

Dissecting the steps of CO₂ reduction: 1. The interaction of CO and CO₂ with γ -Al₂O₃: an *in situ* FTIR study†

Cite this: *Phys. Chem. Chem. Phys.*, 2014, 16, 15117

János Szanyi* and Ja Hun Kwak‡

The adsorption of CO₂ and CO was investigated on a pure γ -Al₂O₃ support material that has been used in Pd and Ru catalysts for the reduction of CO₂. The adsorption of CO₂ resulted in the formation of carbonates, bicarbonates and linearly adsorbed CO₂ species. The amount and the nature of the adsorbed species were dependent on the annealing temperature of the alumina support. On γ -Al₂O₃ annealed at 473 K mostly bicarbonates formed, while no adsorbed CO₂ was seen on this highly hydroxylated surface. With increasing calcination temperature the amount of both surface carbonates and linearly adsorbed CO₂ increased, but still the most abundant surface species were bicarbonates. Surface carbonates and adsorbed CO₂ can readily be removed from the alumina surface, while bicarbonates are stable to elevated temperatures. The interaction of CO with γ -Al₂O₃ is much weaker than that of CO₂. At room temperature 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 CO₂ on the 773 K-annealed γ -Al₂O₃ surface, but it does not result in the desorption of CO₂, rather in the increased production of weakly held carbonates. After the removal of adsorbed CO, CO₂ moves back to its original adsorption sites, *i.e.*, Lewis acidic Al³⁺ centers. The exposure of a CO₂-saturated γ -Al₂O₃ to H₂O 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 CO₂ on supported Pd and Ru catalysts.

Received 11th February 2014,
Accepted 23rd May 2014

DOI: 10.1039/c4cp00616j

www.rsc.org/pccp

Introduction

The critical role of the nature of the support material in determining the product selectivity of CO₂ reduction over supported metal catalysts has long been realized and studied extensively.^{1,2} In our own studies of CO₂ reduction over alumina-supported Pd and Ru catalysts we have observed that Al₂O₃ was not merely a support for the active metal particles, but an active participant in the CO₂ 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 La₂O₃ to the 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 and/or products. The modification of the electronic state of the active metal centers may influence the interaction between the reactants and the catalyst, the stability 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 CO₂ with the γ -Al₂O₃ support itself (part 1), and also with Pd/ γ -Al₂O₃ catalysts we have tested before in the reduction of CO₂ with H₂ (part 2).

The interaction of CO₂ with oxide surfaces has extensively been studied previously for the characterization of the basicity of these materials.^{5–8} Since γ -Al₂O₃ is one of the most widely used support materials in industrial catalytic processes, its interaction with CO₂ has attracted a lot of attention and has

Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, WA 99352, USA. E-mail: janos.szanyi@pnnl.gov

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4cp00616j

‡ Current address: Department of Chemical Engineering, UNIST, 100 Banyeon-Ri, Ulsan 689-798, Korea.

been investigated since the early days of the application of IR spectroscopy in catalysis. In general, the interaction of CO₂ with γ -Al₂O₃ is rather weak. The exposure of γ -Al₂O₃ to CO₂ results in a number of adsorbed species: weakly held, adsorbed CO₂ and carbonates and bicarbonates, and all of these species can conveniently be characterized by IR spectroscopy.^{9,10} The amount of surface carbonates formed and the structure of the bicarbonate species have been shown to strongly depend on the extent of dehydration and dehydroxylation which are proportional to the calcination temperature. Calcination at low sample temperature, *i.e.* the removal of adsorbed H₂O primarily, resulted in the formation of B1 type of bicarbonates, a very small amount of carbonates, and no adsorbed CO₂.⁷ With increasing calcination temperature, *i.e.* with the increasing extent of dehydration and subsequent dehydroxylation, B2 type of bicarbonates formed, and the amount of both weakly held carbonates and adsorbed CO₂ increased significantly. Bicarbonates form *via* the reaction between surface -OH groups and CO₂, while carbonates are produced by the interaction of basic surface O²⁻ ions and CO₂. CO₂ can also adsorb on surface defect sites, consisting of, primarily, sites which were formed by dehydroxylation (Lewis acid sites). The interaction of CO with γ -Al₂O₃ has also been investigated in detail; 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 γ -Al₂O₃ 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 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 CO₂ adsorption studies over a γ -Al₂O₃ support (part 1) and three Pd/ γ -Al₂O₃ catalysts (0.5, 2.5 and 10 wt% Pd loadings) (part 2) studied in the reduction of CO₂ with H₂. The aim of this work was to identify the species that formed on the surfaces of these materials and that might be relevant mechanistically in the CO₂ reduction process. We conducted these adsorption experiments as a function of either the calcination temperature (γ -Al₂O₃) or the pretreatment environment (calcination, reduction and oxidation) over the Pd/ γ -Al₂O₃ catalysts. Our results show that upon exposure of all the materials investigated in this study (*i.e.*, Al₂O₃ and Pd/ γ -Al₂O₃) to CO₂ at ambient temperature bicarbonates on the alumina support are the dominant surface species formed. Exposing Al₂O₃ to CO at 300 K, in complete agreement with Morterra *et al.*,¹² resulted in the formation of neither carbonate nor bicarbonate species. However, the formation of both carbonates and bicarbonates was observed on Pd/ γ -Al₂O₃ catalysts after

