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Surface Engineering of a Supported PdAg Catalyst for Hydrogenation of CO₂ to Formic Acid: Elucidating the Active Pd Atoms in Alloy Nanoparticles

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ABSTRACT: The hydrogenation of carbon dioxide (CO₂) to formic acid (FA; HCOOH), a renewable hydrogen storage material, is a promising means of realizing an economical CO₂-mediated hydrogen energy cycle. The development of reliable heterogeneous catalysts is an urgent yet challenging task associated with such systems, although precise catalytic site design protocols are still lacking. In the present study, we demonstrate that PdAg alloy nanoparticles (NPs) supported on TiO₂ promote the efficient selective hydrogenation of CO₂ to give FA even under mild reaction conditions (2.0 MPa, 100 °C). Specimens made using surface engineering with atomic precision reveal a strong correlation between increased catalytic activity and decreased electron density of active Pd atoms resulting from a synergistic effect of alloying with Ag atoms. The isolated and electronically promoted surface-exposed Pd atoms in Pd@Ag alloy NPs exhibit a maximum turnover number of 14,839 based on the quantity of surface Pd atoms, which represents a more than ten-fold increase compared to the activity of monometallic Pd/TiO₂. Kinetic and density functional theory (DFT) calculations show that the attack on the C atom in HCO₃⁻ by a dissociated H atom over an active Pd site is the ratedetermining step during this reaction, and this step is boosted by PdAg alloy NPs having a low Pd/Ag ratio.

Introduction

The selective transformation of carbon dioxide (CO_2) to useful chemicals or fuels has the potential to alleviate both climate change and future demands for fossil fuels.¹⁻⁴ The hydrogenation of CO₂ to produce formic acid (FA; HCOOH) is a promising strategy, since the target product is a valuable commodity chemical commonly used for preservative and antibacterial purposes.⁵⁻⁶ Because FA has a relatively high hydrogen content (53 $g \cdot L^{-1}$) and is a less-toxic, nonflammable liquid under ambient conditions, it is also regarded as a promising hydrogen storage material. Using this compound, chemically stored hydrogen could be liberated in a controlled manner in the presence of appropriate catalysts, even at room temperature.⁷⁻¹⁴ Recently, FA has also been considered as an alternative to methanol as a fuel source for direct liquid fuel cell systems generating electricity.¹⁵ The current industrial FA production methods traditionally include the hydrolysis of methyl formate and oxidation of biomass.¹⁶⁻¹⁷ Thus, the application of CO₂ hydrogenation catalysts to generate FA must be researched in order to ensure efficient CO₂ utilization and the realization of economically-viable CO2-mediated hydrogen energy cycles.¹⁸

The gas phase hydrogenation of CO₂ to FA involves a positive free energy change ($\Delta G = 33 \text{ kJ mol}^{-1}$), while the same reaction in aqueous solution proceeds more readily because of the relatively low (negative) free energy ($\Delta G = -4 \text{ kJ mol}^{-1}$).¹⁹ Significant efforts have been devoted to the research of homo-ACS Paragon geneous transition metal complexes as catalysts for FA production, especially those based on Ir and Ru, and interesting results have been obtained.^{8, 11, 20-23} Unfortunately, the development of heterogeneous catalysts lags significantly in spite of the obvious practical advantages of such materials.^{5, 24-32} Thus, heterogeneous catalysts still require the use of high catalyst concentrations, extremely elevated pressures and organic solvents.

The immobilization of existing molecular organometallic complexes on insoluble matrixes could combine the tunability of the well-defined active centers in homogeneous catalysts and the operational simplicity of heterogeneous materials.³³ Surface-grafted silica-based substances having a variety of functional groups allow the coordination of analogous metal complexes.³⁴ Porous organic framework (POF) materials, including metal organic frameworks (MOFs), are also potential supports for single-atom active centers, based on the utilization of the framework skeleton to provide suitable coordination sites.³⁵⁻³⁶ The design of this category of catalysts is relatively simple because the resulting coordination environments are similar to those of their homogeneous counterparts.

However, to date, there have been few insights with regard to the most promising design strategies for active catalyst sites in supported metal nanoparticles (NPs). Pd-, Au- and Rubased catalysts have all been shown to be active for the target reaction and their activity can be enhanced by the appropriate selection of support materials, by increasing the NP dispersion Environment

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and by altering the electronic structures of the active metals. The electronic and geometric effects associated with bimetallic NPs, whose architectural configuration involves two metals, can be surface engineered to obtain random alloys, segregated or core–shell structures. This flexibility offers significant opportunities to maximize catalytic activity and selectivity compared with monometallic counterparts, owing to the unique interactions between neighbouring metals.³⁷⁻³⁹ As a result, there has been remarkable progress in the development of supported bimetallic NP catalysts, with the creation of novel catalysts based on a well-understood design strategy. However, although it is well known that catalytic performance can be modified as a result of alloying, additional elucidation of the catalytically active species during the hydrogenation of CO_2 to FA is required.

