Experimental details

Catalyst preparation

The catalyst was prepared by incipient wetness impregnation using a commercial γ-Al_2O_3 support obtained from Sasol Germany GmbH (Puralox SBA 200, specific surface area 250 m^2/g). The amount of precursor salt (Pd(II)nitrate dihydrate, Fluka) required for a final metal loading of 2 wt% was dissolved in water followed by stirring at room temperature for 1 hour. After drying over night at 100°C calcination was carried out at 500°C for 3 hours in static air. Reduction was done in situ (in the reaction cell) in pure hydrogen at 573 K, immediately before a respective measurement. Pure Al_2O_3 was calcined and pretreated under the same conditions.

Characterization

The metal dispersion was determined by hydrogen chemisorption in a volumetric system after pretreatment in hydrogen at 573 K and keeping this temperature in vacuum (approx. 10^{-6} mbar) for 1 h to desorb hydrogen and formed water. H_2 isotherms were then collected at 293 K at increasing partial pressures. Two isotherms were measured consecutively with room temperature evacuation in between in order to distinguish between surface-adsorbed and absorbed hydrogen. Based on the amount of chemisorbed hydrogen a mean Pd particle size of 4.5 nm (dispersion 25%) was obtained, assuming spherical particles and a H:Pd ratio of 1. The mean particle size agreed with that observed by high resolution TEM-EDX (FEI Tecnai F20-FEG S-Twin operated at 200 kV) and powder X-ray diffraction (Philips X`Pert PRO). Quantitative chemisorption studies of CO were performed at 293 K using the same volumetric system, assuming a CO:Pd ratio of 0.5.

IR spectroscopic measurements

Transmission FT-IR spectra were recorded on a Bruker IFS 28 spectrometer equipped with an MCT detector at a resolution of 4 cm^{-1}. The catalyst was pressed to a disc (amount of catalyst: approx. 10-20 mg), mounted on a ring-shaped furnace and placed inside an IR cell connected to a turbo-molecular pump. Additionally, the IR cell is equipped with liquid nitrogen cooling, which allows measurements at low temperature (~100 K). Adsorption of probe molecules or reactants is carried out under static vacuum conditions with the gases introduced via a leak valve.

Prior to the adsorption studies, the samples were reduced in the cell at 573 K for 30 min, followed by treatment in vacuum at the same temperature for one hour, and cooled down to 293 K in vacuum (approx. 10^{-6} mbar). CO adsorption was carried out at 293 K, exposing to 5 mbar CO until saturation, and followed by evacuation of gas phase CO at the same temperature. Adsorption of CO_2 was performed under the same conditions. Apart from $^{12}C^{16}O$ and $^{12}C^{16}O_2$, the following CO and CO_2 isotopes (Isotec) were used: $^{13}C^{18}O$ (min. 99 atom% ^{13}C, 95 atom% ^{18}O), $^{13}C^{18}O_2$ (min. 99 atom% ^{13}C, 97 atom% ^{18}O) and $^{13}C^{16}O_2$ (min. 99 atom% ^{13}C).

Supplementary data

IR spectroscopic measurements

The following table summarizes the frequencies of the main carbonate bands observed upon exposure of the various CO and CO_2 isotopes.

Table 1: Carbonate band frequencies and shifts observed upon exposure of $^{12}C^{16}O$, $^{13}C^{18}O$, $^{12}C^{16}O_2$, $^{13}C^{16}O_2$ and $^{13}C^{18}O_2$ on 2 wt% Pd-alumina at 293 K.

Exposed Gas	Carbonate main band positions (cm^{-1}) (νC=O *bd*; ν_{sy}COO *bc*)	$\Delta\nu$ compared to $^{13}C^{18}O$ exposure (cm^{-1})	$\Delta\nu$ compared to $^{12}C^{16}O/^{12}C^{16}O_2$ exposure (cm^{-1})
$^{12}C^{16}O$ or $^{12}C^{16}O_2$	1650; 1436	36; 41	--
$^{13}C^{18}O$	1614; 1395	--	36; 41
$^{13}C^{16}O_2$	1609; 1399	5; 4	41; 37
$^{13}C^{18}O_2$	1594; 1382	20; 13	56; 54

bd = bidentate carbonate; bc = bicarbonate