The mechanism of carbonate formation on Pd–Al_2O_3 catalysts†

Karin Föttinger,[a] Robert Schlögl[b] and Günther Rupprechter*[a]

Received (in Cambridge, UK) 28th August 2007, Accepted 15th October 2007
First published as an Advance Article on the web 25th October 2007
DOI: 10.1039/b713161e

Vibrational spectroscopic investigations of the adsorption of isotopically labelled and unlabelled CO and CO_2 reveal that carbonate formation on Pd–alumina catalysts occurs *via* an "oxygen down" reaction of CO with hydroxyl groups on the support, whereas CO dissociation on Pd can be excluded.

The formation of carbonates on oxide supported metal catalysts upon exposure to CO or CO_2 is a well-known effect that can be monitored by infrared spectroscopy or temperature-programmed methods. However, its exact mechanism is still unclear, although several explanations were proposed in the literature, for example for Pd–Al_2O_3 or Pd–MgO catalysts. One model attributed the formation of carbonates to the dissociation/disproportionation of CO on Pd (2 CO → CO_2 + C), followed by reaction of CO_2 with the support (with basic O^{2-} and OH^- ions forming CO_3^{2-} and HCO_3^-, respectively) [*e.g.* ref. 1,2]. However, a considerable number of both experimental and theoretical studies rather excluded CO dissociation on Pd (for CO pressures up to 1 bar and temperatures up to 500 K).[3–6] A second model explained the formation of carbonates *via* a "water gas shift" reaction between CO and the hydroxyl groups of the oxide support (CO + OH → CO_2 + ½ H_2) followed by CO_2 reaction with other OH groups or O^{2-}.[1,7–9] A presence of carbonates already before CO adsorption has also been reported.[10] On pure oxides (without metal) reactive adsorption of CO has been mostly reported for basic oxides, such as MgO, CaO or ZrO_2 [*e.g.* ref. 7,11]. For alumina, the discussion of the formation of carbonates upon CO adsorption is still controversial [*e.g.* ref. 12,13].

This work was motivated by the differing results in the literature concerning the ability of Pd to dissociate CO and, in particular, concerning the origin of the carbonate species on Pd–alumina. We present an IR spectroscopic investigation of well-defined Pd–alumina catalysts taking advantage of isotope-labelled CO and CO_2 that allowed us to assess the validity and relevance of the proposed mechanisms. This also led us to suggest a procedure to selectively probe the reactive sites on alumina and other oxides *via* the adsorption of $^{13}C^{18}O$.

A 2 wt% Pd catalyst supported on a commercial γ-Al_2O_3 (Sasol Germany GmbH, Puralox SBA 200) was prepared by incipient wetness impregnation using Pd(II) nitrate dihydrate as precursor, followed by calcination at 773 K and reduction at 573 K. Pure alumina without Pd was used for comparison and pretreated under the same conditions.

The Pd particle size was determined by TEM, by XRD line broadening and by H_2 chemisorption using a volumetric system (sorption – back-sorption method[14]), with all methods indicating a mean particle diameter of approximately 4.5 nm. According to TEM and IR spectra of adsorbed CO the Pd particles were well-faceted cuboctahedral particles exhibiting mostly (111) and (100) surface facets.[15]

FT-IR measurements were carried out in transmission mode on a Bruker IFS 28 FT-IR spectrometer. After *in situ* reduction at 573 K in pure hydrogen for 30 min, followed by evacuation at the same temperature for one hour, static CO or CO_2 adsorption was performed at 300 K and 5 mbar pressure.

