Pd$_2$Ga-Based Colloids as Highly Active Catalysts for the Hydrogenation of CO$_2$ to Methanol

Andrés García-Trenco, Edward R. White, Anna Regoutz, David J. Payne, Milo S. P. Shaffer, and Charlotte K. Williams

1. INTRODUCTION

The hydrogenation of CO$_2$ to methanol, using H$_2$, derived from renewable or off-peak power, is a promising strategy to reduce our dependence on fossil resources.$^1$ The methanol produced is an important chemical feedstock but is also an attractive liquid energy carrier suitable for energy storage and transportation applications. It can be used directly as fuel or in blends with gasoline,$^2$ in conventional combustion engines, or for use in fuel cells.$^3$ Methanol is currently produced on a large scale from natural gas through a syngas route. Steam methane reforming produces a mixture of CO, CO$_2$, and H$_2$ that is subsequently converted to methanol using heterogeneous Cu-ZnO-Al$_2$O$_3$ catalysts.$^4$ Isotopic labeling and modeling studies suggest that the methanol derives from the CO$_2$ in the syngas, under the typical industrial reaction conditions.$^5$ It is known that Cu-ZnO-Al$_2$O$_3$ catalysts are also active for the direct hydrogenation of CO$_2$ to methanol, although with only moderate activity and insufficient stability.$^6$ Over the past decade, Fischer and co-workers have pioneered the use of mixtures of colloidal Cu and ZnO nanoparticles (NPs) for the synthesis of methanol from syngas, reporting activities comparable to or slightly better than those obtained for the benchmark Cu-ZnO-Al$_2$O$_3$ heterogeneous catalysts.$^9$–$^12$ This approach has also been studied and applied successfully by our group in the hydrogenation of CO$_2$ to methanol, as well as in the direct synthesis of DME from syngas.$^{13}$–$^{15}$ Colloidal Cu and ZnO NPs exhibit high surface areas, and mixtures readily form the Cu/ZnO interface thought to be the active site for methanol synthesis.$^{16}$–$^{18}$ The colloidal system allows a number of properties to be easily tuned, including catalyst composition, particle size, solubility, and surface functionality.$^{19}$ These stabilized colloidal catalysts are applied in liquid-phase reactors where the temperature gradients can be easily controlled, a feature which may be desirable to obviate the typical deactivation attributed to the poor temperature control fixed-bed technologies.$^{20}$ In fact, a commercial liquid-phase methanol synthesis process (LPMEOH) has been developed, on the basis of conventional heterogeneous catalysts used as a slurry;...
however, a solubilized catalyst may offer improved kinetics, mass transport, and high intrinsic activity. One of the challenges in optimizing colloidal Cu/ZnO catalysts lies with controlling the interaction between the Cu NPs with their counterpart ZnO NPs to maximize the formation of active sites; individually Cu or ZnO NPs are hardly active in isolation.\textsuperscript{16,21}

Despite the promise of the Cu/ZnO system, there is also interest in exploring other metal/oxide combinations in order to maximize performance. Heterogeneous catalysts using palladium as the active metal have shown significant promise in a range of hydrogenation and reforming reactions.\textsuperscript{22,23} Fujitani et al. reported the first use of Pd/Ga\textsubscript{2}O\textsubscript{3} catalysts for the synthesis of methanol from CO\textsubscript{2} and H\textsubscript{2}.\textsuperscript{57} obtaining activity higher than that for the Cu/ZnO system. Since then, several groups have developed Pd/Ga\textsubscript{2}O\textsubscript{3} catalysts for methanol synthesis, as well as in related reactions such as methanol steam reforming or methanol decomposition.\textsuperscript{24,27,30,31,34,39} Pd\textsubscript{2}Ga NPs have mostly been studied for the hydrogenation of CO\textsubscript{2} and Ga\textsubscript{2}O\textsubscript{3} phases in the reaction mechanism, it is accepted that the formation of Pd–Ga intermetallic compounds, mainly the Pd\textsubscript{2}Ga phase, is strongly implicated in controlling catalytic activity.\textsuperscript{24,27} Pd\textsubscript{2}Ga NPs have mostly been studied previously in fixed-bed reactors, as heterogeneous catalysts on solid supports including MgO/MgGa\textsubscript{2}O\textsubscript{4},\textsuperscript{34,32} α, β, and γ-Ga\textsubscript{2}O\textsubscript{3} polymorphs,\textsuperscript{24,27} and SiO\textsubscript{2}.\textsuperscript{57} The syntheses typically employ the decomposition of ternary hydrotalcite-like compounds,\textsuperscript{34} simple coprecipitation,\textsuperscript{39} or an incipient wetness impregnation of Ga and Pd precursors.\textsuperscript{24,27} Recently, a strong metal–support interaction was found specifically between the polar (002) Ga\textsubscript{2}O\textsubscript{3} surface and supported Pd NPs, which facilitates electron transfer and the formation of PdGa\textsubscript{2}.\textsuperscript{31,32}

Although there is still a lack of consensus about the role of the Pd and Ga\textsubscript{2}O\textsubscript{3} phases in the reaction mechanism, it is accepted that the formation of Pd–Ga intermetallic compounds, mainly the Pd\textsubscript{2}Ga phase, is strongly implicated in controlling catalytic activity.\textsuperscript{24,27,50,31,34,39} Pd\textsubscript{2}Ga NPs have been studied previously in fixed-bed reactors, as heterogeneous catalysts on solid supports including MgO/MgGa\textsubscript{2}O\textsubscript{4},\textsuperscript{34,32} α, β, and γ-Ga\textsubscript{2}O\textsubscript{3} polymorphs,\textsuperscript{24,27} and SiO\textsubscript{2}.\textsuperscript{57} The syntheses typically employ the decomposition of ternary hydrotalcite-like compounds,\textsuperscript{34} simple coprecipitation,\textsuperscript{39} or an incipient wetness impregnation of Ga and Pd precursors.\textsuperscript{24,27} Recently, a strong metal–support interaction was found specifically between the polar (002) Ga\textsubscript{2}O\textsubscript{3} surface and supported Pd NPs, which facilitates electron transfer and the formation of PdGa\textsubscript{2}.\textsuperscript{31,32}