In this paper, we present a new catalyst based on PdAg alloy NPs supported on TiO₂, intended to promote heterogeneous CO_2 hydrogenation to produce FA. This material was used because surface engineering with atomic precision can provide PdAg alloys with different surface compositions. When using this catalyst, isolated and electron-rich Pd atoms created with the aid of neighbouring Ag atoms at a low Pd/Ag ratio boost the electronegativity of the dissociated hydride species. This ultimately enhances the rate determining HCO₃⁻ hydrogenation step, as demonstrated by kinetic and density functional theory (DFT) calculations.

Results and Discussion

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Supported PdAg catalysts were prepared using a conventional method. Briefly, TiO₂ (JRC-TiO-6, BET surface area $(S_{BET}) = 100 \text{ m}^2 \text{ g}^{-1}$, rutile) was impregnated with an aqueous solution of [Pd(NH₃)₄]Cl₂ and AgNO₃. The Pd/Ag ratio in the resulting material was controlled by varying the concentration of Ag while maintaining a constant Pd loading of 1.0 wt%. The samples obtained in this manner were subsequently reduced with NaBH₄ without calcination, affording PdAg allov NPs supported on TiO₂ having different atomic ratios. For comparison purposes, various other supports, including layered double hydroxide (LDH), MgO, CeO₂ and Al₂O₃, were also employed for the deposition of PdAg alloy NPs. In addition, Pd-based alloy NPs supported on TiO₂ were synthesized along with Cu, Zn, Au or Ni precursors as the second metal by the same impregnation method, followed by reduction with NaBH₄.

We initially attempted to identify the optimal catalyst for the hydrogenation of CO₂ to FA, and generated the data summarized in Table 1. A typical reaction was performed in a 25 mL stainless steel reactor in a basic aqueous solution containing 1.0 M NaHCO₃ under a total pressure of 2.0 MPa (H₂:CO₂) = 1:1) at 100 °C over 24 h. FA was obtained with >99 % selectivity for all catalysts and any other products cannot be observed. The support used for the alloy NPs was regarded as a crucial parameter because the support can provide additional heterogeneous catalytic sites, and may also modify particle sizes and electronic properties. The PdAg/TiO₂ (Pd:Ag=50:50) specimen was found to be an efficient heterogeneous catalyst. with a high turnover number (TON) of 748 (entry 1) after 24 h. In addition, trials without a catalyst or using only the TiO₂ support material showed no activity. We recently reported that strongly basic LDH can act as an efficient support for a singlesite Ru catalyst during the hydrogenation of CO₂, and the present data show moderate activity was obtained when using PdAg/LDH (entry 2). However, the other heterogeneous PdAg catalysts, such as PdAg/MgO, PdAg/CeO₂ and PdAg/Al₂O₃, were found to be less active (entries 3-5). Interestingly, PdAg/TiO₂ exhibited considerably high activity compared with the corresponding PdCu, PdZn, PdAu and PdNi catalysts supported on TiO₂ (entries 6-9). In the Pd K-edge X-ray absorption near-edge structure (XANES) spectra, the edge position of the PdAg/Al₂O₃ was lower than that of the PdAg/TiO₂ (**Figure S1**), which presumably ascribed to the differences in the work functions between Al₂O₃ (4.70 eV) and TiO₂ (6.21 eV). This result also suggests that the moderate interaction between PdAg NPs and TiO₂ is suitable for attaining active catalysts for this target reaction.

 Table 1. Screening results for CO₂ hydrogenation to formic acid over various catalysts.^a

Entry	Metal NPs	Molar ratio (Pd:M)	Support	TON@24h
1	PdAg	1:1	TiO ₂	748
2	PdAg	1:1	LDH	342
3	PdAg	1:1	MgO	200
4	PdAg	1:1	CeO_2	142
5	PdAg	1:1	Al_2O_3	40
6	PdCu	1:1	TiO ₂	353
7	PdZn	1:1	TiO ₂	344
8	PdAu	1:1	TiO ₂	251
9	PdNi	1:1	TiO ₂	120
10	Pd	1:0	TiO ₂	281

 a Conditions: catalyst (50 mg), 1.0 M aqueous NaHCO3 solution (10 mL), H_2:CO2 (1:1, total 2.0 MPa), 100 °C.



Figure 1. (A) TON values (based on Pd atoms) versus the mole fraction of Ag in PdAg/TiO₂ catalysts having different Pd and Ag concentrations. (B) TEM image of a single PdAg/TiO₂ NP and the elemental distributions as determined by cross-sectional EDX line profiling.