annealing and oxidation. No carbonate/bicarbonate species formed over the Pd/ γ -Al₂O₃ catalysts after reduction in H₂. These results seem to suggest that oxygen bound to either the Pd particles or, more probably, the Pd/alumina interface can readily react with CO and is responsible for the formation of CO₂ that, in turn, produces surface carbonates/bicarbonates on the alumina support material.

Experimental

The γ -Al₂O₃ used throughout these studies was a commercial SBA-200 Puralox material from Condea with a BET surface area of $\sim 200 \text{ m}^2 \text{ g}^{-1}$. 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 cm^{-1} resolution. Each spectrum reported was the average of 256 scans, and was 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 (γ -Al₂O₃ support and Pd/ γ -Al₂O₃ 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 2×10^{-8} and 760 Torr. Oxygen and hydrogen gas used for cleaning and reduction of the samples were used as received (both gases were of research purity). The CO and CO₂ 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 CO₂ 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 (CO₂ 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. CO₂ adsorption at 295 K

The interaction of CO₂ 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 the active catalytic component (*i.e.*, Pd metal).

All the CO₂ 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 CO₂ in a step-wise manner, *i.e.*, CO₂ was introduced into the IR cell in increasing amounts, and an IR spectrum was collected after the introduction of each CO₂ aliquot. (The resulting series of IR spectra for each of the four annealed samples are shown in Fig. S1 in the ESI.† The assignments of IR peaks observed after exposure of the alumina sample to CO₂ are summarized in Table S1 in the ESI.†) IR spectra collected at the highest CO₂ 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 CO₂ adsorption on γ -Al₂O₃¹⁵ and on η -Al₂O₃.⁷ 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⁻¹.^{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 are also some weak IR features in the spectrum, suggesting the presence of weakly held carbonates (1798, 1532, 1267 and 1206 cm⁻¹)^{7,15} and “free” carbonates (1409 cm⁻¹).⁵ Note the almost complete absence of IR signatures in the 2350–2380 cm⁻¹ spectral region that is characteristic of ends-on CO₂ complexes adsorbed onto Lewis acid sites (Al³⁺ 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⁻¹). The very intense δ_{OH} IR feature of bicarbonates at 1230 cm⁻¹ 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 γ -Al₂O₃ at 573 K brings about significant changes in the IR spectrum after CO₂ exposure. Most notable are the large decrease in the intensity of the 1438 cm⁻¹ feature and the appearance of the IR features at 1469, 2360 and 3610 cm⁻¹. In addition, the bands of surface carbonates became more intense, as the weak shoulder on the high frequency side of the 1798 cm⁻¹ band became much more intense and developed into a new feature at around 1751 cm⁻¹. All these changes can be attributed to small, but definitely noticeable dehydroxylation of the γ -Al₂O₃ 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 at 773 K. After the 773 K calcination pretreatment, the $\nu_{\text{O-H}}$ feature of the surface bicarbonates observed at 3620 cm⁻¹ after 473 and 573 K annealing becomes very sharp and intense and red shifts to ~ 3609 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 cm⁻¹, characteristic of weakly held, Lewis acid site-bound CO₂, interacting with coordinatively unsaturated, tetrahedral Al³⁺ ions (the weak band centered at ~ 2406 cm⁻¹ can also be assigned to a similar undercoordinated tetrahedral Al³⁺ site in a different crystallographic location on the alumina surface) [ref. 12 and references therein]. Another significant consequence of the extensive dehydroxylation is the large intensity gain of a series of IR bands in the 1700–1900 cm⁻¹ spectral region, paralleled by the increase in the intensity of the IR feature at 1206 cm⁻¹.