Given the success of the aforementioned heterogeneous catalysts, the development of colloidal Pd\textsubscript{2}Ga NPs catalysts for the hydrogenation of CO\textsubscript{2} to methanol is a desirable and as yet unexplored target. Here, a simple strategy to synthesize colloidal Pd\textsubscript{2}Ga NPs, together with their detailed characterization and catalytic performance, is demonstrated.

2. EXPERIMENTAL SECTION

2.1. Preparation of the Catalytic Precursors. Gallium-(III) stearate (Ga(OSt))\textsubscript{3} was prepared by modifying a reported method used for the synthesis of other metal stearates.\textsuperscript{40,41} In brief, 3 equiv of stearic acid (extra pure, Fischer Scientific) was dissolved in methanol and then neutralized with a methanol solution of tetramethylammonium hydroxide (TMAOH, 98% Alfa Aesar). Afterwards, 1 equiv of Ga(NO\textsubscript{3})\textsubscript{3} (99.9% Alfa Aesar) dissolved in methanol was added dropwise into the neutralized solution. The white Ga(OSt)\textsubscript{3} precipitate was filtered, washed extensively with methanol, and finally dried in a vacuum oven at 50 °C. C and H contents (%), were determined by elemental analysis (Table S1 in the Supporting Information) and were in good agreement with the nominal values. FTIR spectroscopy (Figure S1 in the Supporting Information) showed the CH\textsubscript{2} vibrations (2850 and 2917 cm\textsuperscript{-1}) of the stearate chain, along with absorptions at 1449 and 1560 cm\textsuperscript{-1} assigned to the carboxylic symmetric and asymmetric stretches, respectively.\textsuperscript{50,42} Pd(II) acetate (Pd\textsubscript{(OAc)}\textsubscript{2}) was obtained commercially from Acros Organics (47.5 wt % Pd). A commercial precursor to the methanol synthesis catalysts, based on the ternary CuO-ZnO-Al\textsubscript{2}O\textsubscript{3} material, was previously in a range of hydrogenation and reforming reactions.\textsuperscript{22,23} The Cu or ZnO NPs are hardly active in isolation.\textsuperscript{16,21}

2.2. Characterization Techniques. Fourier transform infrared (FTIR) spectroscopy was performed with a PerkinElmer Spectrum 100 Fourier Transform IR spectrometer using a deuterated triglycine sulfate (DTGS) detector and an attenuated total reflection (ATR) accessory. Elemental analysis (EA) was carried out using a Carlo Erba Flash 2000 Elemental Analyzer. Thermogravimetric analysis (TGA) was conducted using a PerkinElmer Pyris 1 TGA instrument under N\textsubscript{2} flow from 100 to 700 °C, at a heating rate of 10 °C min\textsuperscript{-1}

Powder X-ray diffraction (XRD) was carried out using an X’pert Pro MPD diffractometer (PANalytical BV) operating at 40 kV and 40 mA, using nickel-filtered Cu K\textsubscript{α} radiation (λ = 1.542 nm). To prevent contact with air during the measurements, the samples were covered by a polymide film tape (Agar Scientific). The average crystal size of Pd(0), Cu(0), and Pd\textsubscript{2}Ga particles were determined by applying the Scherrer equation (shape factor of 0.9) to the most intense and not overlapped reflections at 39.9 (111), 43.5 (111), and 44.8° (020), respectively.

Transmission electron microscopy (TEM) samples were prepared by drop-casting a toluene solution onto a 300 mesh Cu holey-carbon grid with an ultrathin 3 nm carbon film (Agar Scientific). Annular dark field scanning TEM (ADF-STEM) and energy dispersive X-ray (EDX) mapping were performed with a JEOL JEM 2100F scanning transmission electron microscope operated at 200 kV and equipped with an Oxford X-Max 80 SDD EDX detector. High-resolution TEM (HR-TEM) images were obtained with an aberration-corrected FEI Titan instrument operated at 300 kV. For HR-TEM imaging, samples were loaded and sealed into a Gatan Environmental Holder, under a nitrogen atmosphere in a glovebox, preventing any atmospheric exposure that might lead to inadvertent sample oxidation during transfer to the microscope. The average NP sizes were determined using HR-TEM and ADF-STEM by measuring approximately 200 NPs for each sample.

