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Boosting the activity of PdAg alloy nanoparticles during H₂ production from formic acid induced by CrO_x as an inorganic interface modifier†

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Interfacial modification of PdAg nanoparticles supported on mesoporous carbon (MSC) functionalized with weakly basic phenylamine groups was performed using an amorphous CrO_x phase. The resulting PdAgCr/amine-MSC catalyst was found to promote the efficient dehydrogenation of formic acid (HCOOH) serving as a liquid organic hydrogen carrier. A maximum turnover frequency of 6898 h⁻¹ (based on the mass of Pd employed) was achieved, which was 1.6 times larger than the value previously obtained using a PdAg catalyst. Physicochemical characterization and density functional theory calculations indicated that electronic interactions with the CrO_x phase induced a significant electronic gap. This effect, in turn, generated unique ensemble sites on the PdAg nanoparticle surfaces at which electron-deficient Ag^{δ+} and electron-rich Pd^{δ-} atoms were adjacent. Kinetic analyses and theoretical investigations demonstrated that O–H bond dissociation was assisted by amine groups on the support surface. Enhanced C–H bond dissociation and H₂ desorption resulting from the cooperative action at the ensemble sites were found to play a crucial role in increasing the catalytic activity. The present system is easily synthesized, does not require additives, can be recycled and effectively suppresses CO formation, meaning that this material is a suitable candidate for practical applications in fuel cells.

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Broader context

Formic acid (FA, HCOOH) has emerged as one of the most promising hydrogen storage compounds because it is non-flammable, relatively nontoxic, and contains 4.4 wt% (53.4 g L⁻¹) hydrogen. There have been extensive studies in developing catalysts targeted for efficient H₂ delivery. Our own group has demonstrated that the dispersed PdAg nanoparticles supported on phenylamine-functionalized mesoporous carbon display an extremely high turnover frequency (TOF) of 5638 h⁻¹ during the dehydrogenation of FA, and this work has provided advanced insights into the architecture of catalytically-active sites for this target reaction (*ACS Catal.*, 2018, 8, 2277). In this study, interfacial modification of PdAg nanoparticles was performed using highly dispersed CrO_x. The resulting ternary PdAgCr/amine-MSC is proven to display a maximum TOF of 6898 h⁻¹, which is 1.6 times larger than that with our previously reported binary catalyst. On the basis of kinetic and theoretical investigations, we demonstrated that the significant enhancement of activity is attributed to the interplay of unique ensemble sites on the PdAg nanoparticle surface, where electron-deficient Ag^{δ+} and electron-rich Pd^{δ-} are adjacent. We are sure that these findings are of sufficiently immediate interest to a general chemistry research readership.

1. Introduction

Hydrogen (H₂) has a high gravimetric energy density of 33.3 kW h kg⁻¹, which is three times the value for gasoline, and produces only water as a by-product when converted into energy in an internal combustion engine or a fuel cell.^{1,2} Hence,

H₂ is a potentially important energy source. However, the development of safe and efficient methodologies for the storage and transportation of hydrogen gas is required to realize a sustainable hydrogen-based economy.^{3,4} Conventional storage technologies, including pressurization and/or cryogenic liquefaction, suffer from a tradeoff relationship between storage density and efficiency.⁵ As such, chemical hydrogen storage in liquid organic hydrogen carriers (LOHCs) may be a viable alternative to physical hydrogen storage.^{6–8} In an LOHC system, hydrogen is stored by converting a hydrogen-lean compound into its hydrogen-rich counterpart *via* a catalytic hydrogenation reaction, while hydrogen is released by dehydrogenation of the hydrogen-rich compound. There are several LOHC systems,

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including cyclohexane–benzene, methylcyclohexane–toluene, decalin–naphthalene and perhydro-*N*-ethylcarbazole–*N*-ethylcarbazole, that have been recognized as suitable candidates.^{9–13}

Formic acid (FA, HCOOH) has emerged as a prominent LOHC component over the last decade. FA is of interest because of its high hydrogen content (4.4 wt%; 53.4 g L⁻¹), low toxicity and low flammability (flashpoint of 69 °C, which is much higher than the values for methanol (12 °C) and gasoline (-40 °C)) under ambient conditions.^{14,15} The use of FA could allow economical CO₂-mediated hydrogen storage energy cycling based on the regeneration of FA through the hydrogenation of CO₂ with H₂.¹⁶ The selective dehydrogenation of FA is favored thermodynamically ($\Delta G = -48.4$ kJ mol⁻¹), which is necessary to ensure that pure H₂ is generated without the formation of CO and H₂O *via* the competitive dehydration pathway ($\Delta G = -28.5$ kJ mol⁻¹). This factor is especially important because the CO byproduct is toxic to Pt-based fuel-cell catalysts. For all these reasons, numerous investigations have been conducted in attempts to identify catalysts, both homogeneous and heterogeneous, capable of promoting FA dehydrogenation under mild conditions.^{17–23}