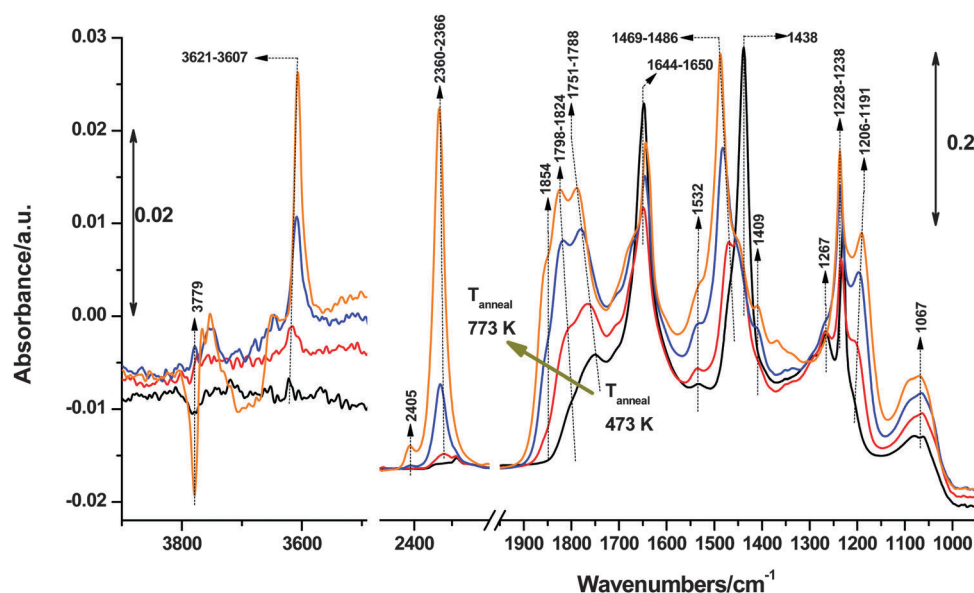


Fig. 1 IR spectra collected from a γ -Al₂O₃ sample after CO₂ exposure at 295 K. Prior to CO₂ adsorption the sample was annealed from 473 K (bottom, black spectrum) to 773 K (top, orange spectrum).

These IR bands represent weakly held surface carbonates (bridging carbonates,¹² bridging CO₂ surface species¹⁷), 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 bicarbonates, as evidenced by the interconversion of the 1438 cm⁻¹ band to the one centered at 1486 cm⁻¹, in exactly the same fashion as it has been shown by Morterra *et al.* for η -Al₂O₃.⁷ It is also interesting to note that the development of the B2 type bicarbonate species coincides with a large decrease in the intensity of one of the $\nu_{\text{O-H}}$ vibrational features of γ -Al₂O₃, specifically the least acidic one positioned at 3779 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 is calcined at temperatures lower than 473 K mostly B1 bicarbonates are formed, while above 673 K almost exclusively B2 bicarbonates are formed. 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 most probably interact with a 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 ~ 3610 cm⁻¹). When the concentration of surface hydroxyls was significantly reduced ($T > 673$ K) only B2 type of bicarbonates were 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 CO₂ lose, to a 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, CO₂-saturated γ -Al₂O₃ samples is shown in Fig. S2 (ESI†). All the IR spectra were collected at 300 K sample temperature. The intensities of IR features representing weakly adsorbed carbonates (IR bands in the 1700–1900 cm⁻¹ range) and Lewis acid site-adsorbed CO₂ molecules (~ 2365 and 2407 cm⁻¹) decrease rapidly as the sample is heated from 300 to 400 K. The bicarbonate species are rather stable, and retain some of their intensities even after annealing at 600 K (bottom spectrum). Concomitant with the decrease in the intensity of all the bicarbonate-related IR features is the increase in the intensity of the Al-O-H band at 3779 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 1300–1600 cm⁻¹ spectral region most probably represent bidentate (“organic”) carbonates.⁹

2. CO adsorption at 100 K

Parallel with the CO₂ 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 ref. 12 and references therein]. At these low temperatures CO can interact with hydroxyl groups (weakly) and also with different types of coordinatively unsaturated Al³⁺ ions¹² 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 h and then exposed to increasing amounts of CO at 100 K sample temperature, and IR spectra were collected after the introduction of each CO aliquot (series of spectra collected during these experiments are presented in Fig. S3, ESI†). (The assignments of IR features observed after exposure of the alumina sample to CO are summarized in Table S2 in the ESI†.) Three spectral regions of ν_{OH} (3250–3850 cm⁻¹), ν_{CO} (2050–2300 cm⁻¹) and ν_{AlO} (950–1150 cm⁻¹) can easily be distinguished. The IR spectra obtained from the 473 K-annealed γ -Al₂O₃ sample show only very weak features in the ν_{OH} and ν_{AlO} regions, due to the presence of an almost fully hydroxylated surface under the mild calcination applied prior to CO adsorption. In the ν_{CO} region there are only two, albeit high intensity, bands assigned to CO adsorbed on surface hydroxyls (2158–2155 cm⁻¹) *via* weak hydrogen bonding and CO adsorbed on Lewis acid sites (2194–2186 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. In the IR spectra of adsorbed CO on γ -Al₂O₃ annealed at higher temperatures (mainly at 673 and 773 K) this IR feature is much sharper, since

