ABSTRACT: Tailoring the interfacial sites between metals and metal oxides can be an essential tool in designing heterogeneous catalysts. These interfacial sites play a vital role in many renewable applications, for instance, catalytic CO₂ reduction. Postsynthesis deposition of metal oxide on supported metal catalysts can not only create such interfacial sites but also prevent particle sintering at high temperature. Here, we report a sol–gel-based strategy to synthesize an atomically dispersed "precatalyst". In contrast to the deposition on catalysts containing preformed nanoparticles, overcoating this material before reductive treatment can inhibit particle growth during thermal activation steps, yielding highly accessible, sintering-resistant Pd clusters that are less than 2 nm in diameter. This synthetic approach allows us to engineer interfacial sites while maintaining high metal accessibility, which was difficult to achieve in previous overcoated materials. Notably, engineering the Pd–ZrO₂ interface into an inverted interface with an amorphous ZrO₂ overcoat might facilitate a C–O cleavage route instead of a mechanism containing a bicarbonate intermediate during CO₂ hydrogenation. We also observed that carbon deposition occurring on methanation sites could be a key factor for improving CO selectivity. Alteration of the reaction pathway, along with the deactivation of certain sites, led to 100% CO selectivity on the ZrO₂@Pd/ZrO₂ catalyst. This work demonstrated that overcoated materials could represent a promising class of heterogeneous catalysts for selective CO₂ conversion over noble metals, which have higher rates and thermal stability compared to state-of-the-art Cu-based catalysts.

KEYWORDS: sol–gel chemistry, heterogeneous catalysis, catalyst overcoating, CO₂ hydrogenation, metal support interface

INTRODUCTION

Heterogeneous catalysis is an essential workhorse of the chemical industry and for the production of bulk commodity chemicals.¹ Since the last decade, focus has been placed on identifying different active sites and gaining new insights into structure–reactivity relations in order to design more selective catalysts for converting renewable feedstocks (e.g., biomass and CO₂). The importance of metal–metal oxide interfaces has been recognized for the catalytic transformation of CO₂.²–⁴ Such interfacial sites can be tailored by controlling the size of nanoparticles, through the occurrence of in situ encapsulation with strong metal support interactions and postsynthesis modification.⁵ Postsynthesis via metal oxide overcoating is a particularly attractive set of methods because of the flexibility of metal oxides that can be used. Additionally, the metal oxide overcoat can inhibit the sintering of nanoparticles during catalytic reactions, thus lengthening the catalysts’ life time.⁶,7 Another intriguing characteristic of overcoated catalysts is the formation of a "metal oxide overcoat–metal–metal oxide support" interface, as opposed to the uncoated "metal–metal oxide support" configuration, which sometimes leads to higher stabilities and/or different catalytic properties.⁸,⁹ Because of this unique catalyst structure, overcoated catalysts have been referred to as "inverted catalysts".¹⁰ Creating interfacial sites using overcoating strategies also has the potential to lower the cost during catalyst synthesis because nanoparticles can be supported on a less expensive support with high surface area (e.g., silica) and be further functionalized with another metal.

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oxide overcoat. However, postdeposition is still facing several challenges. For instance, metal oxide overcoats usually impede the accessibility of active sites, which could be due to the dense texture of the overcoat and/or the interactions between metal oxide precursors and nanoparticles.\textsuperscript{11,12} Moreover, current metal oxide deposition techniques often rely on gas-phase deposition techniques such as atomic layer deposition (ALD).\textsuperscript{13} When overcoating catalyst powders with high surface area, large excess quantities of precursors and long exposure time are sometimes needed to overcome mass transfer limitations. The need for a specialized high vacuum instrument also greatly increases the cost. In addition, although the highly conformal and dense films produced by ALD are ideal for specific applications such as electronics, they are not necessarily adapted to catalyst synthesis, where more porous overcoats with improved accessibility might be more desirable.

In this context, we have developed several liquid-phase methods that might lower the costs of catalyst overcoating, including an approach relying on stoichiometric injection of metal alkyl precursors in the liquid phase, which produced the overcoats that could match the quality and conformality of ALD,\textsuperscript{14} and others using sol–gel precursors that led to conformal but less dense overcoat.\textsuperscript{15–18} Nevertheless, the loss of active sites after coating still remains a significant challenge to prepare an active catalyst, not merely in the materials prepared by ALD but also for catalysts with less dense overcoats synthesized using wet-chemistry methods.\textsuperscript{6,19}

Here, we report a sol–gel-based approach to prepare an atomically dispersed "precatalyst" by combining the surface reaction of alkoxysilane and the coordination chemistry of palladium and ethylenediamine (en). Liquid-phase-based overcoating was then performed on this precatalyst to restrain the growth of the Pd particle during thermal treatments and engineer a new metal oxide–Pd interface. The resulting overcoated catalysts have highly accessible sub-nanometer Pd clusters with an engineered metal oxide interface. We found that the ZrO\textsubscript{2}–Pd interface that formed on the relatively inactive SiO\textsubscript{2} surface substantially increased the activity toward CO\textsubscript{2} activation. We also observed an altered CO\textsubscript{2} hydrogenation mechanism on the new ZrO\textsubscript{2}–Pd interface, which is distinct from that on the uncoated Pd–ZrO\textsubscript{2} interface. Although maintaining high conversion, the altered mechanism leads the reaction over the ZrO\textsubscript{2}@Pd/ZrO\textsubscript{2} catalyst to achieve 100\% CO selectivity. The overcoated catalyst is also more sintering-resistant than the uncoated Pd/ZrO\textsubscript{2}. The enhancement of both catalyst selectivity and stability makes this synthetic approach highly promising in designing catalysts for CO\textsubscript{2} conversion.