On Pd–Al_2O_3 carbonate bands were observed at the following positions: the main peaks appeared at 1650, 1436 and 1229 cm^{-1}, a shoulder was observed at 1470 and a weak peak at 1264 cm^{-1} (Fig. 1A). The same bands were found on the pure support without Pd. The assignment of the IR peaks is not straightforward, because adsorbed carbonates can exist in different structures. The following assignments were reported in the literature[16–18]: Free carbonate ions on the oxide support give rise to a band at 1440 cm^{-1} ($\nu_{as}CO_3^{2-}$). Monodentate species are characterized by bands at 1530–1470 cm^{-1} ($\nu_{as}COO^-$) and 1370–1300 cm^{-1} ($\nu_{sy}COO^-$). Bidentate carbonates lead to νC=O bands at 1670–1530 cm^{-1} and ν_{as}COO at 1270–1220 cm^{-1}. Bicarbonates exhibit bands at 1625–1600 cm^{-1} (ν_{as}COO), 1440–1415 cm^{-1} (ν_{sy}COO) and 1250–1180 cm^{-1} (δCOH). Furthermore, formation of formates can occur on oxide surfaces [*e.g.* ref. 7,16,19,20], but these species would lead to additional bands in the C–H stretching vibration region that did not appear in our measurements. Considering these assignments, bidentate carbonates and hydrogencarbonates have been formed on our catalyst upon CO adsorption. Adsorption of CO_2 produced the same bands (Fig. 1A), with an additional smaller peak at 1709 cm^{-1}. However, upon exposure to CO_2 the carbonate bands had a higher intensity pointing to a higher surface carbonate concentration.

The OH stretching region should provide a direct answer whether support OH groups are involved in carbonate formation or not. In fact, adsorption of CO led to changes in the OH stretching region, both for the pure alumina support as well as for Pd-containing samples (Fig. 1B). Sharp OH bands at 3766, 3726 and 3663 cm^{-1} strongly decreased in intensity (negative peaks in Fig. 1B) and a broad band appeared at lower frequency (around 3300 cm^{-1}). The latter presumably indicates formation of water (OH + H) or adsorbed H_2, because the same effect occurred upon adding H_2 to Al_2O_3 or Pd–Al_2O_3 (without CO). This observation strongly supports the formation of CO_2 *via* reaction of CO with the surface OH groups, which was corroborated by the fact that

---

[a] *Institute of Materials Chemistry, Veterinärplatz 1, A-1210, Vienna, Austria. E-mail: grupp@imc.tuwien.ac.at; Fax: +43 1 25077 3890; Tel: +43 1 25077 3813*
[b] *Fritz Haber Institute, Max Planck Society, Faradayweg 4-6, 14195, Berlin, Germany. Fax: +49 30 8413 4404; Tel: +49 30 8413 4401*

† Electronic supplementary information (ESI) available: Experimental and supplementary IR data. See DOI: 10.1039/b713161e