Additionally, the catalytic activity was greatly affected by the composition of the PdAg alloy NPs. **Figure 1A** plots TON values versus the Ag content in various specimens. The monometallic Pd/TiO₂ gave poor results, while the reaction using monometallic Ag/TiO₂ was also extremely sluggish (TON = 7). The TON increased with increases in the Ag proportion up to 70%, after which it decreased. This "volcano" type variation in activity based on the Pd/Ag ratio suggests the formation of a uniform PdAg alloy structure on the surface of the TiO₂ as well as a synergic effect originating from the integration of the Pd and Ag.⁴⁰ High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) im-

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ages demonstrated highly dispersed PdAg alloy NPs with a narrow size distribution on the TiO₂ support in the case of the PdAg/TiO₂ (Pd:Ag = 30:70), with a mean particle diameter (d_{ave}) of 3.3 nm (**Figure S2**). This value is similar to that obtained for the Pd/TiO₂ ($d_{ave} = 3.2$ nm, see **Figure S3**). Energydispersive X-ray spectroscopy (EDX) line analysis revealed that both Pd and Ag were situated on the same particles, confirming the formation of a random PdAg alloy (**Figure 1B**). In contrast, the mean particle size of the PdAg NPs on the Al₂O₃, which exhibited activity substantially inferior to that observed using TiO₂, was 9.5 nm with a wide size distribution (**Figure S4**). The formation of small PdAg NPs with a narrow size distribution could therefore be one important factor contributing to the high catalytic activity of the PdAg/TiO₂.

As discussed, the maximum activity was obtained with a low Pd/Ag ratio (Pd:Ag = 30:70) in trials using random PdAg alloy NPs. This result indicates that Pd atoms surrounded by excess Ag atoms can efficiently facilitate the hydrogenation of CO_2 . Based on these data, we investigated the effect of surface-exposed active Pd atoms in alloy NPs on the catalytic activity, applying a surface engineering approach.



Figure 2. TEM images of and elemental distributions along single NPs of (A) $Pd@Ag/TiO_2$ and (B) $Ag@Pd/TiO_2$ as determined by cross-sectional EDX line profiling.

Because of the complete solid solubility and similar reduction potentials of Pd and Ag ions $(E^0(Pd^{2+}/Pd^0) = +0.99 V)$, $E^{0}(Ag^{+}/Ag^{0}) = +0.80$ V), random PdAg alloy NPs can be readily formed via the co-reduction of Pd and Ag precursors. Thus, we were able to tune the surface composition of PdAg NPs to form Pd_{core}Ag_{shell} structures via the successive reduction of metal precursors. This was accomplished by first impregnating the TiO_2 with $[Pd(NH_3)_4]Cl_2$ followed by reduction with NaBH₄ to form the Pd core. Next, AgNO₃ impregnation was carried out and the material again subjected to reduction with NaBH₄ to form a Ag shell, affording Pd@Ag/TiO₂. To produce AgcorePdshell catalysts, Ag@Pd/TiO2 was also synthesized by the same successive reduction method but in the opposite order. Pd:Ag molar ratio was unified to 30:70 for fair comparison. In this paper, the term of alloy was used for both randomly distributed PdAg NPs core-shell type nanoparticles.

Elemental analysis confirmed that the average composition of the NPs in both types of materials was Pd₃₀Ag₇₀. HAADF-STEM images also showed highly dispersed PdAg NPs with average diameters of 3.1 and 3.2 nm for the Pd@Ag/TiO₂ and Ag@Pd/TiO₂, respectively (**Figures S5 and S6**). EDX line scans confirmed the successful surface engineering of the NPs, such that Pd atoms were preferentially located in the core region, while the Ag atoms were situated in the shell region in the Pd@Ag/TiO₂ (**Figure 2A**). Conversely, the Pd and Ag atoms had the opposite distribution for the Ag@Pd/TiO₂ (Figure 2B).



Figure 3. (A) Pd K-edge and (B) Ag K-edge FT-EXAFS spectra of PdAg/TiO₂, Pd@Ag/TiO₂, Ag@Pd/TiO₂, Pd/TiO₂ and reference materials.