### RESULTS AND DISCUSSION

**Catalyst Synthesis Using Atomically Dispersed Precatalysts and Metal Oxide Overcoats.** Ethylenediamine is a bidentate ligand that can form complexes with noble metals.\textsuperscript{20,21} A combination of molecules containing this chelating functionality and an alkoxysilane has been used to prepare SiO\textsubscript{2}-supported metal catalysts through sol–gel processing.\textsuperscript{22} Our synthesis approach relies on the same chemistry. Specifically, the chelated Pd was grafted on the SiO\textsubscript{2} surface through the condensation of Si-(OCH\textsubscript{3})\textsubscript{3} with silica’s surface hydroxyl groups (step 1, Scheme 1), which produced an atomically dispersed Pd/SiO\textsubscript{2} [Pd(en)\textsubscript{2}/SiO\textsubscript{2}]. The completion of grafting could be simply observed from the color change of silica and the reaction medium (Figure S1).

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis of the resulting material revealed the presence of two bands at 2937 and 2883 cm\textsuperscript{-1} that could be assigned to C–H stretching, which confirmed the presence of the Pd complex on the silica surface (Figure S2).\textsuperscript{23} Pd(en)\textsubscript{2}/SiO\textsubscript{2} was then overcoated with ZrO\textsubscript{2} using a kinetically controlled sol–gel method similar to what we had previously reported for alumina and niobia.\textsuperscript{16,24} Specifically, we slowed down the hydrolysis and condensation rates of Zr(t-BuO)\textsubscript{4} by adding ethyl acetoacetate (EAA) to form a chelated ZrO\textsubscript{2} precursor.\textsuperscript{25} The resulting kinetically controlled precursor was injected into a Stöber solution (i.e., an ethanol solution containing targeted quantities of NH\textsubscript{3} and H\textsubscript{2}O), which was
mixed with dispersed \( \text{Pd(en)}_2/\text{SiO}_2 \) to grow a \( \text{ZrO}_2 \) overcoat (step 2, Scheme 1). Importantly, the \( \text{Pd(en)}_2 \) complex remained unreactive because of the strong interaction between ethylenediamine and Pd. Therefore, the Pd that was grafted on the surface did not leach when performing liquid-phase coating during which another chelating agent (EAA) was also present in solution. In addition to our presented method, an alternate method for immobilizing Pd using arginine was also reported where the amine group of arginine was used to coordinate Pd, and the resulting complex was anchored on the surface via the carboxylic acid group. Nevertheless, such a Pd−arginine complex likely interacted with silica by electrostatic interaction rather than by covalent bonding. In this study, we grafted the \( \text{Pd(en)}_2 \) complex by forming a covalent siloxane linkage, which is more stable than electrostatic forces. We had also tried to overcoat an impregnated silica containing a strongly electrostatically adsorbed Pd complex, but most of the Pd leached during the coating procedure, which was likely caused by the complexation between EAA (i.e., one of our overcoating reagents) and Pd. Accordingly, we proposed that using an organo-functionalized silane could result in the most stable material that is compatible with kinetically controlled sol−gel coating. In the last step, the atomically dispersed precatalyst overcoated with \( \text{ZrO}_2 \) (\( \text{ZrO}_2@\text{Pd(en)}_2/\text{SiO}_2 \)) was first calcined at 400 °C to remove any impurities containing C and N from the synthesis reagents and then reduced to form the final Pd catalyst by flowing H\(_2\) at 400 °C. The same thermal treatments were also performed on uncoated \( \text{Pd(en)}_2/\text{SiO}_2 \) to form g-Pd/\( \text{SiO}_2 \) (where g stands for the material prepared from the grafted \( \text{SiO}_2 \)) in order to compare the effect of the overcoat on the nanoparticle size distribution.

We first determined the dispersions of \( \text{ZrO}_2@\text{Pd}/\text{SiO}_2 \) and g-Pd/\( \text{SiO}_2 \) using CO chemisorption and inductively coupled plasma optical emission spectroscopy (ICP-OES). The Pd dispersion on \( \text{ZrO}_2@\text{Pd}/\text{SiO}_2 \) (38%, Table 1) was twice higher than that on g-Pd/\( \text{SiO}_2 \) (19%, Table 1). Scanning transmission electron microscopy (STEM) further confirmed a larger average Pd particle size for g-Pd/\( \text{SiO}_2 \) (3.4 nm, Figure 1a).

Table 1. Summary of the Characterization Results of Reference and Overcoated Catalysts

<table>
<thead>
<tr>
<th>catalyst</th>
<th>loading (a) (%)</th>
<th>( S_{\text{BET}} ) (m(^2)·g(^{-1}))</th>
<th>( \text{Pd}_{\text{surface}} ) (( \mu \text{mol} )·g(^{-1}))</th>
<th>( d_{\text{Pd}} ) (nm)</th>
<th>dispersion (d) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-Pd/( \text{SiO}_2 )</td>
<td>0.39</td>
<td>170.1</td>
<td>6.9</td>
<td>3.4</td>
<td>19</td>
</tr>
<tr>
<td>( \text{ZrO}_2@\text{Pd}/\text{SiO}_2 )</td>
<td>0.28</td>
<td>162.1</td>
<td>9.9</td>
<td>N/A</td>
<td>38</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3@\text{Pd}/\text{SiO}_2 )</td>
<td>0.32</td>
<td>170.9</td>
<td>12.0</td>
<td>1.4</td>
<td>40</td>
</tr>
<tr>
<td>( \text{ZrO}_2@\text{Pd}/\text{ZrO}_2 )</td>
<td>0.34</td>
<td>76.8</td>
<td>22.1</td>
<td>N/A</td>
<td>70</td>
</tr>
<tr>
<td>Pd/( \text{Al}_2\text{O}_3 )</td>
<td>0.4</td>
<td>164.1</td>
<td>13.4</td>
<td>2.6</td>
<td>36</td>
</tr>
<tr>
<td>Pd/( \text{ZrO}_2 )</td>
<td>0.57</td>
<td>64.3</td>
<td>47.3</td>
<td>N/A</td>
<td>89</td>
</tr>
</tbody>
</table>

(a) Determined by ICP-OES. (b) Determined by CO chemisorption. Although CO with two- and threefold coordination may also be present, we still assume the stoichiometric ratio between Pd and CO to be 1. A discussion justifying the choice of this stoichiometric number is given in the Supporting Information. (c) Determined by STEM. Pd supported on \( \text{ZrO}_2 \) or with \( \text{ZrO}_2 \) overcoat cannot be observed because of the insufficient contrast. (d) Pd dispersion, calculated by \( \text{Pd}_{\text{surface}}/\text{total Pd} \).