The surface of the samples was characterized using X-ray photoelectron spectroscopy (XPS). The spectra were recorded on a Thermo Scientific K-Alpha+ X-ray photoelectron spectrometer system operating at 2 × 10\textsuperscript{-9} mbar base pressure. This system incorporates a monochromated, microfocused Al K\textsubscript{α} X-ray source (hv = 1486.6 eV) and a 180° double-focusing hemispherical analyzer with a 2D detector. The X-ray source was operated at 6 mA emission current and 12 kV anode bias, and a flood gun was used to minimize sample charging. A small shift in binding energy (BE) caused by charging was observed for the sample PdGa290/3:1, and all spectra relating to this sample were corrected by a shift of −250 meV. Samples were mounted using conductive carbon tape and transferred to the spectrometer using a special glovebox module which prevented any exposure to air. Data were collected at 20 eV pass energy for both core level (Pd 3d, Ga 2p\textsubscript{1/2} and Ga 3d) and valence band spectra using an X-ray spot size of 400 μm\textsuperscript{2}. All data were analyzed using the Avantage software package. For the calculation of the inelastic electron mean free path (IMFP), following the Tanuma, Powell, and Penn (TPP-2M) method, the QUASES software package was used.\textsuperscript{43}

Pd/Ga pre- and postcatalysis samples analyzed by XRD, XPS, and TEM were prepared using typical air-sensitive techniques, in order to prevent any air exposure. As such, the samples were withdrawn from the reactor to a Schlenk tube, under a N\textsubscript{2} atmosphere, via a cannula with a high flow rate of N\textsubscript{2} (400 mL min\textsuperscript{-1}), washed several times with dry toluene (distilled from sodium and degassed by performing at least three freeze–
2.3. Synthesis of the Pd/Ga Colloids and Catalytic Experiments. The synthesis and reaction tests were performed in a 300 mL continuous flow stirred-tank reactor (CSTR; Parr), with mechanical stirring at 1500 rpm and with vertical baffles to ensure the homogeneous mixing of the liquid and gas phases. Squalane (16 ppm of water, by Karl Fischer titration) was used as the solvent, as it exhibits a high boiling point and good gas solubility of the feed gases; it has already been reported to be an excellent solvent for the liquid-phase methanol synthesis and is widely used.9,44 In a typical preparation procedure, the required amounts of Pd(OAc)₂ and Ga(OSt)₃ were suspended in 100 mL of squalane (3.18 mmolPd+Ga L⁻¹), and the mixture was degassed with N₂ (400 mL min⁻¹) for 30 min. Then, the temperature was increased to 190 °C (6 °C min⁻¹), and after 1 h under N₂ flow (400 mL min⁻¹), the reactor was cooled to 100 °C. The resulting sample, prepared with a Pd:Ga molar ratio of 2:1, is labeled as PdGa₁₉₀N₂. In the second preparation step, the reduction was performed by passing a 200 mL min⁻¹ stream of 5% H₂/N₂ at 0.5 MPa and 210, 250, or 290 °C (3 °C min⁻¹) for 2 h. The Pd/Ga colloids are labeled as PdGaₓ/y/z, where x is the reduction temperature and y/z the Pd:Ga molar ratio used.

In order to perform the methanol synthesis run, the prepared Pd/Ga colloid (still in the CSTR) was submitted to the methanol synthesis conditions, which were 5.0 MPa, 210 °C, GHSV = 18.9 L mmolPd+Ga⁻¹ h⁻¹ of a gas mixture comprising 96 vol % (75% H₂/25% CO₂), and 4 vol % Ar (used as internal standard for GC analysis) for 15 h. The benchmark commercial Cu-ZnO-Al₂O₃ catalyst was tested as a reference material. The choice of catalyst loading was dictated by normalization considerations, making sure that the total amount of metals (Cu, Zn, Al, Mg) in moles was the same as that in the Pd/Ga colloids (3.18 mmolMetal⁻¹ L⁻¹), GHSV = 18.9 L mmolMetal⁻¹ h⁻¹).39 Before any catalysis experiments were conducted, the reference catalyst was activated using a diluted H₂ stream (5 vol % H₂/N₂) at 0.45 MPa and 240 °C.

Figure 1. XRD spectra for the Pd/Ga samples (a) at different stages in the preparation and reduction temperatures and (b) prepared with different Pd/Ga composition. Asterisks denote diffraction from the polyimide film tape used to prevent the air exposure of the samples.

“X denotes an O⁻/OH or CO₂⁻/CO₂H terminal group.
Research Article

Ga(0), Pd

XRD patterns of the Pd/Ga products revealed only broad Pd(OAc)2 and Ga(OSt)3 to 190 ºC, which showed that heating a mixture of palladium acetate (Pd(OAc)2) precursor with the byproducts being mostly acetic acid and CO2. XRD confirmed that the resulting black colloid (PdGa190N2) consists of Pd(0) crystallites with an average size of 2.8 nm (Figure 1a). The XRD pattern is shifted by 0.6º to lower 2θ angles in comparison to the reference Pd(0) crystalline phase, due to an expansion in the Pd-Pd interatomic distance known to occur for Pd(0) NPs of such a small size.46 During the bulk preparation step, the acetic acid and CO2. XRD confirmed that the resulting black colloid (PdGa190N2) consists of Pd(0) crystallites with an average size of 2.8 nm (Figure 1a). The XRD pattern is shifted by 0.6º to lower 2θ angles in comparison to the reference Pd(0) crystalline phase, due to an expansion in the Pd-Pd interatomic distance known to occur for Pd(0) NPs of such a small size.46 During the bulk preparation step, the acetic acid and CO2, the catalyst concentration was doubled (Figure 1a); no other crystalline phases such as Pd(0), Ga(0), Pd–Ga alloys, or oxidized phases were identified. More defined Pd,Ga reflections are obtained on increasing the reduction temperature, indicating a slightly larger Pd,Ga NP size (increasing from 4.6 to 5.7 nm). It is noteworthy that, in contrast to many intermetallic compounds that exhibit precisely defined stoichiometry, the Pd,Ga phase can exist over a relatively broad compositional range and should more correctly be referred to as Pd2−xGa1+x.47,48 In good agreement with the XRD characterization, HR-TEM analyses of the Pd/Ga colloids show the presence of well-defined spherical NPs with a lattice spacing consistent with the Pd,Ga crystalline phase (Figure 2).