Table 2. Curve fitting results for Pd and Ag K-edge EXAFS data.

sample	edge	shell	CN	CN_{total}	<i>R</i> /Å	$\Delta\sigma^2\!/{\AA^2}$
	Pd K	Pd–Pd	3.1	7.1	2.77	0.086
PdAg/TiO ₂		Pd–Ag	4.0		2.85	0.018
Pd/Ag = 30/ 70	Ag K	Ag–Ag	5.1	9.5	2.86	0.095
		Ag–Pd	4.4		2.80	0.035
	Pd K	Pd–Pd	3.3	8.1	2.75	0.098
Pd@Ag/TiO2		Pd–Ag	4.8		2.80	0.079
Pd/Ag = 30/70	Ag K	Ag–Ag	4.5	8.8	2.83	0.011
		Ag–Pd	4.3		2.78	0.036
	Pd K	Pd–Pd	1.8	5.6	2.75	0.047
Ag@Pd/TiO2		Pd–Ag	3.8		2.79	0.010
Pd/Ag = 30/70	Ag K	Ag–Ag	7.0	10.7	2.84	0.011
		Ag–Pd	3.7		2.79	0.036

X-ray absorption measurements were carried out to precisely determine average local structural information for the Pd and Ag atoms. The shapes of the normalized X-ray absorption near-edge structure (XANES) spectra at the Pd K-edge and the edge positions of three PdAg samples resembled those of Pd foil and monometallic Pd/TiO₂ but differed from those of PdO. These results suggest that the oxidation state of the Pd atoms was close to Pd⁰ (Figure S7). More detailed inspection found two distinct peaks at approximately 24,367 and 24,385 eV, corresponding to the allowed $1s \rightarrow 5p$ transition in the PdAg samples. These peaks were slightly shifted to lower energy values compared to the Pd/TiO2, indicating that the symmetry of the Pd metal face centered cubic (fcc) structure was slightly disordered by integration with the Ag.⁴¹ The Pd K-edge Fourier transform-extended X-ray absorption fine structure (FT-EXAFS) spectra contained a single sharp peak associated with Pd–Pd bonds at approximately 2.6 Å that was also suggestive of metallic Pd (Figure 3A). However, the Pd-Pd distance in the PdAg samples was found to be slightly longer compared to the values for Pd foil and Pd/TiO₂, indicating the presence of heteroatom Pd-Ag bonds. No peaks due to Pd-O or Pd-O-Pd bonds (expected at approximately 1.6 and 3.0 Å in the case of PdO) were observed. The Ag K-edge XANES spectra of these three PdAg samples were also found to resemble those of Ag foil and monometallic Ag/TiO2, confirming the presence of metallic Ag (Figure S8). Their FT-EXAFS spectra contained a single intense peak ascribed to contiguous Ag-Ag bonds with a length of approximately 2.7 Å (Figure 3B). This peak was shifted to a slightly shorter interatomic distance compared with those of pure Ag foil and Ag/TiO₂, again suggesting Pd-Ag bonds.

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Coordination numbers (CNs) and bond lengths (R) obtained from EXAFS curve fitting can provide critical information regarding the composition of the bimetallic NPs, and these data are presented in Table 2. The Pd-Pd bond distances were evidently shorter than those of Pd-Ag bonds, which in turn were shorter than Ag-Ag bonds. These results are consistent with the shifts of the main peaks due to metallic bonding in the FT-EXAFS spectra. It is widely accepted that the atoms inside an fcc lattice are completely coordinated with a CN of 12, while the surface atoms are coordinately unsaturated with a CN of 7, 8 or 9 for (110), (100) and (111) facets, respectively.⁴² As a result, the CN of the shell atoms will typically be less than that of the core atoms, since atoms at the surface have fewer neighbors than those in the core.⁴³ In the present case, the d_{ave} for the three PdAg NP samples were all approximately 3 nm, meaning that the total CN was considerably less than 12. The CN_{total} ($CN_{Pd-Pd} + CN_{Pd-Ag}$) at the Pd Kedge for PdAg/TiO₂ made with a random alloy was found to be 7.1, which is lower than the value of 9.5 ($CN_{Ag-Ag} + CN_{Ag-}$ Pd) at the Ag K-edge because the Pd concentration was substantially lower than that of Ag (Pd:Ag = 30:70). As expected, the CN_{total} at the Pd K-edge for the Pd@Ag/TiO2 was increased, while the Ag K-edge was decreased, confirming a Pd_{core}Ag_{shell} structure. The opposite trend was observed in the case of the Ag@Pd/TiO2 with a AgcorePdshell structure.