Figure 1. TEM images and Pd particle size distributions of (a) g-Pd/\( \text{SiO}_2 \) and (b) \( \text{Al}_2\text{O}_3@\text{Pd}/\text{SiO}_2 \) and EDX mappings of (c) \( \text{Al}_2\text{O}_3@\text{Pd}/\text{SiO}_2 \) and (d) \( \text{ZrO}_2@\text{Pd}/\text{SiO}_2 \). The sub-nanometer Pd clusters observed in panel b are highlighted by red circles.
We were unable to observe Pd particles and measure the particle size distribution on ZrO2@Pd/SiO2 because of the poor contrast between Pd and ZrO2 (Figure S3). Therefore, we prepared Al2O3@Pd/SiO2 using a similar kinetically controlled approach,16 as we expected that the higher contrast between Al2O3 and Pd would enable us to analyze Pd particles using STEM. Indeed, a much better contrast was obtained and many sub-nanometer Pd clusters were observed when analyzing Al2O3@Pd/SiO2. STEM analyses showed that its average particle size was significantly smaller (1.4 nm) than that of g-Pd/SiO2 (Figure 1b). The dispersion of Al2O3@Pd/SiO2 was also obtained using CO chemisorption and ICP-OES. Because the dispersion of Al2O3@Pd/SiO2 was very close to that of ZrO2@Pd/SiO2 (Table 1), we inferred that ZrO2@Pd/SiO2 also has similarly small Pd clusters. These results strongly suggested that the overcoat can inhibit the growth of Pd particles during thermal activation and further highlighted the potential of combining overcoating techniques and atomically dispersed materials for synthesizing sintering-resistant catalysts with high dispersion.28,29 The energy-dispersive X-ray (EDX) mapping (Figure 1c,d) also showed that kinetically controlled sol−gel methods can uniformly grow both ZrO2 and Al2O3 on high-surface-area SiO2 (Aerosil 200), which is a more industrially relevant support. In contrast to a recently reported analogous approach, the strategy presented here does not require expensive organometallic complexes or an ALD instrument.30 Although organometallic complexes are known precursors for preparing atomically dispersed catalysts, they are typically moisture sensitive, which is not compatible with sol−gel processes where water is present in the reaction media. Pd(en)2/SiO2 is fairly inert and can be stored in an ambient environment. This stable characteristic makes Pd(en)2/SiO2 an ideal precatalyst for synthesizing catalysts with a metal oxide overcoat−metal−metal oxide support configuration, which may possess different catalytic properties from that of supported catalysts with regular metal−metal oxide interfaces.

Here, we took advantage of the stabilization effects of the overcoat and illustrated the use of Pd(en)2/SiO2 for synthesizing ultrasmall Pd clusters with Al2O3−Pd or ZrO2−Pd interfaces. The characterization results of g-Pd/SiO2 suggested that preparing a well-dispersed Pd/SiO2 is challenging even at low loading because the interaction between Pd and SiO2 is not particularly strong.31 In contrast to the case where larger-sized Pd particles had been formed prior to catalyst overcoating, the use of atomically dispersed Pd(en)2/SiO2 during catalyst preparation could minimize the loss of the external Pd surface occurring in the thermal reduction step.

Figure 2. XPS spectra and deconvolution results for (a) g-Pd/SiO2, (b) Pd/Al2O3, (c) Al2O3@Pd/SiO2, (d) Pd/ZrO2, (e) ZrO2@Pd/SiO2, and (f) ZrO2@Pd/ZrO2.
In addition to SiO₂, the Pd complex can also be grafted on other metal oxide supports using the same procedure. We prepared Pd(en)₂/ZrO₂ and overcoated it with ZrO₂ to form ZrO₂@Pd/ZrO₂. This catalyst displayed a higher dispersion (70%, Table 1) than that of ZrO₂@Pd/SiO₂, which could be explained by the stronger interaction between Pd and the ZrO₂ support. We also prepared a reference Pd/ZrO₂ using a standard wet impregnation method with the same Pd precursor and found that Pd was also highly dispersed (89%, Table 1). The slightly lower dispersion of the overcoated catalyst is likely due to coverage by the overcoat. Irreversible loss of active sites during overcoating is an issue that is challenging to solve. Density functional theory (DFT) simulations have explained this coverage effect for ALD processes by showing that metal oxide precursors can interact with specific facets of nanoparticles. Our past work showed that only 38% of Cu remained accessible after overcoating of Cu/Al₂O₃ with analogous chelation chemistry-based sol−gel coating. The overcoat formed using a nonhydrolytic sol−gel method even blocked up to 80% of the Pt sites of nanoparticles supported on SBA-15. This smaller dispersion of ZrO₂ overlayer was likely due to coverage by the overcoat. Irreversible loss of active sites during overcoating is an issue that is challenging to solve.11–13

**Overcoat Effects on the Physical and Chemical Properties of the Catalysts.** The physical and chemical properties of the overcoated and reference catalysts were further characterized. The N₂ physisorption isotherms showed that Al₂O₃@Pd/SiO₂ and ZrO₂@Pd/SiO₂ have nearly the same hysteresis loops as that of g-Pd/SiO₂ (Figure S4a). These three catalysts also had similar BET surface areas (with less than a 10% reduction after overcoating and sometimes a slight increase). These results were distinct from previous observations of ZrO₂−ALD processes where the overcoated catalysts showed reduced BET surface areas (with less than a 10% reduction after overcoating and sometimes a slight increase). These results were distinct from previous observations of ZrO₂−ALD processes where the overcoated catalysts showed reduced BET surface areas (with less than a 10% reduction after overcoating and sometimes a slight increase). These results were distinct from previous observations of ZrO₂−ALD processes where the overcoated catalysts showed reduced BET surface areas (with less than a 10% reduction after overcoating and sometimes a slight increase).