To ensure that practical systems are developed, current research has focused on the use of reliable heterogeneous catalysts such as Au, Pt and especially Pd, which exhibits excellent catalytic activity. Alloying these elements with additional metals that possess superior resistance to CO poisoning is another promising strategy.^{24–28} Our group previously developed binary nanoparticle (NP) catalysts based on Pd combined with coinage metals such as Au, Ag or Cu that exhibited superior activity compared with monometallic catalysts.^{29–31} The synergistic effect provided by these materials is attributed to the electronic activation of Pd species by charge transfer resulting from the different work functions of the two metals. This prior work suggested possible design strategies for producing catalytically active sites promoting the dehydrogenation of FA.

Research regarding the nano-engineering of catalysts for efficient dehydrogenation of FA has indicated that precise tuning of the NP architecture at the angstrom level is required to provide the appropriate activity and selectivity. Controlling particle size can provide large surface-area-to-volume ratios and also optimize the relative proportions of low- and high-coordination surface atoms within regular arrangements of the NPs.^{32,33} The catalytic behavior of NPs is also affected by morphology due to differences in the preferential exposure of particular crystallographic planes.³⁴ Many supports, including zeolites, silica, carbon and metal–organic frameworks, have been investigated in attempts to obtain strong metal–support interactions, with frequent reports of unique synergistic effects at the interfaces between NPs and supports.^{35–41} Surface modification with organic molecules can also inhibit the agglomeration of NPs, thus allowing control over the adsorption kinetics of reactants or intermediates through specific geometric phenomena or metal–ligand electronic effects.^{42,43}

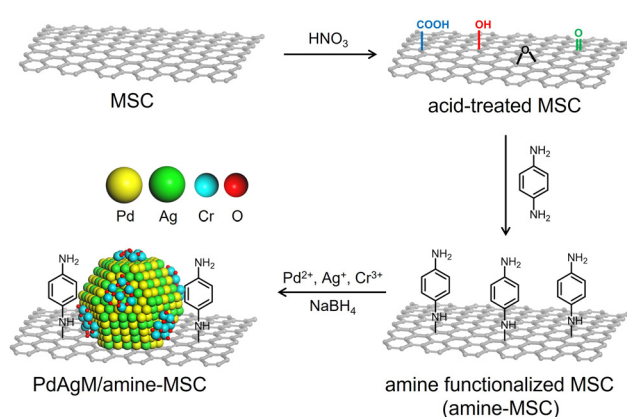
We have previously reported that the PdCuCr ternary NPs within a macroreticular basic resin that possesses -N(CH₃)₂ functional groups are responsible for the efficient production

of H₂ from formic acid, which is attributed to the stabilization effect of surface Cr clusters and a synergistic effect to boost the C–H bond dissociation step.⁴⁴ Inspired by our previously obtained insight, the present study utilized a highly dispersed amorphous CrO_x phase as an inorganic interface modifier to alter the electronic state of PdAg NPs supported on mesoporous carbon (MSC) functionalized with a weakly basic phenylamine. Unlike organic ligands, which exhibit Lewis basicity, metal centers connected with oxide (O₂⁻) groups in CrO_x are positively charged, while those in the periphery of the Cr³⁺ atoms are highly negatively charged. Thus, the modification of these materials with CrO_x improves catalytic activity during dehydrogenation of FA compared with a pure binary PdAg catalyst. These electronic interactions generate unique ensemble sites at which electron-deficient Ag^{δ+} and electron-rich Pd^{δ-} atoms are adjacent, and ultimately lead to a rate-determining step involving the dissociation of C–H bonds in FA, as demonstrated by kinetics analyses and density functional theory (DFT) calculations.

2. Results and discussion

2.1. Characterization of catalysts

The synthetic procedure employed to produce catalysts comprising PdAgCr supported on phenylamine-functionalized MSC (denoted herein as PdAgCr/amine-MSC) is illustrated in Scheme 1. In this procedure, the MSC was treated with an aqueous nitric acid solution, which resulted in the formation of surface O-based functional groups such as -COOH and -OH (Fig. S1A, ESI[†]). The surface of the acid-treated MSC was subsequently functionalized with *p*-phenylenediamine to afford amine-MSC. During this step, the surface O-based functional groups reacted with the amine groups to generate amide and C–N bonds. The concentration of amine groups grafted onto the MSC was determined to be approximately 0.57 mmol g⁻¹ based on CHN elemental analysis (Table S1, ESI[†]), in good agreement with the value of 0.53 mmol g⁻¹ obtained from thermogravimetric analysis (Fig. S1B, ESI[†]). Pd, Ag and Cr were deposited by mixing the amine-MSC support with aqueous



Scheme 1 Schematic illustration of the synthesis of the PdAgCr-supported amine-MSC catalyst.



solutions containing $\text{Pd}(\text{NO}_3)_2$, AgNO_3 and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Finally, each sample was reduced using NaBH_4 , affording PdAgCr/amine-MSc.