32 We also characterized the surface PdAg NPs by Fourier 33 transform infrared (FT-IR) experiments following CO adsorp-34 tion (Figure 4A). In a preliminary DFT calculation, the ad-35 sorption energies (E_{ad}) of CO adsorbed at a Pd site on the Pd 36 (111) and PdAg (111) surfaces were determined to be 31.7 and 37 33.9 kcal/mol, which are noticeably larger than 12.9 and 12.5 38 kcal/mol at an Ag site on the Ag (111) and PdAg (111) surfac-39 es, respectively (Table S1). In addition, the amount of CO in the pulsed CO adsorption measurement of monometallic 40 Ag/TiO₂ was 0.009 cm³/g, which was ca.0.2% of the theoretical value, by assuming monodentate type adsorption onto Ag 42 atoms (Table S2). These results suggest that the CO molecules 43 are predominantly adsorbed on the Pd atoms rather than the 44 Ag atoms. Monometallic Pd/TiO₂ generated two distinct peaks 45 assignable to the linear and bridging stretching vibrations of 46 adsorbed CO at 2076 and 1943 cm⁻¹, respectively.⁴⁴ The contribution of bridging-type CO decreased as the Pd/Ag ratio 48 was lowered, and was completely absent in the case of the Pd@Ag/TiO2, suggesting the isolation of Pd atoms. Addition-49 ally, linear-type CO was predominantly observed for all sam-50 ples, and the peaks were gradually shifted to lower wavenumbers with decreases in the Pd/Ag ratio. Thus, the Pd atoms 52 in the PdAg NPs were evidently electron enriched by charge 53 transfer from Ag atoms owing to the net difference in ioniza-54 tion potential between the two metals (Pd: 8.34 eV, Ag: 7.57 55 eV). A similar tendency was observed in the XPS data. The Pd 56 3d peaks generated by the PdAg samples were shifted to lower 57 binding energies than those of the Pd/TiO₂, and this shift was 58

observed to decrease in the order of $Pd(a)Ag/TiO_2 >$ $PdAg/TiO_2 > Ag@Pd/TiO_2$ (Figure 4B).



Figure 4. (A) FT-IR spectra of CO chemisorbed on Pd and PdAg samples. (B) XPS spectra of Pd and PdAg samples. (C) Relationship between the TON for CO₂ hydrogenation based on surfaceexposed Pd atoms (as determined by CO pulse adsorption) and the Pd 3d binding energy (as determined by XPS).

The catalytic activities of a series of supported PdAg catalysts having different surface compositions, and of Pd/TiO₂, were assessed during CO₂ hydrogenation, with the results provided in Figure 5. Comparing the TON values based on the total quantities of Pd employed, the Pd@Ag/TiO2 exhibited an elevated TON (2,496) despite the low density of surface exposed Pd atoms. In an effort to elucidate the cause of these activities, the dispersion of Pd species was determined by pulsed CO adsorption measurements (Table S2). As a result, a maximum TON value of 14839 was obtained from the Pd@Ag/TiO₂ based on the quantity of surface Pd atoms, which represents a more than ten-fold increase compared with the Pd/TiO2. These TON values obtained under relatively mild conditions are superior to those reported previously for other heterogeneous catalysts, including Au/Al₂O₃ (580 at 4 MPa),²⁹ Ru/γ-Al₂O₃ (139 at 13.5 MPa),²⁶Pd/mpg-C₃N₄ (85 (24 h) at 100 °C, 4 MPa),³⁰ Ru/LDH (698 (24 h) at 100 °C, 2 MPa),¹⁸ Au/TiO₂ (215 (20 h) at 70 °C, 4 MPa),²⁹ Ir-PN₄₅ PEI@TNT(Na⁺) (1012 (20 h) at 140 °C, 2 MPa),⁴ PdAg/SBA-15-phenylamine (874 (24 h) at 100 °C, 2 MPa)38 and PdAg/amine-modified mesoporous carbon (839 (24 h) at 100 °C, 2 MPa).³⁷ Moreover, a TEM image of the recovered catalyst confirmed that the particle sizes remained essentially unchanged without significant agglomeration of the NPs and the average diameter was determined to be 3.7 nm (Figure S9A). EXAFS analysis also demonstrated no significant variations in the alloy structure (Figure S9B-E). Furthermore, the spent catalyst keeps its original activity even second reaction.

The high catalytic activity of the Pd@Ag/TiO₂ can be ascribed to the generation of isolated and electron-rich Pd atoms with the aid of the surrounding Ag atoms, since the average diameters estimated by TEM revealed no significant differences in NP size. There is also evidently a correlation between the TON based on surface Pd atoms and the Pd 3d_{5/2} binding

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energy determined by XPS analysis (Figure 4C). The importance of the electronic state of the active center to the hydrogenation of CO_2 to FA has been reported previously. As an example, the strong electron-donating ability of PNP pincertype ligands or N-heterocyclic carbenes in Ir(III) complexes are responsible for promoting the reaction.⁴⁶⁻⁴⁷ In prior work, our own group also identified a correlation between catalytic activity and the Ru 3p binding energy for a series of Ru-based LDH-supported catalysts, in which the TON based on Ru content increased as the binding energy decreased.¹⁸



Figure 5. Comparison of the catalytic activities of a series of supported PdAg catalysts with different surface compositions and Pd/TiO₂ during CO₂ hydrogenation. Conditions: catalyst (10 mg), 1.0 M aqueous NaHCO3 solution (10 mL), H₂:CO₂ (1:1, total 2.0 MPa), 100 °C.