The thickness of a ZrO₂ monolayer (0.075 nm) was greater than that of Pd/ZrO₂ prepared using ALD (0.02 nm/cycle). Furthermore, ZrO₂@Pd/ZrO₂ showed approximately 20% larger surface area, and its hysteresis loop was slightly modified compared to the uncoated Pd/ZrO₂ (Figure S4b). All these results indicated that the sol−gel method produced a more porous metal oxide overcoat compared to gas-phase ALD, which was in agreement with our previous work.7,24

Several studies have shown that the chemical state of Pd (Pd/PdO ratio) was dependent on the metal oxide support, and this property could have important effects for certain catalytic applications.34,35 In this work, we first used overcoating to create additional surface functionality on a catalyst with a relatively inert support (e.g., SiO₂). X-ray photoelectron spectroscopy (XPS) was then performed to characterize the overcoated and reference catalysts. The deconvoluted spectra showed that 95% of Pd was in its metallic form (Figure 2a) when being supported on SiO₂. In comparison, Al₂O₃@Pd/SiO₂ had an increased atomic fraction of Pd(II) with a Pd(II)/Pd(0) ratio of 0.18, which was similar to that of Pd/Al₂O₃ (Figure 2b,c), indicating that the Al₂O₃ overcoat could form an Al₂O₃−Pd interface and thus alter the chemical state of the Pd nanoparticles. Deconvoluting XPS data for the catalysts containing ZrO₂ was more challenging because of the presence of two intense Zr 3p peaks in the same binding energy region. The Pd signal was barely detectable on ZrO₂@Pd/SiO₂ (likely resulting from its lower metal loading) but could be observed on both ZrO₂@Pd/ZrO₂ and Pd/ZrO₂ (Figure 2d-f). The deconvolution models showed that ZrO₂@Pd/ZrO₂ had three times higher Pd(II)/Pd(0) ratio than that of uncoated Pd/ZrO₂. Given the relatively small size of the peaks of interest versus the intense Zr 3p signal, the consistency of the deconvolution models for these two catalysts was assessed by performing Monte Carlo (MC) simulations (details are described in the Supporting Information, Section 2.5). The distributions of Pd(II)/Pd(0) were obtained using the resulting simulated datasets (Figure S5). The median values for this ratio were 0.96 and 1.29 for Pd/ZrO₂ and ZrO₂@Pd/ZrO₂, respectively. In addition, the intervals of the distributions without the upper and lower 5% tails were [0.29,2.48] for Pd/ZrO₂ and [0.14,6.44] for ZrO₂@Pd/ZrO₂. Although the relatively high overlap between the distributions made the assessment less conclusive, the simulation result still suggested that ZrO₂ had a statistically significant effect on Pd and then increased its oxidation state.
CO (~80%, Table 2) but a very low conversion (approximately 2%, Figure S6), which was in agreement with previous work. Selectivities toward CO and CH₄ for this control catalyst remained stable over 20 h on stream. The low conversion of g-Pd/SiO₂ could be attributed to the slow activation of CO₂ on the relatively inert silica support. Using Pd supported on Al₂O₃ significantly increased the conversion (Figure 3a). Although the higher conversion could be partially ascribed to the higher dispersion of Pd/Al₂O₃, the rate of this catalyst was one order of magnitude higher than that of g-Pd/SiO₂. Dispersion thus cannot explain the lower reaction rate of g-Pd/SiO₂ alone. Instead, we attributed the increased rate to the formation of a Pd–Al₂O₃ interface that likely facilitated CO₂ activation. The result was in agreement with a previous study showing that Al₂O₃ and La₂O₃ could serve as a promoter for CO₂ activation. Although Pd/Al₂O₃ had a higher activity, it was less selective toward CO (~60%, Table 2). However, we also observed that the yield of CO rapidly dropped with prolonged time on stream, while the conversion fluctuated between 5 and 10% and the CH₄ selectivity remained below 5% throughout the measurement. The reduced carbon balance indicated that this catalyst was likely catalyzing the formation of carbonaceous deposits. The formation of such carbon species is not uncommon during hydrocarbon conversion over acidic catalysts (e.g., zeolites). The Pd clusters located on the mixed Al₂O₃–SiO₂ interface appeared to have distinct catalytic properties from those of either Pd/Al₂O₃ or Pd/SiO₂. We assume that this Al₂O₃–SiO₂ interface forms acid sites and converted reaction intermediates into carbon deposits. NH₃-TPD also revealed that Al₂O₃@Pd/SiO₂ had more acid sites compared to uncoated Pd/Al₂O₃ (Figure S7). Consequently, even though some interesting properties and initial CO selectivity were observed using Al₂O₃@Pd/SiO₂, the poor carbon balance over an extended period of time significantly limits its practical use. In addition to Al₂O₃, ZrO₂ has also frequently been used to prepare catalysts, especially for producing methanol from CO₂. Both theoretical calculations and in situ experiments have shown that CO₂ can chemisorb and then be activated on the ZrO₂ surface. For this reason, we prepared and tested another series of catalysts with ZrO₂, which was used both as a support and overcoat. Similar to Al₂O₃@Pd/SiO₂, the activity was significantly improved after overcoating ZrO₂ on Pd/SiO₂, confirming the high activity of Pd–ZrO₂ interfaces for catalyzing CO₂ reduction (Figure 4a). More importantly, ZrO₂@Pd/SiO₂ outperformed any catalysts containing Al₂O₃. Because Pd/Al₂O₃, Al₂O₃@Pd/SiO₂, and ZrO₂@Pd/SiO₂ have similar dispersions and loadings (Table 1), we concluded that the Pd–ZrO₂ interface is more active for catalytic CO₂ activation than the Pd–Al₂O₃ interface. Moreover, the use of ZrO₂@Pd/SiO₂ not only led to a high CO selectivity (~80%, Table 2) but also showed little deactivation. Unlike Al₂O₃@Pd/SiO₂ that led to pronounced carbon deposition over time, ZrO₂@Pd/SiO₂ maintained a carbon balance over 95% (Table 2) and CH₄ selectivity slightly decreased during the reaction (Figure S8a). Because the comparison of catalytic results of Al₂O₃@Pd/SiO₂ and Pd/Al₂O₃ indicated that distinct catalytic properties could appear when a mixed oxide interface was introduced, we subsequently studied Pd/ZrO₂ to see whether this reference catalyst showed substantially different catalytic activity.