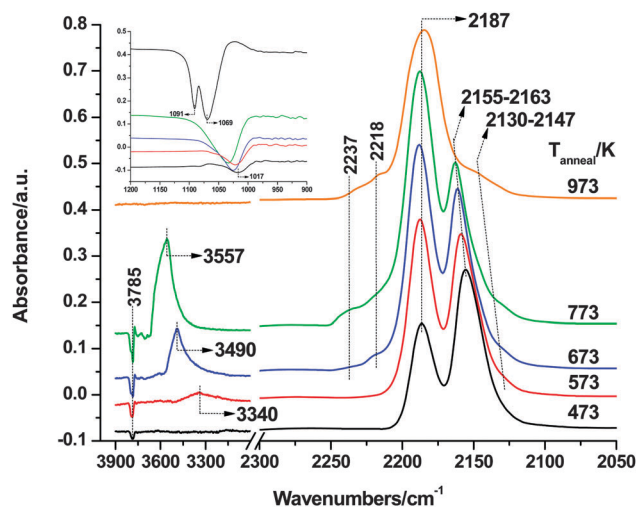


Fig. 2 IR spectra collected from annealed (from 473 to 973 K) γ -Al₂O₃ samples after the conclusion of CO adsorption at 100 K ($P_{\text{CO, equilibrium}} = 0.035$ Torr).

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^{-1} 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 ($2197\text{--}2188\text{ cm}^{-1}$). With increasing annealing temperature the number of surface Lewis acid sites increases, and therefore, more CO can adsorb. The intensity of the OH-bound CO feature ($2163\text{--}2159\text{ cm}^{-1}$) 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 $\sim 1050\text{ cm}^{-1}$ increases as well. Note also the increase in the intensities of the negative IR features at 3794 and 3787 cm^{-1} of surface ν_{OH} vibrations, and the appearance of a broad, weak feature at $\sim 3340\text{ cm}^{-1}$ which is the result of the shift in the ν_{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 ν_{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, and the intensity of the ν_{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 ν_{OH} feature red shifted by the interaction with CO. Besides the two intense ν_{CO} features we have discussed so far, two new, low intensity bands appear on the 673 K-annealed sample at ~ 2220 and 2240 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 ν_{CO} vibrational features increase as the sample is heated to 773 K. At this temperature the surface is extensively dehydroxylated as evidenced by the large intensity gain 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 the 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 decreases (large intensity drop of the 2155 cm^{-1} band), the intensity of the shifted ν_{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 ν_{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 ν_{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), and/or 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 earlier the stability of these adsorbed CO species on the alumina surface was rather low. Fig. 3 displays two series of IR spectra collected from the CO saturated, 473 K (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 spectral acquisition.) The intensity of the IR feature ($\sim 2155\text{ cm}^{-1}$) representing the most weakly adsorbed CO species drops significantly even

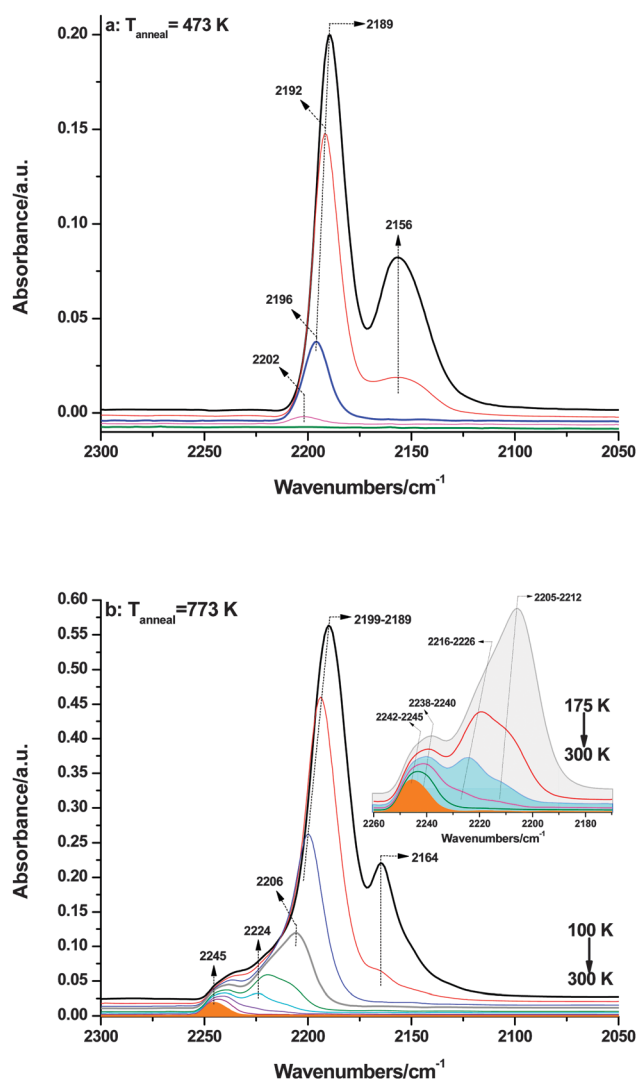


Fig. 3 IR spectra collected during the stepwise annealing following CO adsorption at 100 K on the 473 K (panel a) and 773 K (panel b) annealed $\gamma\text{-Al}_2\text{O}_3$ samples. The temperature interval between two consecutive IR spectra is 25 K. All the spectra were collected at 100 K sample temperature. The inset in panel b shows the IR spectra collected from 175 to 300 K.