Considering previous experimental and theoretical studies regarding the reaction mechanisms of metal NPs,^{29, 37-38, 48} we propose a possible catalytic cycle for CO₂ hydrogenation over supported PdAg NPs (Figure 6A). The reaction is initiated by the dissociation of H₂ to afford a metal-hydride species (step 1). This is followed by the adsorption of HCO_3^{-} generated under basic conditions (step 2), which undergoes hydrogenation to give a formate intermediate (step 3). The reduction of HCO₃⁻ is energetically more likely to proceed if active H attacks the C atom of HCO₃⁻ rather than the O atoms. Finally, the production of formate accompanied by H₂O regenerates the initial active species (step 4). NaHCO₃ and NaOH gave almost similar activity as an additive, while the use of trimethylamine showed moderate result (Figure S10). The activity without additives is quite low because of the limited solubility of CO₂ in aqueous solution. Kinetic studies showed almost zero-order dependence in CO₂ pressure (Figure S11). The FT-IR spectrum of the Pd@Ag/TiO2, upon treatment in an aqueous NaHCO₃ solution at 1.0 MPa of CO₂ showed the peak due to v (CO₃) band of the adsorbed HCO₃⁻ was observed at around 1454 cm⁻¹ (Figure S12).⁴⁹ These results suggest that the present catalytic system mainly proceeds via the reduction of HCO₃⁻ transformed from gaseous CO₂ under basic aqueous solutions, while the involvement of the direct CO₂ activation is the minor pathway. The origin of the FA during this hydrogenation process was investigated using ¹³CO₂ in D₂O as a solvent (with 0.5 M NaOH) followed by analysis of the products by ¹³C NMR spectroscopy. Deprotonated H¹³COO⁻ generated a sole peak at 170. 8 ppm without the formation of byproducts (Figure S13).⁵⁰ Additionally, HCO₃ was used as a sole carbon source without gaseous CO₂, the attained TON

significantly decreased. These experiments provide firm evidence that the FA originates from the CO_2 .

In the case of a reaction under a flow of H₂ and D₂ through the catalyst, the TOF for HD formation was almost independent of the surface composition, as shown in **Figure 7A**.⁵¹ On the contrary, the effect of the HCO₃⁻ concentration was greatly dependent on the surface composition (**Figure 7B**). The reaction order decreased as follows; Pd/TiO₂ (0.67) > Ag@Pd/TiO₂ (0.36) > PdAg/TiO₂ (0.33) > Pd@Ag/TiO₂ (0.22), which is consistent with the TON values based on the quantity of surface exposed Pd atoms for the CO₂ hydrogenation. These kinetic investigations demonstrate that the elementary steps involving HCO₃⁻ species (*step 2 or 3*) is the ratedetermining step, rather than the dissociation of H₂ (*step 1*).



Figure 6 (A) Possible reaction mechanism and (B) potential energy profiles for CO₂ hydrogenation to formic acid.

To better understand the positive effect of alloving with Ag, potential energy profiles were obtained using DFT calculations, employing Pd₂₂, Pd₁₁Ag₁₁ and Pd₆Ag₁₆ clusters as models for monometallic Pd and alloy NPs (Figure 6B). In the case of Pd_{22} , the dissociation of H_2 (step 1) occurs at Pd sites via TS_{I/II} with a barrier of 13.9 kcal/mol. Following this, HCO₃⁻ is adsorbed on the Pd to produce intermediate III (step 2), followed by reduction through the attack of a hydride via TS_{III/IV}, with a barrier of 77.4 kcal/mol (step 3). The energy barrier to step 4, in which formate is spontaneously generated along with H₂O when the OH of HCO₃⁻ is attacked by another hydride, is negligibly small. These results show that the ratedetermining step in the present catalytic cycle is step 3. In the cases of the Pd₁₁Ag₁₁ and Pd₆Ag₁₆ clusters, the dissociation of H₂ occurs with a barrier of 11.9 and 11.0 kcal/mol, respectively. These activation energies are similar to that obtained with the Pd_{22} , but differ from the 39.0 kcal/mol calculated for an Ag₂₂ cluster model. These results agree with the kinetic data obtained from the HD formation reaction, and show that alloying with Ag does not affect the H₂ dissociation step. In sharp contrast, the activation energy for the reduction of HCO₃⁻ via $TS_{III/IV}$ was decreased with increases in the proportion of Ag atoms, with calculated values of 58.7 and 46.2 kcal/mol for $Pd_{11}Ag_{11}$ and Pd_6Ag_{16} , respectively. These results are also in good agreement with the kinetic investigation into the effect of HCO_3^- concentration, and further demonstrate that the PdAg alloy NPs with a low Pd/Ag ratio plays a pivotal role in boosting the rate-determining step. In a preliminary calculation, the energy barrier in the dissociation of H_2 on Ag atom of Pd_6Ag_{16} cluster was determined to be 38.9 kcal/mol, which is almost similar to that on the Ag₂₂ cluster, but is substantially larger than those on the Pd atoms of Pd_{22} , $Pd_{11}Ag_{11}$, and Pd_6Ag_{16} , respectively. This result definitely excludes the participation of Ag atoms on the catalytic cycle as an active center even after the formation of Pd@Ag core-shell structure.