Table 2. Summary of CO₂ Hydrogenation Results of the Reference and Overcoated Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Observed selectivity (%)</th>
<th>Selectivity at 20 h (%)</th>
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<tbody>
<tr>
<td>g-Pd/SiO₂</td>
<td>0.16</td>
<td>0.14</td>
</tr>
<tr>
<td>ZrO₂@Pd/SiO₂</td>
<td>3.9</td>
<td>2.9</td>
</tr>
<tr>
<td>Al₂O₃@Pd/SiO₂</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>ZrO₂@Pd/ZrO₂</td>
<td>3.6</td>
<td>2.0</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>2.3</td>
<td>1.8</td>
</tr>
<tr>
<td>Pd/ZrO₂</td>
<td>4.5</td>
<td>2.2</td>
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<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Observed rate (mmol CO₂·g⁻¹·Pd·s⁻¹)</th>
<th>CO</th>
<th>CH₄</th>
<th>CO</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-Pd/SiO₂</td>
<td>0.16</td>
<td>79</td>
<td>21</td>
<td>83</td>
<td>17</td>
</tr>
<tr>
<td>ZrO₂@Pd/SiO₂</td>
<td>3.9</td>
<td>79</td>
<td>22</td>
<td>87</td>
<td>12</td>
</tr>
<tr>
<td>Al₂O₃@Pd/SiO₂</td>
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<td>5</td>
<td>23</td>
<td>0</td>
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<tr>
<td>ZrO₂@Pd/ZrO₂</td>
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<td>91</td>
<td>9</td>
<td>100</td>
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<td>Pd/Al₂O₃</td>
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<td>60</td>
<td>44</td>
<td>56</td>
<td>43</td>
</tr>
<tr>
<td>Pd/ZrO₂</td>
<td>4.5</td>
<td>77</td>
<td>23</td>
<td>92</td>
<td>6</td>
</tr>
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</table>

*Calculated using the conversion before deactivation (0 h time on stream). The calculated rates and selectivities were based on the data shown by the solid line in Figures 3 and 4. For the most active series of catalysts (containing ZrO₂), all the relevant conversions were within the range between 30 and 40%. Because the active site (metal–metal oxide interface) for CO₂ hydrogenation is difficult to precisely define and probe, the rate was normalized by the total number of Pd atoms.*

Figure 3. Conversion, CO selectivity, and CH₄ selectivity during CO₂ hydrogenation over (a) Pd/Al₂O₃ and (b) Al₂O₃@Pd/SiO₂. The details of the reaction condition are described in the Supporting Information.
while CH4 selectivity decreased (Figure S8b). Although the selectivity towards CO increased over time (to 92% at 20 h), similar high CO selectivity (77%, Table 2). Interestingly, the catalyst also had a better dispersed (89%, Table 1). This catalyst also had a rate after applying such a normalization (≈10.3 CO2 g^−1 h^−1). These results suggested that the energy barrier of the rate-determining step might be the lowest when Pd was supported on a SiO2—ZrO2 mixture. However, because Pd^surface measured by CO adsorption does not necessarily represent the active site of the rate-determining step (which was hypothesized to be Pd—metal oxide interfaces), whether supporting Pd on a SiO2—ZrO2 is particularly favorable for converting CO2 will require further investigation. Even though the initial conversion of ZrO2@Pd/ZrO2 was the lowest among the catalysts containing ZrO2, the CO selectivity of ZrO2@Pd/ZrO2 was the highest (91%, Table 2), and it quickly increased to 100% within 2 h (Figure 4c). No CH4 was detected from 2 to 20 h time on stream (Figure S8c). Among several metals that catalyze CO2 hydrogenation, Cu-based catalysts have been reported to have a selectivity of 100% toward CO at atmospheric pressure because they had very little activity for methanation.54,55 Nevertheless, noble metals typically catalyze methanation, which decreases CO selectivity. Importantly, ZrO2@Pd/ZrO2 could not only selectively convert CO2 to CO but also outperform the benchmark Cu/ZnO/Al2O3 (a benchmark catalyst used in industry that has nearly the same activity, when considering accessible surface Pd as measured by CO chemisorption (≈5.1 CO2 g^−1 h^−1). Pd^surface^−1 and had the highest rate after applying such a normalization (≈10.3 CO2 g^−1 h^−1). Interestingly, ZrO2@Pd/SiO2 had the highest rate after applying such a normalization (≈10.3 CO2 g^−1 h^−1). These results suggested that the energy barrier of the rate-determining step might be the lowest when Pd was supported on a SiO2—ZrO2 mixture. However, because Pd^surface measured by CO adsorption does not necessarily represent the active site of the rate-determining step (which was hypothesized to be Pd—metal oxide interfaces), whether supporting Pd on a SiO2—ZrO2 is particularly favorable for converting CO2 will require further investigation. Even though the initial conversion of ZrO2@Pd/ZrO2 was the lowest among the catalysts containing ZrO2, the CO selectivity of ZrO2@Pd/ZrO2 was the highest (91%, Table 2), and it quickly increased to 100% within 2 h (Figure 4c). No CH4 was detected from 2 to 20 h time on stream (Figure S8c). Among several metals that catalyze CO2 hydrogenation, Cu-based catalysts have been reported to have a selectivity of 100% toward CO at atmospheric pressure because they had very little activity for methanation.54,55 Nevertheless, compared to Cu, noble metals such as Pd usually have a higher rate for CO2 conversion. For instance, at atmospheric pressure, the rate of Cu/ZnO/Al2O3 (a benchmark catalyst used in industry that can also be employed to produce methanol at more elevated pressures) at 600 °C was reported as 1.2 mmol CO2 g^−1 Cu s^−1 with 100% CO selectivity, whereas the rate for the reference Pd/Al2O3 catalyst we measured here reached 2.3 mmol CO2 g^−1 Pd s^−1 at 450 °C.55 Nevertheless, noble metals typically also catalyze methanation, which decreases CO selectivity. Importantly, ZrO2@Pd/ZrO2 could not only selectively convert CO2 to CO but also outperform the benchmark Cu/ZnO/Al2O3 in terms of the CO2 conversion rate (with a stable activity of 2 mmol CO2 g^−1 Pd h^−1 for dash lines) (d) CO chemisorption measurements of the fresh and spent catalysts (targeting total and reversible deactivations by first and second titrations, respectively).