during evacuation at 100 K, and it almost completely disappears after annealing at 125 K (the shifted ν_{OH} vibrational feature at around 3555 cm^{-1} loses most of its intensity after flashing the sample to 125 K). Besides the large intensity drop of the 2155 and 3555 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 cm^{-1} . The Lewis site bound CO feature of the 473 K-annealed sample loses its intensity very fast, and after annealing at 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 at 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 only the low intensity IR feature at 2240 cm^{-1} , representing ν_{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 ν_{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 a slight difference in the acid strength of 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 ($2223\text{--}2220\text{ cm}^{-1}$) appears, 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 the 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 stability of the two lower frequency IR features is very low, and a short period of time evacuation completely eliminates them. The intensity of 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_2 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

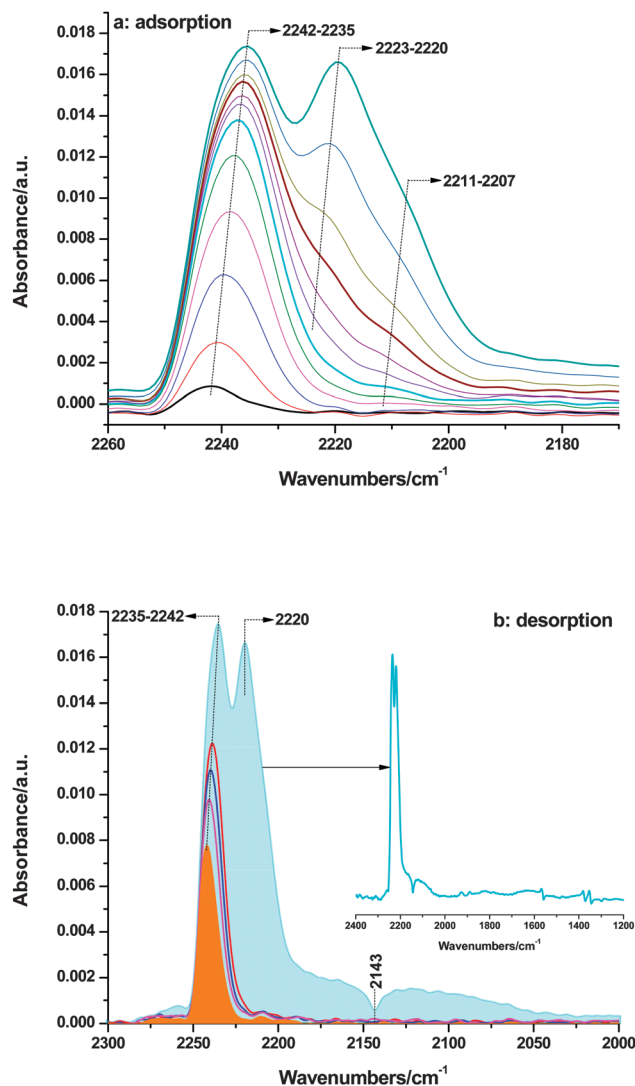


Fig. 4 IR spectra collected during the stepwise CO adsorption on a 773 K-annealed $\gamma\text{-Al}_2\text{O}_3$ sample (panel a) and during subsequent evacuation (panel b) at 295 K.

$\gamma\text{-Al}_2\text{O}_3$ and $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ systems they found that regardless of the presence or absence of Pd, significant amounts of bicarbonates were produced on the alumina surface.¹³ These contradicting findings are even more puzzling in light of the similarities of the $\gamma\text{-Al}_2\text{O}_3$ samples studied in ref. 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 temperature. 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 reveals 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 $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$

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 γ -Al₂O₃ may need to be re-evaluated.

Co-adsorption of CO₂ with CO and H₂O at 295 K

Since the reaction we are interested to investigate on γ -Al₂O₃-supported metal catalysts (CO₂ reduction with H₂) produces water and CO we also studied the co-adsorption of CO and CO₂, and H₂O and CO₂ on the 773 K-annealed clean support material at 295 K. First the 773 K-annealed alumina was saturated with CO₂ at 295 K, and the excess CO₂ (gas phase CO₂) 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 in Fig. 5 (panel a: 1050–2000 cm⁻¹, and panel b: 2100–3850 cm⁻¹ spectral ranges). In the spectral range of carbonates/bicarbonates very minor variations in the IR spectra can be seen: a slight increase in intensity in the weakly held carbonates at \sim 1195 and 1725–1900 cm⁻¹. The intensities of the bicarbonate features do not seem to vary at all. The most significant change in the IR spectrum as a result of CO exposure of the CO₂-saturated alumina is the fast intensity drop of the chemisorbed linear CO₂ feature at \sim 2365 cm⁻¹, and the appearance of the Lewis acid site bound CO feature at \sim 2240 cm⁻¹. At higher CO amounts (when the presence of gas phase CO can clearly be seen) the intensity of almost all chemisorbed CO₂ signal disappears, and the lower frequency adsorbed CO feature at \sim 2220 cm⁻¹ appears. These results unambiguously substantiate that CO and CO₂ are competing for the same adsorption sites. Although CO₂ adsorbs stronger to these Al³⁺ 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 CO₂-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 CO₂ 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 of the bicarbonates). These results clearly indicate that during CO exposure as CO replaces CO₂ on Al³⁺ sites CO₂ does not desorb, but rather converts to weakly held carbonates. Then, when adsorbed CO is removed by evacuation CO₂ moves back to its original adsorption sites. These observations are in full agreement with those of Morterra *et al.* on the CO/CO₂ co-adsorption on η -Al₂O₃.⁷