3. RESULTS AND DISCUSSION

3.1. Formation of the Colloidal Pd2Ga-Based Catalysts

The colloidal catalysts were prepared by a two-step procedure whereby first the thermal decomposition of palladium acetate (Pd(OAc)2) precursor was achieved, at 190 ºC in squalane, and subsequently the colloid was reduced using a dilute hydrogen flow, at a selected temperature (Scheme 1). The first step involving the thermal decomposition reaction was monitored by TGA-MS (Figures S2 and S3 in the Supporting Information), which showed that heating a mixture of Pd(OAc)2 and Ga(OSt)3 to 190 ºC, the catalyst state was attained, typically after ca. 7 h time on stream. No deactivation was observed for the colloidal Pd/Ga catalyst for the 15 h runs. In contrast, the peak activity is given for the reference Cu-ZnO-Al2O3, which exhibited a distinct loss in activity with time. All experiments were conducted under differential reaction conditions, with CO2 conversions always below 2%. Under the reaction conditions employed, the calculated CO2 conversions at the thermodynamic limit (Aspen plus v 8.8 software), considering the methanol synthesis and the side reverse water-gas shift reaction, were 36.9, 31.8, and 26.4% at 190, 210, and 240 ºC, respectively. In this study, all catalytic experiments were performed in the kinetically controlled regime. Selectivities are given on a carbon basis.

Figure 2. TEM analysis of the reduced Pd/Ga samples (PdGa290/2:1) showing the formation of Pd2Ga NPs: (a) representative ADF STEM image; (b) HR-TEM image of an individual Pd2Ga NP; (c) Fourier transform of (b) with reflections indexed by their respective \{hkl\} indices; (d) electron diffraction pattern from many nanoparticles. Rings are labeled with corresponding \{hkl\} families for Pd2Ga.

No other crystalline phases were ever observed, despite the analysis of numerous high-resolution images. Table 1 shows the average size of the Pd2Ga NPs, which slightly increases with the reduction temperature, from 4.8 to 5.8 nm. The increase can be partially attributed to an increase in volume upon incorporation of Ga into Pd to form the alloy, which is estimated to be 48% (14% in radius), or to some ripening at higher reduction temperatures.

The results indicate that the gallium stearate can be reduced to form a Ga(0) alloy at temperatures as low as 210 ºC. It is important to note that no Ga(0)-containing phase was formed without the presence of Pd, as revealed by control experiments (see section 3.2, sample PdGa290/0:1). The role of the palladium can be understood by considering its ability to activate hydrogen, either by forming active hydrides or through hydrogen dissociation,30,49 which mediates the reduction of Pd2Ga. It is, therefore, proposed that the Ga(III) reduction

(1)
only occurs on the surface of the Pd(0) NPs, after which Ga(0) species can diffuse into the Pd(0) core to form the Pd2Ga alloy. It should also be considered that the Pd-mediated reduction of Ga(OSt)3, or its thermal decomposition at $\sim 250^\circ\text{C}$ (Figure S2 in the Supporting Information), likely leads to the formation of stearic acid in the reaction medium, which may itself undergo reduction, in the presence of H2 and high temperatures, to octadecanol.\textsuperscript{9,13} Both species have been reported to effectively stabilize colloidal NPs.\textsuperscript{9,13,51} Given the thermal decomposition of the precursors at 290 $^\circ\text{C}$, and the lack of any other phases or byproducts observed, it is likely that the yield is quantitative; however, due to the difficulties in isolating the product from squalane, an absolute mass yield could not be obtained.

The surfaces of samples at each stage of preparation were also characterized by XPS. In order to analyze the XPS spectra of the sample PdGa190N2, a pure metallic Pd reference sample was prepared, applying the described preparation method using the strongest reduction temperature of 290 $^\circ\text{C}$ (PdGa290/1:0). The formation of the elemental Pd crystalline phase for the PdGa290/1:0 sample was confirmed by XRD and TEM (vide infra). The Pd 3d core level spectrum for PdGa190N2 (Figure 3a) exhibits two contributions: one at the binding energy position of Pd(0) (335.2 eV) and one at a higher binding energy typical for a Pd−Ga environment (335.7 eV). Some asymmetry from the metallic Pd is still visible in the Pd 3d core level; however, the metallic character of the Pd is much more evident in the valence band (VB) spectra (Figure 3b). In the purely metallic Pd sample, PdGa290/1:0, a high density of states is found at the Fermi energy $E_F$, stemming from Pd 4d states.\textsuperscript{30} Covalent interaction of Pd with, for example, Ga can lead to a shift of the Pd 4d band maximum away from $E_F$, which

Table 1. Average Particle Size for the Pd/Ga Colloids and GaGa2O3/GaPd2Ga Molar Ratio Determined by TEM and XPS, Respectively

| sample       | $\bar{x}$ particle size (nm)\textsuperscript{a} (standard deviation) | Ga \textit{2p}$_{3/2}$ Ga 3d |
|--------------|---------------------------------------------------------------|-------------------|
| PdGa290/1:0  | 5.0 ± 0.1 (1.1)                                               | 1.27 0.61         |
| PdGa210/2:1  | 4.8 ± 0.1 (1.4)                                               | 0.79 0.19         |
| PdGa250/2:1  | 5.8 ± 0.1 (1.8)                                               | 1.00 0.78         |
| PdGa290/3:1  | 5.8 ± 0.1 (1.6)                                               | 0.79 0.19         |
| PdGa290/2:1  | 5.6 ± 0.1 (1.7)                                               | 1.00 0.78         |
| PdGa290/1:1  | 5.5 ± 0.1 (1.5)                                               | 1.63 1.00         |
| PdGa290/1:2  | 5.7 ± 0.1 (1.3)                                               | 2.03 1.38         |

\textsuperscript{a}Average particle size and standard error were determined by TEM. The standard error of the mean is defined as standard deviation/(no. of measures)$^{1/2}$.