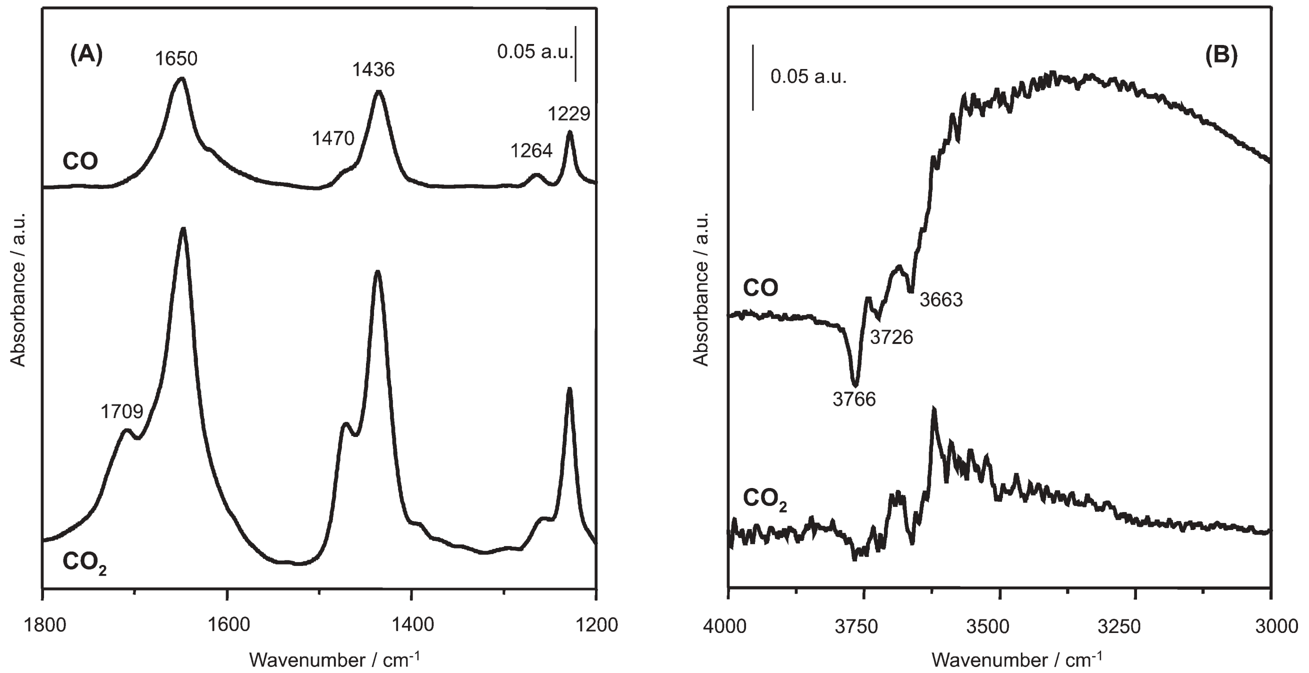


Fig. 1 Vibrational IR spectra after adsorption of CO and CO_2 (5 mbar, 293 K) on Pd–Al_2O_3 and Al_2O_3: (A) carbonate region and (B) OH stretching region. Difference spectra are displayed, obtained by subtracting the corresponding spectra acquired before gas exposure.

upon CO_2 adsorption the sharp OH bands were not affected or decreased only slightly (and, therefore, do not show up in the difference spectrum) and no broad OH band was produced (*i.e.* CO_2 did not react away surface OH and rather produced CO_3^{2-}) (Fig. 1B).

The observed changes in the OH region and the fact that carbonates were also produced on the pure support clearly suggest the reaction of CO with surface hydroxyl groups as pathway for carbonate formation. However, at this point one cannot exclude a second (faster?) pathway of carbonate formation in the presence of Pd metal *via* CO disproportionation.

In order to assess this suggestion, adsorption of isotopically labelled $^{13}C^{18}O$ was performed. This should allow distinguishing between CO_2 formed by CO disproportionation ($2\ ^{13}C^{18}O \rightarrow {}^{13}C^{18}O_2 + {}^{13}C$) and CO_2 produced *via* "water gas shift" reaction ($^{13}C^{18}O + {}^{16}OH_{supp.} \rightarrow {}^{13}C^{18}O^{16}O + ½\ H_2$). After further reaction of CO_2 with the support, one should observe mainly $^{13}C^{18}O$ vibrations in the first case, while the second pathway should lead to vibrational bands of both $^{13}C^{16}O$ and $^{13}C^{18}O$. In order to confirm the calculated frequency shifts, experiments were also carried out with isotope-exchanged $^{13}C^{18}O_2$ and $^{13}C^{16}O_2$ ($^{13}C^{18}O^{16}O$ was not available).

When $^{13}C^{18}O$ was exposed, carbonate bands appeared at 1614, 1395 and 1224 cm^{-1}, with shoulders at 1650 and 1430 cm^{-1} (Fig. 2a). The same bands were found for the pure alumina support (without Pd). Comparison with the vibrational bands observed after adsorption of $^{13}C^{18}O_2$ (Fig. 2c) shows no match which immediately excludes CO dissociation as source of CO_2. In contrast, the IR peaks agree well with calculations for $^{13}C–^{16}O$ vibrations, which suggests the water gas shift route. However, the readsorption of $^{13}C^{18}O^{16}O$ should lead to both $^{13}C–^{16}O$ and $^{13}C–^{18}O$ vibrations, but the latter was not observed (upon $^{13}C^{18}O$ dosing).

Based on these results and the reference measurements discussed below we suggest the following model for carbonate formation (Scheme 1): $^{13}C^{18}O$ reacts "oxygen down" with the alumina