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Figure 7. (A) Comparison of activity during the HD exchange reaction using Pd and PdAg catalysts. (B) Effect of HCO_3^- concentration on TOF values using Pd and PdAg catalysts



Figure 8. Representative Mulliken atomic charges as determined by DFT calculations in the reaction intermediate C for (A) Pd_{22} , (B) $Pd_{11}Ag_{11}$ and (C) Pd_6Ag_{11} clusters.

As discussed above, the electronic state of the active Pd atoms is important to the hydrogenation of CO₂, and there is a strong correlation between the TON based on surface Pd atoms and the extent to which the Pd atoms are electron rich. The significant enhancement of the rate-determining step by the PdAg alloy NPs having a low Pd/Ag ratio can be explained by considering the electronic state in reaction intermediate III. Figure 8 depicts the highest occupied molecular orbital (HOMO) level of reaction intermediate III and the representative Mulliken atomic charges of selected atoms as determined by DFT calculations for Pd₂₂, Pd₁₁Ag₁₁ and Pd₆Ag₁₆ clusters. The HOMO can be tuned through coupling of the electronic structure as the NP composition is varied, and is elevated (from -1.65 to -1.51 eV) when Pd atoms are surrounded by more Ag atoms. This higher HOMO level would be expected to increase the extent to which the Pd atoms are electron rich and so to decrease the electronic charge of the Pd atoms that

participate in the dissociation of H₂. Thus, these charges decrease in the order of $-0.115 (Pd_{22}) > -0.168 (Pd_{11}Ag_{11}) >$ 0.216 (Pd₆Ag₁₆). These results are supported experimentally by the FT-IR spectra following CO adsorption as well as the XPS analysis. Such changes accordingly decrease the electronegativity of the dissociated hydride species on the Pd atoms. In contrast, the electronic charges of the C atoms of the adsorbed HCO₃⁻ are almost constant for all cluster models, and maintain their positive charges. Therefore, electronically promoted hydride species on the Pd₆Ag₁₆ will tend to attack the C atoms of the adsorbed HCO3, whereas electronic repulsion between the less negative hydride species on the Pd₂₂ and the positively charged C atoms results in a greater activation energy. It can be concluded that the electronic ligand effect resulting from the interplay of the neighboring Ag atoms explains the enhanced activity for CO₂ hydrogenation.

Conclusion

In summary, we have elucidated the effects of highly active Pd sites surrounded by Ag atoms during CO₂ hydrogenation to FA. By tuning the surface-exposed Pd atoms in the alloy NPs, the optimized Pd atoms in Pd@Ag/TiO₂ performed as an efficient catalyst even under low pressure conditions. Excellent selectivity was obtained owing to the electronic ligand effect caused by the Ag atoms, with activity greater than that of monometallic Pd/TiO₂ by a factor of more than ten. The enhanced electronegativity was found to facilitate the rate determining reduction step of the adsorbed HCO₃⁻ species, as evidenced by kinetic and DFT calculations. This study provides advanced insights into the architecture of catalytically active sites for CO₂ hydrogenation to FA. This work also emphasizes the importance of the surface engineering of alloy NPs with atomic precision for optimization of the target reaction. Further improvement of the catalytic performance by the enhancement of CO₂ adsorption properties may lead to the development of environmentally-benign CO2-mediated hydrogen storage/release systems.

Experimental Section

Materials: TiO_2 (JRC-TiO6) was kindly supplied by the Catalysis Society of Japan. $[Pd(NH_3)_4]Cl_2$ was obtained from the Aldrich Chemical Co., AgNO₃ was purchased from Nacalai Tesque and NaHCO₃ was purchased from Wako Pure Chemical Industries, Ltd. All commercially-available compounds were used as-received. Distilled water was employed as the reaction solvent.