\textsuperscript{b}Molar ratio of the Ga forming Ga2O3 and the Pd$_2$Ga alloy determined by XPS at different core levels.

Figure 3. XPS spectra for Pd/Ga samples at different preparation steps and reduction temperatures, including (a) Pd 3d core level, (b) valence band spectrum, (c) Ga \textit{2p}$_{3/2}$ core level, and (d) Ga 3d core level. Parts (a) and (b) also include spectra for the pure Pd sample (PdGa290/1:0) as reference. All spectra were normalized to the Pd 3d$_{5/2}$ peak.
in turn also leads to the loss of asymmetry in the Pd 3d core level.\(^{52}\) The valence band of PdGa\(_{190}\) still shows predominantly Pd(0) character, although a small shift away from \(E_F\) is already noticeable. There is clear evidence in both Pd 3d and VB spectra for the formation of metallic Pd, in accordance with XRD characterization. To understand whether Pd\(_2\)Ga is already formed, at this stage, one has to consider the Ga core levels shown in Figure 3c,d. Both show one high binding energy feature typical for the precursor Ga(OST)\(_3\), at 1119.1 eV (Ga 2p\(_{3/2}\)) and one at 21.1 eV (Ga 3d). No additional peaks toward lower binding energy are observed, which excludes the formation of Pd\(_2\)Ga at this stage.

Pd/Ga samples reduced at 210 and 290 °C show a symmetric Pd 3d core level typical of an alloy phase with the Pd 3d\(_{5/2}\) line at a binding energy of 335.8 eV. This position agrees well with the values previously reported for Pd\(_2\)Ga in the literature,\(^{30,52,53}\) as well as with the XRD and TEM characterization. The asymmetry characteristic for metallic Pd(0) has been completely lost, and its absence is further confirmed by the strong shift at the top of the valence band away from the Fermi energy \(E_F\). When the Ga 2p\(_{3/2}\) and Pd 3d core levels are compared, it is evident that both comprise two resolved components with differences in BE of 1.1 and 1.3 eV, respectively, with varying relative intensities (Figure 3c,d). These features are consistent with Ga species forming Pd\(_2\)Ga and Ga\(_2\)O\(_3\) and will be discussed in more detail later. Furthermore, the Ga 2p\(_{3/2}\) peak in particular shows some tailing on its higher BE side, most probably due to the presence of residual Ga(OST)\(_3\).

### 3.2. Influence of the Pd/Ga Composition

A series of colloidal Pd/Ga catalysts were prepared, using the method described, at different molar ratios of the Pd(OAc)\(_2\) and Ga(OST)\(_3\) precursors, while the overall loading of metals was kept constant, and at a reduction temperature of 290 °C, which favors the formation of the Pd\(_2\)Ga alloy. The XRD patterns (Figure 1b) show that, with the use of only Pd(OAc)\(_2\), the sample PdGa\(_{290}/1:0\) produces pure crystalline Pd(0) NPs, with an average crystallite size of 4.6 nm. The use of a Pd:Ga molar ratio of 3:1 yields a product featuring the presence of Ga and oxygen species where this amorphous phase was located, indicating the formation of a Ga\(_2\)O\(_3\) phase on the surface of the Pd\(_2\)Ga NPs.

XPS (Figure 5a,b) shows a striking difference between the mixed Pd/Ga samples and the pure Pd sample (PdGa\(_{290}/1:0\)). As discussed previously, the Pd 3d core level and corresponding valence band spectrum of PdGa\(_{290}/1:0\) show the characteristic features of metallic Pd, including the BE position (335.2 eV) and a strong asymmetry of the core line shape, which is directly related to a large density of states at the Fermi energy \(E_F\) from Pd 4d states. While the VB of Pd\(_2\)Ga is still dominated by Pd 4d states with only a slight influence from the Ga 4s and 4p states, the Pd 4d core level maximum shifts away from \(E_F\). A nonzero intensity at \(E_F\) remains in Pd\(_2\)Ga and leads to a metal-type behavior of this alloy. The low-intensity features below the main valence band of Pd\(_2\)Ga are due to Pd 5s and Ga 4s states.\(^{54}\) The Pd 3d\(_{5/2}\) core level maximum of the mixed Pd/Ga samples lies at 335.6 eV, which is in accordance with previously reported values for the formation of the Pd\(_2\)Ga alloy.\(^{30,52,53}\)

