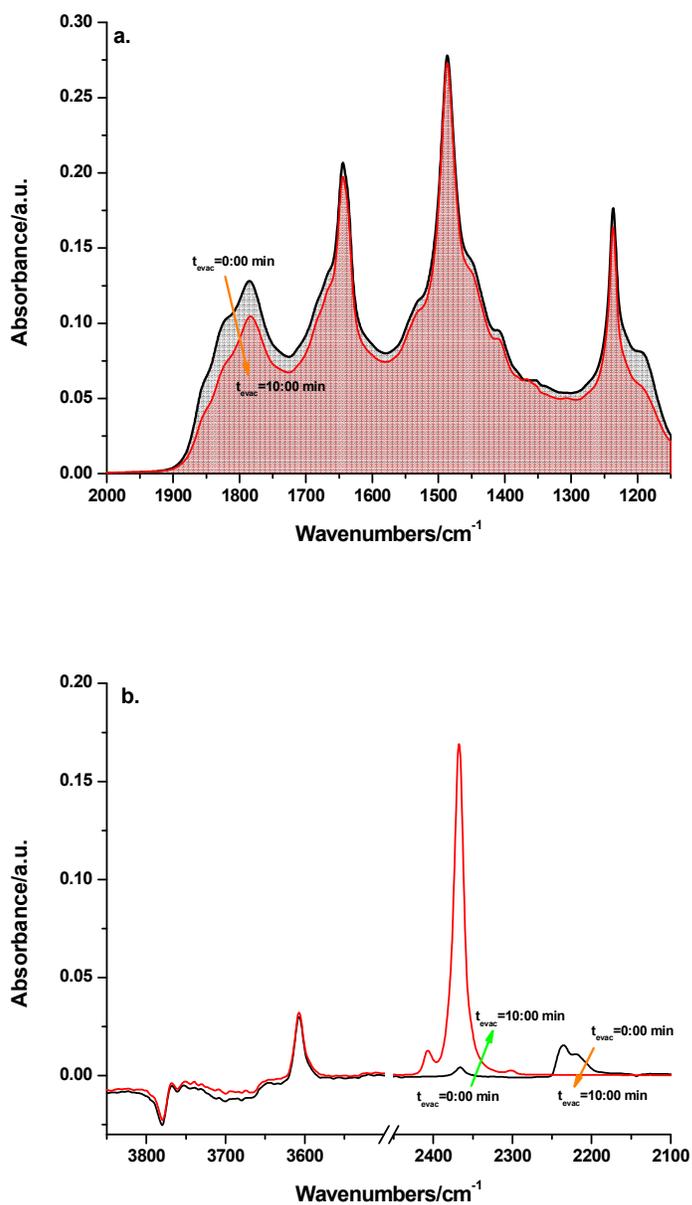
**Figure 4.** IR spectra collected during the stepwise CO adsorption on a 773 K-annealed  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample (panel a) and during subsequent evacuation (panel b) at 295 K.



**Figure 5.** IR spectra collected during the stepwise CO adsorption on a CO<sub>2</sub>-saturated, 773 K-annealed  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample. Both CO<sub>2</sub> saturation and CO adsorption were carried out at 295 K sample temperature. (The shaded areas highlight the spectral regions where intensity variations occurred as a result of CO adsorption on CO<sub>2</sub>/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.)



**Figure 6.** IR spectra collected from a CO<sub>2</sub>-saturated, 773 K-annealed  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample after CO adsorption (black spectrum) and subsequent evacuation for 10 min (red spectrum) at 295 K in two spectral regions: a: 1150-200 cm<sup>-1</sup>, and b: 2100-3850 cm<sup>-1</sup>.



TOC