Catalyst synthesis: TiO₂ (0.5 g) was dispersed in 100 mL of an aqueous solution containing $[Pd(NH_3)_4]Cl_2$ (0.047 mmol) and AgNO₃ (0.047 mmol), followed by stirring at room temperature for 1 h. The suspension was evaporated under vacuum and the obtained powder was dried overnight. Subsequently, the sample was reduced with NaBH₄ (0.28 mmol) and washed with distilled water several times to yield PdAg/TiO₂ (Pd: 1.0 wt%, Pd/Ag molar ratio = 1/1). Using the same correduction procedure, the support, the second metal in the alloy and the Pd/Ag molar ratio were all changed. During the synthesis of the Pd@Ag/TiO₂ catalyst (Pd: 1.0 wt%, Pd/Ag molar ratio = 3/7), TiO₂ was first impregnated with Pd(NH₃)₄]Cl₂, followed by reduction using NaBH₄, after which AgNO₃ was added, followed by a second reduction with NaBH₄.

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reduction method but in the opposite order. Analysis by inductively couple plasma atomic emission analysis (ICP-AES) clearly indicated that the desired amounts of metal species were successfully loaded onto each of the catalysts.

General procedure for the catalytic hydrogenation of CO₂: CO₂ hydrogenation to FA was conducted with a batch reactor system using a stainless steel autoclave (60 mL). In each trial, the catalyst (10 mg) and a 1.0 M aqueous NaHCO₃ solution (10 mL) were transferred into the reactor and the pressure was set to 2.0 MPa by adding H₂:CO₂ (1:1). The system was subsequently heated to 100 °C and stirred for 24 h. FA yields were determined by high performance liquid chromatography (HPLC), using a Shimadzu instrument equipped with a Bio-Rad Aminex HPX-87H ion exclusion column (300 × 7.8 mm) and 5 mM H₂SO₄ (0.5 mL/min) as the mobile phase, at 40 °C. TON values were determined by dividing the quantity of FA produced after 24 h by the moles of either total Pd or surface-exposed Pd.

Characterization: Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku Ultima IV diffractometer with Cu K α radiation (λ =1.54056 Å). TEM images were obtained with a Hitachi HF-2000 FE-TEM instrument operating at 200 kV. Nitrogen adsorption-desorption isotherms were acquired at -196 °C using a BELSORP-max system (MicrotracBEL Corp.). Samples were degassed at 150 °C for 3 h under vacuum to vaporize physisorbed water prior to each trial. Specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption data over the range from $p/p_0 = 0.05$ to 0.35. XPS was performed with a Shimadzu ESCA-3400 system, using Mg Kα radiation (hv = 1253.6 eV) as the excitation source. The binding energy values of the spectra were calibrated using the contaminant C 1s core level at 284.5 eV. Metal concentrations in the samples were determined by ICP-AES analysis with a Nippon Jarrell-Ash ICAP-575 Mark II instrument. STEM images and elemental maps were obtained using a JEOL-ARM 200F apparatus equipped with a Kvex energy-dispersive X-ray detector (JED-2300T) operating at 200 kV. CO pulse adsorption was performed by using a BEL-METAL-1 instrument (BEL Japan, Inc.) to measure the amount of surface exposed Pd. The samples were pretreated under a helium flow at 323 K for 15 min, and subsequently under a H₂ flow at 323 K for 30 min. The CO adsorption was measured at 323 K at a CO flow rate of 20 cm³ min⁻¹. Pd and Ag K-edge XAFS spectra were recorded using a fluorescence yield collection technique at the 01B1 beamline station at the SPring-8 facility, JASRI, Harima, Japan (proposal nos. 2017B1081 and 2017B1084), with a Si(111) monochromator. Data reduction was performed using the REX2000 software program (Rigaku). Fourier transformation of the k3-weighted normalized EXAFS data was carried over the range of 3.0 Å < k/Å-1 < 12 Å to obtain radial structure functions, and backscattering amplitudes and phase shift parameters for curve fitting analyses were calculated with the FEFF8.40 code.

DFT calculations. All DFT calculations were performed with the DMol³ program in the Materials Studio 17.2 software package.⁵²⁻⁵³ The generalized gradient approximation (GGA) exchange-correlation functional proposed by Perdew, Burke and Ernzerhof (PBE) was combined with the double numerical basis set plus polarization functions (DNP). Pd₂₂, Pd₁₁Ag₁₁ and Pd₆Ag₁₆ clusters were chosen as models of monometallic Pd and PdAg alloy NPs, with the lower two layers fixed at the

corresponding bulk position and the top layer allowed to relax during geometry optimizations.

ASSOCIATED CONTENT

Supporting Information is available free of charge via the Internet at http://pubs.acs.org. TEM, CO adsorption, XANES, ¹³CNMR.

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