The effect of water on the adsorption of CO₂ on a 773 K-annealed γ -Al₂O₃ was investigated in two different experiments: in one of the experiments the sample was first saturated with CO₂ at 295 K followed by evacuation to remove the excess CO₂ from the IR cell, and then the sample was exposed to H₂O

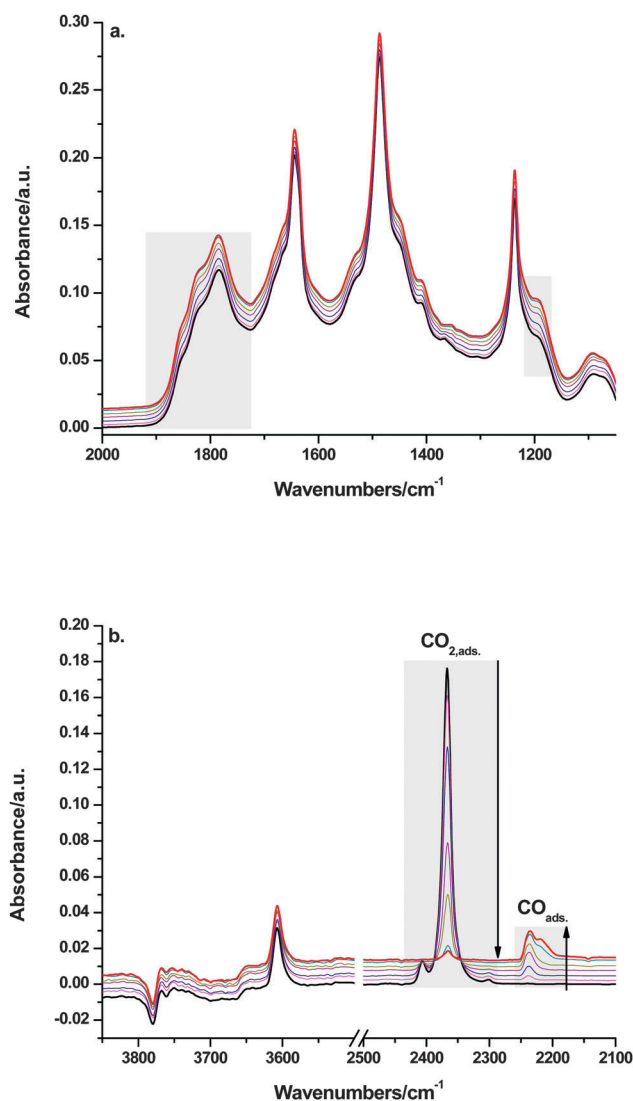


Fig. 5 IR spectra collected during the stepwise CO adsorption on a CO₂-saturated, 773 K-annealed γ -Al₂O₃ sample. Both CO₂ saturation and CO adsorption were carried out at 295 K sample temperature. (The shaded areas highlight the spectral regions where intensity variations occurred as a result of CO adsorption on CO₂/ γ -Al₂O₃.)

in a stepwise manner. In the second experiment the alumina was first exposed to H₂O at 295 K and then to a large dose of CO₂, and the variations in the IR spectra were followed as a function of exposure time. The series of IR spectra obtained during the exposure of a CO₂-saturated γ -Al₂O₃ sample to H₂O is displayed in Fig. S4 (ESI†). The most striking observation is the invariance of the IR features associated with adsorbed CO₂, as well as with carbonates/bicarbonates, to the introduction of water onto the CO₂-saturated sample. The only new IR features appearing as a result of H₂O exposure are the ones associated with adsorbed H₂O at >3000 cm⁻¹. These broad bands arise from the strong hydrogen bonding among adsorbed water molecules. The intensity of the 3608 cm⁻¹ O–H vibrational feature of the bicarbonate species decreases significantly as these hydroxyl groups interact with adsorbed water. This interaction results in