As mentioned above, the Ga 2p and 3d core lines consist of two resolved components (Figure 5c,d). Their average BE positions are 1116.6 and 1117.9 eV in Ga 2p\(_{3/2}\) and 18.6 and 20.0 eV in Ga 3d, with an average variation of 0.3 eV around these values. The lower BE component agrees well with literature data for Pd\(_2\)Ga,\(^{50,52,53,55}\) while the higher BE feature corresponds to Ga\(_2\)O\(_3\).\(^{56–58}\) The relative ratios of these two components vary between samples but also between the two
core levels. The variation between Ga 2p and 3d stems from a large difference in the kinetic energy $E_K$ of the photoelectrons, with $\Delta E_K$ being on the order of 1 keV. The surface sensitivity of the two signals is starkly different, with the lower energy Ga 2p being a great deal more surface sensitive than Ga 3d. Using the approach by Tanuma, Powell, and Penn (TPP-2M method), the inelastic electron mean free path (IMFP) can be calculated, which is a good measure for the depth sensitivity of certain core levels.\(^4\) As a close approximation, the IMFP values were correlated for gallium at the average binding energies of the Ga 2p\(^{3/2}\) and Ga 3d core levels, 1117 and 19 eV, respectively. Calculations on the basis of these values result in an approximately 3 times higher IMFP for Ga 3d, with the exact values being 11.28 Å for Ga 2p\(^{3/2}\) and 31.07 Å for Ga 3d. As the intensity of the Ga\(_2\)O\(_3\) component is comparatively larger in the Ga 2p than in the Ga 3d core level, it can be concluded that the Ga\(_2\)O\(_3\) is predominantly located on the surface of the Pd\(_2\)Ga NPs. When samples prepared with different Pd:Ga ratios are compared, the sample containing insufficient Ga to form the Pd\(_2\)Ga alloy (PdGa\(_{290}/3:1\)) is the only one to show a small proportion of Ga oxide in comparison to Pd\(_2\)Ga regardless of surface sensitivity. From peak fits to the Ga 2p\(^{3/2}\) and 3d core levels, atomic ratios of the two Ga-containing phases, Pd\(_2\)Ga and Ga\(_2\)O\(_3\), were calculated (Table 1). The \(\text{Ga}_{\text{GaO}}/\text{Ga}_{\text{PdGa}}\) molar ratio increases with the relative amount of Ga in the sample. Furthermore, on comparison of the \(\text{Ga}_{\text{GaO}}/\text{Ga}_{\text{PdGa}}\) values for the same sample, it can also be clearly seen that the Ga\(_2\)O\(_3\) is more predominant in the lower energy Ga\(_{2p}\)\(^{3/2}\) spectra, in accordance with the differences in surface sensitivity discussed above.

The characterization results point to the formation of an amorphous Ga\(_2\)O\(_3\) phase on the surface of the Pd\(_2\)Ga NPs, which is more prominent with increasing Ga content. The formation of this phase can be mostly attributed to the thermal decomposition of the Ga(OSt)\(_3\) precursor during the reduction step. A control experiment treating Ga(OSt)\(_3\) under the same conditions (reduction at 290 °C) revealed only the feature at 1117.9 eV at the Ga 2p\(^{3/2}\) position assigned to the Ga\(_2\)O\(_3\) phase (Figure S5 in the Supporting Information). Furthermore, the XRD spectrum showed no crystalline diffraction features, confirming the amorphous nature of the Ga\(_2\)O\(_3\) phase (Figure S6 in the Supporting Information). Therefore, it is reasonable to infer that the use of excess of Ga(OSt)\(_3\) to form the Pd\(_2\)Ga alloy will evolve into the Ga\(_2\)O\(_3\) phase. However, it is also possible that some Ga species are not fully incorporated into the Pd\(_2\)Ga alloy, particularly when stoichiometric or sub-stoichiometric Pd:Ga ratios are used, leading to the continued formation of a low concentration of the Ga\(_2\)O\(_3\) phase. In fact, the Ga-deficient PdGa\(_{290}/3:1\) sample exhibited weak Ga\(_2\)O\(_3\) features in the XPS (Figure 5). Other routes may explain the Ga\(_2\)O\(_3\) formation for this Pd-rich sample. For instance, adventitious trace oxidants in the precursors, solvent, or

Figure 5. XPS spectra for Pd/Ga samples with different Pd/Ga ratios, including (a) Pd 3d core level, (b) valence band spectrum, (c) Ga 2p\(^{3/2}\) core level, and (d) Ga 3d core level. All spectra were normalized to the Pd 3d\(^{5/2}\) peak.
atmosphere used during the synthesis or for characterization may come into contact with the Pd2Ga NPs. The Pd2Ga surface has recently been reported to be unstable to traces of oxidizing agents, leading to Ga segregation and oxidation on the surface to form a GaOx layer,30,47,52 a pure intermetallic surface can only be achieved under highly reducing atmospheres.32

3.3. Catalytic Experiments. 3.3.1. Influence of the Reduction Temperature. It was important to understand the relationship between the catalyst reduction temperature, applied during synthesis, and catalytic behavior. Therefore, samples with Pd:Ga molar ratios of 2:1 were reduced at different temperatures (210, 250, and 290 °C), and the products were tested in the hydrogenation of CO2 to methanol. The only byproduct identified was CO, which comes from the well-known parasitic reverse water-gas shift reaction (rWGSR). As shown in Figure 6, the methanol synthesis rate normalized according to the amount of Pd present clearly increases with the reduction temperature. Since an increased reduction temperature mostly promotes the decomposition of the Ga(OS)3 precursor and the formation of the Pd2Ga alloy from the initial Pd(0) phase, as discussed, the result underscores the importance of the Pd2Ga phase as the active catalyst for the methanol synthesis.24,39 Indeed, catalysts based only on metallic Pd(0) NPs (with similar particle sizes) or using only Ga2O3 showed no activity for either methanol synthesis or the rWGSR. For the active catalysts, increased reduction temperature leads to a slight enhancement in MeOH selectivity from ca. 45 to 50%, which suggests a high activity toward the rWGSR. Although some authors have attributed the CO formation to unalloyed Pd(0),34 we found that metallic Pd alone is barely active toward the rWGSR, which is in accord with some other studies.23 Here, the data indicate that the rWGSR active sites are related to the Pd2Ga alloy.