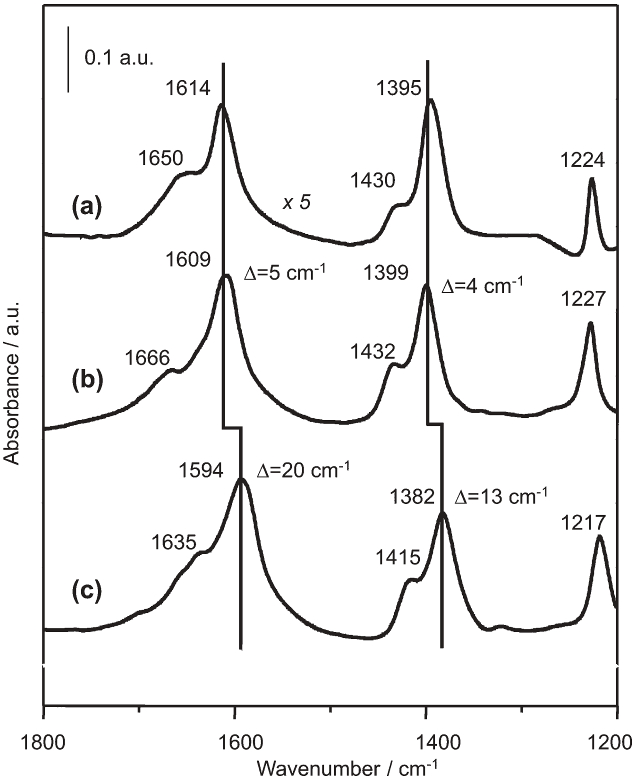
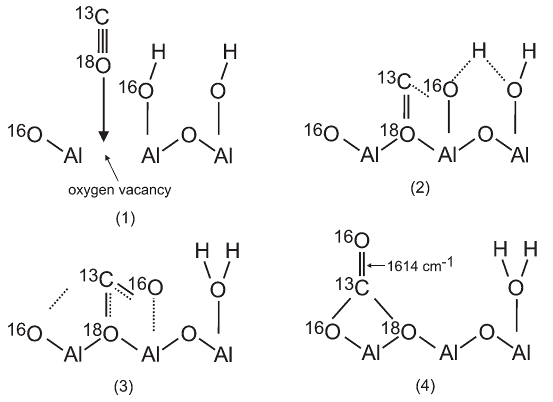


Fig. 2 Adsorption of (a) $^{13}C^{18}O$, (b) $^{13}C^{16}O_2$ and (c) $^{13}C^{18}O_2$ at 5 mbar pressure and 293 K on Pd–Al_2O_3: Difference spectra of the carbonate bands.



Scheme 1 Proposed reaction pathway for carbonate formation.

support, presumably at an oxygen vacancy or Al*cu*‡, before it reacts with a neighbouring surface ^{16}OH group to "CO_2" and hydrogen. There is no desorption and readsorption of CO_2 but it directly reacts with another surface ^{16}oxygen to bidentate carbonate (or with surface ^{16}OH to bicarbonate). This leads to a species for which the internal ^{13}C–^{16}O vibration is most intense.

This model is supported by the following reference measurements: (a) As mentioned, dosing $^{13}C^{18}O_2$ (Fig. 2c) produces a carbonate species for which the ^{13}C–^{18}O vibration is most intense (due to the interaction of one of the two ^{18}O with an oxygen vacancy or Al*cu*). This provides the reference for the internal ^{13}C–^{18}O vibration, which is clearly different from the spectrum after dosing $^{13}C^{18}O$. (b) Dosing $^{13}C^{16}O_2$ (Fig. 2b) produces a carbonate species for which the ^{13}C–^{16}O vibration is most intense (due to the interaction of one of the two ^{16}O with an oxygen vacancy or Al*cu*). This provides the reference for the internal ^{13}C–^{16}O vibration, which is indeed very similar to the spectrum after dosing $^{13}C^{18}O$. The small difference is probably due to the mass difference of one of the two support-bound oxygens.

In summary, we have performed FT-IR studies of the adsorption of unlabelled and isotopically-labelled CO and CO_2 to examine the mechanism of carbonate formation on a Pd–alumina catalyst and on the pure support. Based on the analysis of the carbonate vibrational frequencies we exclude CO disproportionation on the Pd metal at 300 K ($2\,CO \neq CO_2 + C$). Carbonate formation occurs *via* reaction of CO with surface OH ($CO + OH \rightarrow CO_2 + \frac{1}{2} H_2$), followed by instantaneous CO_2 reaction with the oxide support. The isotope studies also indicate an oxygen-down reaction of CO, probably involving oxygen-vacancies or other defects on the alumina support. Future studies will focus on a quantification of the carbonate species which will enable us to use $^{13}C^{18}O$ adsorption to selectively probe and quantify the reactive sites on alumina and other oxides. Preliminary results indicate that approximately $1.5\cdot10^{12}$ carbonate molecules were formed on 1 cm^2 area of alumina.