Figure 4. CO2 hydrogenation catalyzed by (a) ZrO2@Pd/SiO2, (b) Pd/ZrO2, and (c) ZrO2@Pd/ZrO2. To be able to compare the conversions directly, the mass of the catalyst in the reactor was adjusted so as to obtain the same WHSV (1060 L CO2 g^−1 h^−1 for solid lines and 3000 L CO2 g^−1 Pd h^−1 for dash lines) (d) CO chemisorption measurements of the fresh and spent catalysts (targeting total and reversible deactivations by first and second titrations, respectively).
controlling particle size and the porous environment. However, to the best of our knowledge, this is the first Pd-based catalyst to reach 100% CO selectivity. To demonstrate that Pd/ZrO2 cannot reach 100% selectivity toward CO at the same conversion, we reduced the weight of Pd/ZrO2 (to 10 mg) to have the same conversion as the overcoated catalyst (dash line in Figure 4b). The resulting CO selectivity slightly increased but fluctuated at around 90% throughout the test. Although this result emphasized the unique catalytic property of the ZrO2@Pd/ZrO2 material, it also indicated that the selectivity was dependent on conversion. Therefore, we similarly varied the conversion of ZrO2@Pd/ZrO2 by reducing the catalyst’s weight (to 17 mg) in the reactor. The initial CO selectivity of ZrO2@Pd/ZrO2 remained the same (around 90%) at 24% conversion and once again increased to nearly 100% with additional time on stream. Moreover, similar to what we have observed when studying ZrO2@Pd/SiO2, ZrO2@Pd/ZrO2 also deactivated more slowly compared to Pd/ZrO2. ZrO2@Pd/ZrO2 did deactivate in the early stage but the conversion remained relatively stable after 10 h. In contrast, Pd/ZrO2 continuously deactivated throughout the catalytic run. Based on these results, we concluded that not only could the ZrO2 overcoat engineer a new ZrO2−Pd interface and result in an exceptional CO selectivity but it could also mitigate deactivation under harsh reaction conditions (450 °C in the presence of steam).

**Deactivation Study of Catalysts.** To study the deactivation mechanism, CO2 hydrogenation was run using ZrO2@Pd/SiO2, Pd@ZrO2, and ZrO2@Pd/ZrO2 on a Micromeritics Autochem, which allows us to perform CO chemisorption directly on spent catalysts. The initial CO selectivity of ZrO2@Pd/ZrO2 remained the same (around 90%) at 24% conversion and once again increased to nearly 100% with additional time on stream. Moreover, similar to what we have observed when studying ZrO2@Pd/SiO2, ZrO2@Pd/ZrO2 also deactivated more slowly compared to Pd/ZrO2. ZrO2@Pd/ZrO2 did deactivate in the early stage but the conversion remained relatively stable after 10 h. In contrast, Pd/ZrO2 continuously deactivated throughout the catalytic run. Based on these results, we concluded that not only could the ZrO2 overcoat engineer a new ZrO2−Pd interface and result in an exceptional CO selectivity but it could also mitigate deactivation under harsh reaction conditions (450 °C in the presence of steam).

The first CO titration showed that the Pd_{surface} on the three spent catalysts was reduced after 48 h of reaction. The first CO titration showed that the spent ZrO2@Pd/SiO2 had the most Pd_{surface} sites and the spent Pd/ZrO2 had the least Pd_{surface} sites (Figure 4d), which agreed with the observed trend of deactivation rates in the catalysis tests (Figure 4a−c). Interestingly, all spent catalysts showed increased Pd_{surface} after calcination, which suggested the presence of carbonaceous deposits on the spent catalysts. After removing the deposits by calcination, Pd/ZrO2 still lost the largest amount of Pd_{surface} (from 47.3 to 1.2 μmol). Large agglomerated Pd particles were also observed when analyzing the spent Pd/ZrO2 by STEM (Figure S9). These results confirmed that the catalysts with a ZrO2 overcoat were more sintering-resistant under harsh reaction conditions. Among the three spent catalysts, the ZrO2@Pd/ZrO2 catalyst recovered the most Pd_{surface} (from 0.8 to 5 μmol) after calcination. In contrast, calcination had more limited effects on Pd/ZrO2 and ZrO2@Pd/SiO2, which suggested that more carbonaceous deposits formed on ZrO2@Pd/ZrO2. Based on the deactivation study, we concluded that catalyst deactivation was caused by both sintering and carbon deposition. The larger amount of deposits formed over ZrO2@Pd/ZrO2 was particularly interesting, given that the increase in CO selectivity accompanied the initial deactivation (the deactivation slowed down after CO selectivity reached 100%). This selectivity change was unlikely caused by particle sintering because a past work has shown that smaller Pd particles are more selective toward CO when catalyzing RWGS reaction. Additionally, if Pd nanoparticles with a specific size could lead to 100% CO selectivity, the same phenomenon would have been observed on Pd/ZrO2 once the Pd agglomerates had formed. The increase in selectivity toward CO because of dynamic changes of catalysts during CO2 hydrogenation has been previously reported including self-poisoning on Ru/CeO2 and the transformation of methanation sites on Rh/TiO2.56,60 Specifically, the switch from methanation to RWGS sites on Rh/TiO2 was induced by the encapsulation of Rh by a thin
reducible metal oxide overcoat via strong metal support interaction. Because ZrO2 is a nonreducible metal oxide and Pd had been overcoated, active-site transformation was unlikely. Therefore, we propose that the superior CO selectivity of ZrO2@Pd/ZrO2 resulted from the selective carbon deposition on its methanation sites.