The results highlight the need to form the Pd2Ga alloy to obtain active catalysts for the methanol synthesis from CO2; however, XPS also showed the existence of Ga2O3 species on the surface of the Pd2Ga NPs, which may influence catalytic activity, as will be discussed in more detail in the following section.

3.3.2. Influence of Pd/Ga Composition. A series of colloidal Pd/Ga catalysts with variable Pd:Ga ratios (but all reduced at the optimum temperature of 290 °C) were compared in the methanol synthesis reaction. Furthermore, the commercial Cu-ZnO-Al2O3 catalyst was also included as a benchmark. The methanol synthesis rate (Figure 7a) increases gradually with Ga content in the catalyst, reaching the highest value at a Pd:Ga molar ratio of 1:2. Remarkably, the methanol synthesis activity for this PdGa290/1:2 catalyst is nearly 4-fold higher than that obtained for the benchmark Cu-ZnO-Al2O3, when it is normalized for the content of Pd or Cu. On the other hand, considering the activity per total molar metal (Pd + Ga) content, the PdGa290/1:1 (and PdGa290/2:1) catalyst exhibited the maximum performance (Figure S7 in the Supporting Information). While a direct comparison with the current colloidal system is difficult, similar activity improvements have been observed for some fully heterogeneous, fixed-bed systems, with 2-fold23 and 5-fold24 increases reported for heterogeneous Pd/Ga2O3 catalysts relative to the conventional Cu-ZnO-Al2O3, normalized by mass of catalyst and Pd/Cu content, respectively. Other previous heterogeneous catalysts have shown a similar or reduced activity compared to the Cu-ZnO-Al2O3 benchmark.32,34
In parallel with the activity trend, the MeOH selectivity was also moderately enhanced with a reduction in Pd:Ga ratio from 49% (PdGa290/2:1) to 64% (PdGa290/1:2), though the values are still lower than that for the reference catalyst (85%). MeOH selectivity values are in the range reported for heterogeneous catalysts based on supported Pd2Ga NPs, suggesting a similar catalytic behavior.23,24,27,34,39

On the basis of the average particle size and with the assumption of spherical metal particles, turnover frequencies (TOFs) can be estimated, for the methanol production rate, as mol\(_{\text{CH}_3\text{OH}}\) m\(^{-2}\) s\(^{-1}\). For the Pd/Ga samples, the average Pd\(_2\)Ga particle size was obtained by TEM. For the reference Cu-ZnO-Al\(_2\)O\(_3\) catalyst, the methanol rate is generally correlated to the initial Cu(0) surface area.4,59 Therefore, the TOF was estimated from the average Cu(0) particle size after activation (6.3 nm, Figure S8 in the Supporting Information). In this case, Scherrer analysis of the XRD data was used for the size estimate due to agglomeration of the heterogeneous Cu-ZnO-Al\(_2\)O\(_3\) catalyst39 hampering TEM image analysis. Nevertheless, the difference between the particle sizes estimated by XRD and HR-TEM appears to be lower than 10%. As seen in Figure 7b, the TOF increased prominently with a reduction in the Pd:Ga ratio. It is noteworthy that the TOF obtained for the PdGa290/1:2 catalyst was approximately 2-fold higher than that for the reference Cu-ZnO-Al\(_2\)O\(_3\), revealing its higher intrinsic activity toward the methanol synthesis, in agreement with results obtained for heterogeneous catalysts.24,39

On the basis of the effects of varying the Pd:Ga ratio, it seems that the Ga\(_2\)O\(_3\) phase identified on the surface of the Pd\(_2\)Ga NPs plays a crucial role in the catalysis. In fact, there is a strong linear correlation (Figure 8) between the intrinsic activity and the Ga\(_2\)O\(_3\)/Pd\(_2\)Ga molar ratio determined by XPS from the Ga 3d core level for the Pd/Ga catalysts with different Pd:Ga compositions.

The proposed reaction pathway invokes the formation of bi(carbonates), generated by CO\(_2\) adsorption on Ga\(_2\)O\(_3\), surface sites, which are successively hydrogenated to formates, methylenebisoyx and methoxy species, and finally methanol. The ability of Ga\(_2\)O\(_3\) to dissociate and chemisorb H\(_2\) to give Ga–H species, which are able to adsorb CO\(_2\) and hydrogenate the resulting carbonate groups, has been studied by concentration-modulation excitation spectroscopy (MES) in combination with phase-sensitive detection (PDS) experiments.60 The Pd–Ga bimetallic crystallites are proposed to provide atomic hydrogen, via spillover, so as to hydrogenate or increase the concentration of carbonaceous intermediates bonded to Ga\(_2\)O\(_3\).27,60,61

3.3.3. Influence of the Catalysis Conditions. Further methanol synthesis experiments were conducted using the optimized PdGa290/1:1 catalyst, which revealed the highest activity per millimole of metal (Pd + Ga), and the reference Cu-ZnO-Al\(_2\)O\(_3\) catalyst at 190 and 240 °C with the aim of exploring the influence of the reaction temperature. As seen in Figure 9a, the methanol synthesis rate was clearly higher for the Pd/Ga catalyst in comparison to Cu-ZnO-Al\(_2\)O\(_3\) across the temperature range studied, albeit with a lower methanol...
selectivity. As expected, an enhanced activity and decreased methanol selectivity with an increase in reaction temperature was found for both catalytic systems. However, the methanol rate trends significantly differ depending on the catalyst used. The methanol rate of the Cu-ZnO-Al2O3 catalyst gradually rises over the whole range of temperature. On the other hand, the Pd/Ga catalyst experiences a drastic increase in the methanol rate from 190 to 210 °C and then the rate remains nearly constant until 240 °C. This behavior might indicate a detrimental alteration of the methanol synthesis sites at the higher reaction temperature and identifies an optimum reaction temperature of 210 °C for the PdGa290/1:1 catalyst.