This has also implications on a standard method in catalysis, *i.e.* to determine metal particle size (dispersion) *via* quantitative chemisorption of CO [*e.g.* ref. 14,21–23], assuming selective adsorption of CO on the metal. Comparison of CO chemisorption on pure Al_2O_3 and Pd–Al_2O_3 indicated that about 20% of the CO adsorbed on Pd–Al_2O_3 reacted on the support. This leads to an overestimation of Pd dispersion, *e.g.* for the current catalyst (4.5 nm mean particle size; dispersion 25%), the reactive adsorption (carbonate formation) on the support oxide resulted in a smaller "apparent" mean particle size of 3.6 nm (dispersion 31%). This may explain the typical deviation between mean size determination by electron microscopy and CO chemisorption. After correction for the CO amount consumed by carbonate formation, the dispersion values obtained from CO chemisorption agreed with those from hydrogen chemisorption.

Notes and references

‡ Al*cu* is used as abbreviation for coordinatively unsaturated Al ions.

1 H. Dropsch and M. Baerns, *Appl. Catal., A*, 1997, **158**, 163.
2 S. Bertarione, D. Scarano, A. Zecchina, V. Johanek, J. Hoffmann, S. Schauermann, M. Frank, J. Libuda, G. Rupprechter and H.-J. Freund, *J. Phys. Chem. B*, 2004, **108**, 3603.
3 G. Rupprechter, V. V. Kaichev, M. Morkel, H. Unterhalt and V. I. Bukhtiyarov, *Appl. Surf. Sci.*, 2004, **235**, 26.
4 M. Neurock, *Top. Catal.*, 1999, **9**, 135.
5 H. Cordatos, T. Bunluesin and R. J. Gorte, *Surf. Sci.*, 1995, **323**, 219.
6 C. R. Henry, C. Chapon, C. Goyhenex and R. Monot, *Surf. Sci.*, 1992, **272**, 283.
7 K. Pokrovski, K. T. Jung and A. T. Bell, *Langmuir*, 2001, **17**, 4297.
8 O. Demoulin, M. Navez and P. Ruiz, *Appl. Catal., A*, 2005, **295**, 59.
9 S. D. Jackson, B. M. Glanville, J. Willis, G. D. McLellan, G. Webb, R. B. Moyes, S. Simpson, P. B. Wells and R. Whyman, *J. Catal.*, 1993, **139**, 207.
10 T. Lear, N. G. Hamilton and D. Lennon, *Catal. Today*, 2007, **126**, 219.
11 G. Spoto, E. N. Gribov, G. Ricchiardi, A. Damin, D. Scarano, S. Bordiga, C. Lamberti and A. Zecchina, *Prog. Surf. Sci.*, 2004, **76**, 71.
12 C. Morterra and G. Magnacca, *Catal. Today*, 1996, **27**, 497.
13 M. B. Padley, C. H. Rochester, G. J. Hutchings and F. King, *J. Catal.*, 1994, **148**, 438.
14 J. L. Benson, H. S. Hwang and M. Boudart, *J. Catal.*, 1973, **30**, 146.
15 G. Rupprechter, *Adv. Catal.*, 2007, **51**, 133.
16 A. A. Davydov, *Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides*, Wiley, Chichester, 1990.
17 L. Hair, *Infrared Spectroscopy in Surface Chemistry*, Marcel Dekker, New York, 1967.
18 K. I. Hadjiivanov and G. N. Vayssilov, *Adv. Catal.*, 2002, **47**, 307.
19 O. Pozdnyakova, D. Teschner, A. Wootsch, J. Kröhnert, B. Steinhauer, H. Sauer, L. Toth, F. C. Jentoft, A. Knop-Gericke, Z. Paal and R. Schlögl, *J. Catal.*, 2006, **237**, 17.
20 H. Borchert, B. Jürgens, V. Zielasek, G. Rupprechter, S. Giorgio, C. R. Henry and M. Bäumer, *J. Catal.*, 2007, **247**, 145.
21 H. L. Gruber, *J. Phys. Chem.*, 1962, **66**, 48.
22 R. L. Moss, D. Pope, B. J. Davis and D. H. Edwards, *J. Catal.*, 1979, **58**, 206.
23 M. A. Vannice, *J. Catal.*, 1975, **40**, 129.