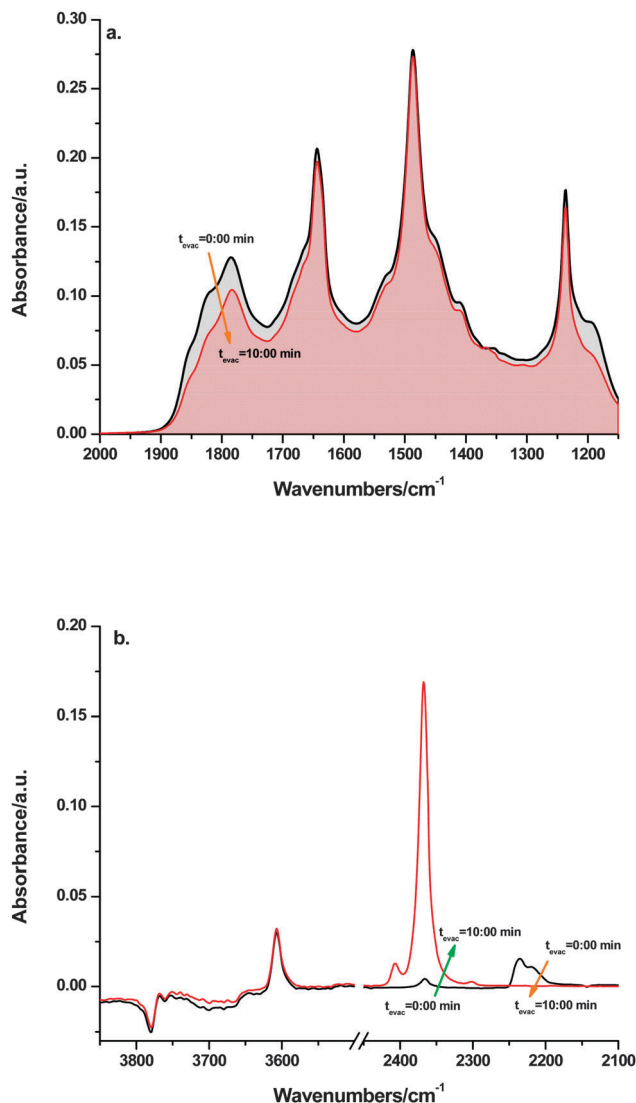


Fig. 6 IR spectra collected from a CO₂-saturated, 773 K-annealed γ -Al₂O₃ sample after CO adsorption (black spectrum) and subsequent evacuation for 10 min (red spectrum) at 295 K in two spectral regions: (a) 1150–200 cm⁻¹ and (b) 2100–3850 cm⁻¹.

the appearance of a new IR band at around 3532 cm⁻¹. The intensity of the IR feature of linearly adsorbed CO₂ (at 2367 cm⁻¹) decreases somewhat with water addition, and concomitantly there is a small increase in intensity in some of the IR features of weakly held (“organic”) carbonates (bands at ~1190 and 1800–1860 cm⁻¹). This is caused by the competition between H₂O and CO₂ for the same adsorption sites (*i.e.*, surface Al³⁺). Similarly to the case of CO/CO₂ co-adsorption discussed above, water exposure of the CO₂-saturated alumina does not result in CO₂ desorption, but rather in the “conversion” of chemisorbed CO₂ into some type of carbonates (“organic”), most probably in bidentate bridging binding configuration. In the second experiment of H₂O/CO₂ co-adsorption first we exposed the 773 K-annealed sample to H₂O and then added a large aliquot of CO₂ to the system, and followed the development of IR features as a function of time (Fig. S5, ESI†). The IR features observed on

this hydrated sample after CO₂ exposure are identical to those seen on the alumina annealed at 773 K prior to H₂O 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 CO₂ was observed (absence of the IR feature at 2365 cm⁻¹), and also B1 bicarbonates formed (characteristic IR band at 1438 cm⁻¹). Furthermore, the intensities of the bidentate carbonate (weakly held carbonate) features (~1190 and 1750–1880 cm⁻¹) 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) γ -Al₂O₃ is not a simple, straightforward process. Exposure of the dehydroxylated alumina surface to water does not eliminate the Lewis acidic Al³⁺ 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 H₂O and then carried out CO₂ 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 the findings of our prior study, where we have shown that the rate of dehydration of ethanol at 473 K was much faster on the 773 K-annealed alumina (Lewis acid sites were present) than on the one that was annealed only at 473 K (only Brönsted acid 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 acid 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 CO₂ with an annealed (from 473 to 973 K) γ -Al₂O₃ support, used for the preparation of supported Pd and Ru catalysts for the catalytic reduction of CO₂, were investigated by *in situ* FTIR spectroscopy. The goal of this study was to understand how γ -Al₂O₃ interacts with the reactant CO₂ 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 CO₂ on γ -Al₂O₃ resulted in the formation of bicarbonates and weakly held surface carbonates, together with linearly adsorbed CO₂. The amount and the nature of carbonates and bicarbonates strongly depended on the calcination temperature of the alumina support. Linearly adsorbed CO₂ 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 CO₂ exposure were bicarbonates, present even

at elevated temperatures following CO₂ 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 have we observed the formation of surface carbonates or bicarbonates upon 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 contradict the findings of some earlier¹¹ and more recent studies.^{13,14} Co-adsorption of either CO or H₂O with CO₂ resulted in competition for the Lewis acidic Al³⁺ sites. Neither CO nor H₂O exposure of the CO₂-saturated alumina resulted in CO₂ desorption, but rather the linearly adsorbed CO₂ was reversibly converted to weakly held bidentate carbonates.