Finally, in order to assess the short-term stability, which is one of the main limitations of the commercial Cu-ZnO-Al2O3 catalysts when they are applied to methanol synthesis from CO2,8 the colloidal PdGa290/1:1 and the Cu-ZnO-Al2O3 catalysts were tested at the reaction temperature of 210 °C for 25 h. While the reference Cu-ZnO-Al2O3 exhibited a deactivation of ca. 50%, typically attributed to the sintering of the Cu and ZnO phases,5,62 the Pd/Ga catalyst was completely stable over this time frame (Figure 9b). The postcatalysis mixture showed some black precipitate, indicating that the colloid might be partially agglomerated under the reaction conditions, but without affecting performance or reducing the effective active surface area. The postcatalysis XRD pattern did not show any significant changes, suggesting that the bulk of the PdGa phase is preserved, without ripening (Figure S9 in the Supporting Information). These findings were confirmed by TEM (Figure S10 in the Supporting Information), where PdGa NPs with an average size of 5.3 ± 0.1 nm were observed (before catalysis 5.5 ± 0.1 nm). The amorphous Ga2O3 phase was again observed to cover the NPs, and the catalyst generally appeared unchanged after reaction.

4. CONCLUSIONS

A simple methodology to prepare colloidal Pd/Ga catalysts for the liquid-phase production of methanol from CO2 is described. The method, which involves the H2 reduction of a mixture of Pd(acetate)2 and Ga(stearate)3 in a high-boiling-point solvent (squalane), is attractive, as it combines high performance with straightforward catalyst preparation. In the first step, palladium acetate is thermally decomposed, in the presence of the gallium stearate precursor, leading to the formation of Pd(0) nanoparticles of 3 nm size. Then, the presence of the gallium stearate precursor, leading to the formation of Pd2Ga NPs with an average size of 5.3 ± 0.1 nm. The amorphous Ga2O3 phase was again observed to cover the NPs, and the catalyst generally appeared unchanged after reaction.

The optimum Pd/Ga catalyst was benchmarked against the commercial Cu-ZnO-Al2O3 using a reaction temperature range of 190–240 °C. The methanol synthesis activity for the Pd/Ga catalyst was higher than that obtained for the commercial catalyst based on Cu-ZnO-Al2O3, although the methanol selectivity was slightly lower, due to higher CO formation. An optimum activity was found at 210 °C, resulting in a 4-fold higher activity in comparison to that for the commercial catalysts (in terms of Pd or Cu molar content). Furthermore, short-term stability studies over 25 h time on stream revealed that the Cu-ZnO-Al2O3 catalyst underwent significant deactivation, in line with the literature results; however, in contrast, no deactivation was observed for the colloidal Pd/Ga catalyst. Additionally, characterization of the sample post-catalysis showed the retention of the nanoscale structure; these data indicate promising stability for the Pd/Ga colloidal catalysts. The new colloidal Pd/Ga catalysts show significant promise in terms of activity, stability, and ability to operate at lower temperatures for the hydrogenation of CO2 to methanol. It is expected that both the method of synthesis and the catalysts themselves should be more broadly applicable to a range of other reduction and catalytic processes and further development of such colloidal systems is warranted.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b02928. Different characterization results (EA, FTIR, TGA, TEM, XPS, XRD) of the precursors, as-synthesized samples, and postcatalysis samples and catalytic results (PDF)

AUTHOR INFORMATION

| Corresponding Authors |
|------------------------|
| *E-mail for D.J.P.: d.payne@imperial.ac.uk. |
| *E-mail for M.S.P.S.: m.shaffer@imperial.ac.uk. |
| *E-mail for C.K.W.: charlotte.williams@chem.ox.ac.uk. |

ORCID

Anna Regoutz: 0000-0002-3747-3763
Charlotte K. Williams: 0000-0002-0734-1575

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The EPSRC is acknowledged for funding (EP/H046380, EP/K035274/1, EP/M013839/1, EP/M028291/1). D.J.P. acknowledges support from the Royal Society (UF100105).

REFERENCES

(1) Kondratenko, E. V.; Mul, G.; Baltrusaitis, J.; Larrazábal, G. O.; Pérez-Ramírez, J. Energy Environ. Sci. 2013, 6, 3112–3135.
(2) Olah, G. A. Angew. Chem., Int. Ed. 2005, 44, 2636–2639.
(3) Palo, D. R.; Dagle, R. A.; Holladay, J. D. Chem. Rev. 2007, 107, 3992–4021.
(4) Baltes, C.; Vukojević, S.; Schütz, F. J. Catal. 2008, 258, 334–344.
(5) Chinchon, G.; Denny, P.; Parker, D.; Spencer, M.; Whan, D. Appl. Catal. 1987, 30, 333–338.
(6) Dutta, G.; Sokol, A. A.; Catlow, C. R. A.; Keal, T. W.; Sherwood, P. ChemPhysChem 2012, 13, 3453–3456.
(7) JadHAV, S. G.; Vaidya, P. D.; Bhanage, B. M.; Joshi, J. B. Chem. Eng. Res. Des. 2014, 92, 2557–2567.
(8) Martin, O.; Martin, A. J.; Mondelli, C.; Mitchell, S.; Segawa, T. F.; Hauert, R.; Drouilly, C.; Curulla-Ferré, D.; Pérez-Ramírez, J. Angew. Chem., Int. Ed. 2016, 55, 6261–6265.