**In Situ DRIFTS Characterization and Reaction Mechanism.** To better understand the higher selectivity of ZrO2@Pd/ZrO2 toward CO and the reaction mechanism, in situ DRIFTS measurements were carried out to identify the reaction intermediates. The catalysts were reduced with a flow of H2 at 300 °C and then, the feed was switched to He. Subsequently, the temperature was elevated to 450 °C, and the first spectrum was measured (black line in Figure 5). The feed was then switched to a mixture of CO2 and H2, and the second spectrum was recorded (green line in Figure 5). ZrO2@Pd/SiO2, ZrO2@Pd/ZrO2, and Pd/ZrO2 displayed similar spectra before beginning the flow of CO2 and H2. The two small bands at 1539 and 1449 cm\(^{-1}\) were assigned to the strongly bound water can be found on the zirconium center that has oxygen vacancies and is more electrophilic. The desorption of water might result from the competitive chemisorbed CO2, and this observation is consistent with a hypothesis suggesting that oxygen vacancy is critical for CO2 activation.

The bicarbonate-mediated mechanism on Pd/ZrO2 is similar to a reported mechanism on an analogous Pd/Al2O3 system (Figure 6a). The first step is the chemisorption of CO2 presumably on the zirconium center with O vacancies according to our DRIFTS measurements. The chemisorbed CO2 then either interacted with surface hydroxyl groups or dissociated H to form bicarbonate-like intermediates. According to Wang et al., these intermediates could be further converted to the adsorbed CO intermediate that can be either bound with an isolated Pd atom linearly \(k_1\) or with Pd atoms with twofold or threefold coordination \(k_2\). CO configuration is known to be particularly influential on CO and CH4 selectivities. The linearly adsorbed CO has a lower desorption barrier, thus eventually forming the CO product, whereas the twofold and threefold coordinated CO are more susceptible to further hydrogenation into CH4. Therefore, several groups have proposed that methanation and RWGS occur on two different sites and reducing the nanoparticles’ size can favor the production of CO because it creates a larger fraction of isolated metal sites that bond CO with a linear configuration. Although chemisorbed CO was not observed during in situ DRIFTS measurements (likely because of the short lifetime of CO intermediates at high temperature), we performed CO chemisorption on Pd/ZrO2 at room temperature, and the signal of linearly bound CO was detected by DRIFTS (Figure S10a). Because of the high dispersion of Pd on ZrO2, many isolated Pd atoms or small clusters sites were likely present on the surface, which favored the production of CO (above 80% selectivity). Because linearly bound CO, twofold and threefold coordinated CO species were also observed, indicating the presence of bigger particles that catalyzed methanation. Because the RWGS reaction and methanation are governed by two different active sites, the aforementioned increased CH4 selectivity at higher conversion can be explained by the competing RWGS and methanation reactions. The equilibrium conversion of RWGS under our condition was calculated as 43%. Therefore, the production of CO was close to the thermodynamic equilibrium in our first run at higher conversion (solid line, Figure 4b). Under such conditions, any excess amount of catalyst would not produce more CO but just contribute to methanation. Once Pd/ZrO2 deactivated, the RWGS reaction was no longer close to the thermodynamic equilibrium, which allowed the active sites to increase the net rates of RWGS compared to methanation and then increased CO selectivity to 90% (similar to that obtained at lower conversion, dashed line, Figure 4b).

As previously mentioned, we did not observe any absorbances representing formate and bicarbonate intermediates when running in situ DRIFTS measurements on the catalysts with ZrO2 overcoat (Figure 5b,d). In the absence of these intermediates and because there are only three known mechanisms of CO2 hydrogenation (bicarbonate mediated, formate mediated, or the direct C–O cleavage pathway), we hypothesized that CO2 was likely converted through the C–O cleavage route on ZrO2@Pd/ZrO2 and ZrO2@Pd/SiO2. Our XPS data showed an increased Pd(II) character in ZrO2@Pd/ZrO2 implying the formation of a new type of interfacial site (i.e., the active site for CO2 activation) with distinct chemical properties, which led to a different catalytic performance. Because the modification of the active site may result from the distinct chemistry of the ZrO2 overcoat synthesized through the sol–gel route, we further performed powder X-ray diffraction to characterize the overcoated and reference catalysts, and the results showed that our ZrO2 overcoat is