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).

References

- 1 J. N. Park and E. McFarland, A highly dispersed Pd–Mg/SiO₂ catalyst active for methanation of CO₂, *J. Catal.*, 2009, **266**, 92–97.
- 2 H. Y. Kim, H. M. Lee and J. N. Park, Bifunctional Mechanism of CO₂ Methanation on Pd–MgO/SiO₂ Catalyst: Independent Roles of MgO and Pd on CO₂ Methanation, *J. Phys. Chem. C*, 2010, **114**, 7128–7131.
- 3 J. H. Kwak, L. Kovarik and J. Szanyi, Heterogeneous catalysis on atomically dispersed supported metals: CO₂ reduction on multifunctional Pd catalysts, *ACS Catal.*, 2013, **3**, 2094–2100.
- 4 J. H. Kwak, L. Kovarik and J. Szanyi, CO₂ reduction on supported Ru/Al₂O₃ catalysts: cluster size dependence of product selectivity, *ACS Catal.*, 2013, **3**, 2449–2455.
- 5 J. C. Lavalley, Infrared spectrometric studies of the surface basicity of metal oxides and zeolites using adsorbed probe molecules, *Catal. Today*, 1996, **27**, 377–401.
- 6 J. Shen, R. D. Cortright, Y. Chen and J. A. Dumesic, Microcalorimetric and Infrared Spectroscopic Studies of gamma-Al₂O₃ Modified by Basic Metal Oxides, *J. Phys. Chem.*, 1994, **98**, 8067–8073.
- 7 C. Morterra, A. Zecchina, S. Coluccia and A. Chiorino, I.R. Spectroscopic Study of CO₂ Adsorption onto γ -Al₂O₃, *J. Chem. Soc., Faraday Trans. 1*, 1977, **73**, 1544–1560.
- 8 A. Vimont, J. C. Lavalley, A. Sahibed-Dine, C. Otero Areán, M. Rodríguez Delgado and M. Daturi, Infrared Spectroscopic Study on the Surface Properties of γ -Gallium Oxide as Compared to Those of γ -Alumina, *J. Phys. Chem. B*, 2005, **109**, 9656–9664.
- 9 C. Morterra and L. Orio, Surface characterization of zirconium oxide. II. The interaction with carbon dioxide at ambient temperature, *Mater. Chem. Phys.*, 1990, **24**, 247–268.
- 10 K. I. Hadjiivanov and G. N. Vayssilov, Characterization of Oxide Surfaces and Zeolites by Carbon Monoxide as an IR Probe Molecule, *Adv. Catal.*, 2002, **47**, 307–511.
- 11 M. B. Padley, C. H. Rochester, G. J. Hutchings and F. King, FTIR Spectroscopic Study of Thiophene, SO₂, and CO Adsorption on Cu/Al₂O₃ Catalysts, *J. Catal.*, 1994, **148**, 438.
- 12 C. Morterra and G. Magnacca, A case study: surface chemistry and surface structure of catalytic aluminas, as studied by vibrational spectroscopy of adsorbed species, *Catal. Today*, 1996, **27**, 497–532.
- 13 K. Föttinger, R. Schlögl and G. Rupprechter, The mechanism of carbonate formation on Pd–Al₂O₃ catalysts, *Chem. Commun.*, 2008, 320–322.
- 14 C. Weilach, C. Spiel, K. Föttinger and G. Rupprechter, Carbonate formation on Al₂O₃ thin film model catalyst support, *Surf. Sci.*, 2011, **605**, 1503–1509.
- 15 N. D. Parkyn, The influence of thermal pretreatment on the infrared spectrum of carbon dioxide adsorbed on alumina, *J. Phys. Chem.*, 1971, **75**, 526.
- 16 J. B. Peri, Infrared study of adsorption of carbon dioxide, hydrogen chloride, and other molecules on “acid” sites on dry silica-alumina and γ -Alumina, *J. Phys. Chem.*, 1966, **70**, 410–417.
- 17 A. M. Turek and I. E. Wachs, Acidic properties of Alumina-Supported Metal Oxide Catalysts: An Infrared Spectroscopy Study, *J. Phys. Chem.*, 1992, **96**, 5000–5007.
- 18 J. H. Kwak, D. Mei, C. H. F. Peden, R. Rousseau and J. Szanyi, (100) facets of γ -Al₂O₃: The Active Surfaces for Alcohol Dehydration Reactions, *Catal. Lett.*, 2011, **141**, 649–655.