![Figure 6](https://dx.doi.org/10.1021/acscatal.0c02146)
amorphous, whereas the commercial ZrO$_2$ support has a monoclinic structure (Figure S11). Accordingly, we attributed the switch of reaction pathways to the presence of this newly engineered interfacial site comprising an amorphous ZrO$_2$ overcoat, which is different from the interface present on Pd over monoclinic ZrO$_2$. On this ZrO$_2$ (amorphous)–Pd interface, CO$_2$ could initially chemisorb on O vacancies, which is similar to the bicarbonate-mediated pathway but follows a different mechanism in the next step. According to the DFT simulation of the C−O cleavage pathway, the dissociation of the first C−O bond was followed by the formation of water (the other product of RWGS reaction), which involved the reaction of dissociated *O (from CO$_2$) and *H (from H$_2$, adsorbed on Pd).\textsuperscript{38,57} Therefore, CO$_2$ cleavage might occur on the ZrO$_2$–Pd interface, and then a CO intermediate was formed (Figure 6b). The DFT study also suggested that the adsorbed CO can either desorb ($k_1$) or further dissociate ($k_2$).\textsuperscript{57} Accordingly, the energy barriers of CO dissociation and desorption are two key factors controlling CO and CH$_4$ selectivities. CO-DRIFTS characterization of ZrO$_2$@Pd/ZrO$_2$ showed that CO could chemisorb on the surface in both linear and bridge configurations (Figure S10b). Similar to what was reported for the bicarbonate-mediated pathway, the different configurations of CO could have led to different energy barriers for C−O cleavage, which governed the final CO/CH$_4$ selectivity. Importantly, DFT simulation showed that the formation of CH$_4$ in the C−O cleavage pathway requires a second C−O cleavage of the CO intermediate, forming *C and *O.\textsuperscript{57} Based on our CO deactivation studies of spent catalysts (Figure 4d), we hypothesized that the adsorbed *C could not only be hydrogenated to CH$_4$ but also nucleate on the surface and form carbonaceous deposits. This hypothesis could explain the self-poisoning phenomenon observed by Aitbekova et al. and us.\textsuperscript{56} On the ZrO$_2$@Pd/ZrO$_2$, a small fraction of the CO intermediate that adsorbed on the sites favoring further C−O cleavage was initially converted into CH$_4$ (at 10% selectivity in our initial measurement). However, carbon deposition likely occurred on the same active sites, which quickly limited methanation (causing the fast initial deactivation), and subsequently, the selectivity toward CO increased to 100%. Interestingly, the monoclinic ZrO$_2$ support seemed to play an important role in this phenomenon because this self-poisoning effect was less discernible when using ZrO$_2$@Pd/SiO$_2$ (its CO selectivity only slightly increased and the calcination treatment led to a smaller recovery of Pd$_{\text{surface}}$). Because a mixed oxide interface might influence this poisoning effect, as an extra control, we synthesized an amorphous ZrO$_2$ support by depositing ZrO$_2$ onto SiO$_2$ (ZrO$_2$@SiO$_2$) and then used it to prepare Pd/ZrO$_2$@SiO$_2$ (which can be used to mostly probe the effect of a Pd–amorphous ZrO$_2$ interface) and use it for CO$_2$ hydrogenation (Figure S12). Although in situ DRIFTS (Figure S13) indicated that Pd/ZrO$_2$@SiO$_2$ also converted CO$_2$ through the direct C−O cleavage pathway, its selectivity toward CO was slightly decreased with extended time on stream. The catalytic behavior of ZrO$_2$@Pd/ZrO$_2$ could be explained by the sensitivity of sub-nanometer metal clusters to their local coordination environment (which was contributed by both the ZrO$_2$ overcoat and support).\textsuperscript{68} As a result, Pd clusters coordinated with two ZrO$_2$ polymorphs could have led to a unique reactivity that facilitated selective carbon deposition. Further elucidation of the factors governing the self-poisoning of methanation sites would require further theoretical and analytical investigations including DFT simulations and more advanced in situ spectroscopies.

## CONCLUSIONS

A sol−gel-based synthetic approach was developed to prepare an atomically dispersed Pd(en)$_2$/SiO$_2$ that served as a precatalyst and was subsequently used in a synthesis procedure featuring kinetically controlled sol−gel overcoating. Overcoating this atomically dispersed material with metal oxides prior to reduction led to a final catalyst containing metal oxide–Pd interface sites with high dispersion. In contrast to the traditional method where Pd particles had been formed on SiO$_2$ prior to coating, this new synthetic approach could limit particle growth during thermal activation, resulting in highly accessible sub-nanometer Pd clusters. Because of the formation of new metal oxide–metal interfaces, both ZrO$_2$@Pd/SiO$_2$ and Al$_2$O$_3$@Pd/SiO$_2$ showed significantly improved activity for CO$_2$ hydrogenation compared to the uncoated g-Pd/SiO$_2$. Moreover, this strategy could be applied to additional metal oxide supports to synthesize catalysts with distinct catalytic properties. Specifically, when using Pd(en)$_2$/ZrO$_2$ to synthesize a ZrO$_2$@Pd/ZrO$_2$ catalyst, the overcoat not only mitigated the agglomeration of Pd under the severe reaction condition but also increased the CO selectivity. This improvement of selectivity was attributed to the self-poisoning of the methanation sites by carbon deposition, which was only favored on the ZrO$_2$@Pd/ZrO$_2$ catalyst, leading to an unprecedented 100% CO selectivity on Pd after 1 h time on stream. The partially deactivated ZrO$_2$@Pd/ZrO$_2$ then maintained a stable reaction rate with prolonged time on stream. These results demonstrate the potential of overcoated supported noble metals in CO$_2$ reduction to CO, especially considering their superior activity, selectivity, and thermal stability.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c02146. Additional characterization data and experimental details including catalyst synthesis, characterizations, and CO$_2$ hydrogenation study (PDF)

## AUTHOR INFORMATION

### Corresponding Author

Jeremy S. Luterbacher − Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland; orcid.org/0000-0002-0967-0583; Email: jeremy.luterbacher@epfl.ch

### Authors

Yuan-Peng Du − Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland; orcid.org/0000-0002-4329-4008

Ali M. Bahmanpour − Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL),
-orcid.org/0000-0003-2092-9215

Luka Mišošević — Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

Florent Héroguèl — Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

Mounir D. Mensi — Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

Oliver Kröcher — Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland; Bioenergy and Catalysis Laboratory, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland; orcid.org/0000-0002-7268-7257

Complete contact information is available at: https://pubs.acs.org/10.1021/acscatal.0c02146

Notes

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