The N_2 adsorption–desorption isotherm for each specimen displayed a characteristic type IV curve with sharp capillary condensation steps and an H1-type hysteresis loop over the relative pressure (p/p_0) range of 0.6–0.9, indicating the presence of ordered and well-preserved cylindrical mesopores (Fig. S2, ESI[†]). These results confirmed that the original pore structure of the MSC was maintained despite the addition of the modifier and metals. The Brunauer–Emmett–Teller surface areas (S_{BET}) and pore volumes (V_p) calculated from the N_2 adsorption–desorption isotherms are summarized in Table S2 (ESI[†]). After amine functionalization to generate amine-MSc ($S_{\text{BET}} = 153 \text{ m}^2 \text{ g}^{-1}$, $V_p = 0.39 \text{ cm}^3 \text{ g}^{-1}$), both S_{BET} and V_p decreased compared with the values for the original MSC ($S_{\text{BET}} = 320 \text{ m}^2 \text{ g}^{-1}$, $V_p = 0.60 \text{ cm}^3 \text{ g}^{-1}$). A further slight decrease was observed after deposition of the metals ($S_{\text{BET}} = 104 \text{ m}^2 \text{ g}^{-1}$, $V_p = 0.24 \text{ cm}^3 \text{ g}^{-1}$).

Fig. 1 presents a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of PdAgCr/amine-MSc, together with energy dispersive X-ray spectroscopy (EDX) maps. The NPs had a mean diameter (d_{ave}) of 1.5 nm and were well dispersed (Fig. 1a). This value was comparable with that obtained for PdAg/amine-MSc ($d_{\text{ave}} = 1.2 \text{ nm}$) and Pd/amine-MSc ($d_{\text{ave}} = 1.8 \text{ nm}$) specimens, as shown in Fig. S3 and S4 (ESI[†]). However, a comparison of the particle sizes clearly demonstrated that the addition of the second and third metals resulted in the formation of smaller NPs. Energy-dispersive X-ray spectroscopy maps indicated that the bright particles were composed of Pd, Ag and Cr atoms that are highly dispersed throughout the amine-functionalized material (Fig. 1b–e).

The electronic state of each metal was investigated by X-ray photoelectron spectroscopy (XPS). In the case of Pd/amine-MSc, the Pd 3d_{5/2} and 3d_{3/2} electron binding energy values were 335.9 and 338.0 eV, and 341.0 and 343.3 eV, respectively. The peaks at lower binding energies were assigned to the Pd⁰ state, while the higher ones were attributed to Pd²⁺ (Fig. 2A). The presence of Pd²⁺ was presumably due to the oxidation of the surface Pd NPs by CrO_x or strong interaction with surface amine groups. The Pd 3d peaks generated by PdAg/amine-MSc



Fig. 2 (A) Pd 3d XPS spectra of (a) PdAgCr/amine-MSc, (b) PdAg/amine-MSc and (c) Pd/amine-MSc; (B) Ag 3d XPS spectra of (a) PdAgCr/amine-MSc and (b) PdAg/amine-MSc; and (C) Cr 2p XPS spectrum of PdAgCr/amine-MSc.

were shifted to lower binding energies by 0.4 eV compared with those obtained from the corresponding monometallic Pd catalyst. This shift was attributed to the ability of Ag atoms to donate electrons to Pd atoms upon alloying, as a consequence of the net difference in the ionization potentials of the two elements (Ag: 7.57 eV, Pd: 8.34 eV). In contrast, the addition of Cr atoms shifted the Pd 3d peaks toward higher binding energies compared with PdAg/amine-MSc. No differences were observed in the Ag 3d XPS spectra acquired from PdAg/amine-MSc and PdAgCr/amine-MSc (Fig. 2B), suggesting that the presence of Ag⁺ was minimal. The Cr 2p spectra could be deconvoluted into two components (Fig. 2C), comprising a main peak at approximately 577.5 eV assigned to Cr³⁺ and a small peak at 580 eV attributed to Cr⁶⁺. These results indicate that the Ag atoms were preferentially located in the core regions of the NPs, while Pd atoms were typically situated on NP surfaces and were partially oxidized by the amorphous chromium oxide (CrO_x) and/or chromium hydroxide ($\text{Cr}(\text{OH})_3$).

X-ray absorption analyses were also performed to elucidate the local structures of the specimens. The shapes of the Pd K-edge X-ray absorption near-edge structure (XANES) spectra of the three Pd-based samples all differed from that of Pd foil but resembled the spectrum of PdO (Fig. 3A). The Fourier-transform extended X-ray absorption fine structure (FT-EXAFS) spectra of all materials exhibited two peaks associated with Pd–O(N) and contiguous metallic Pd–Pd bonds, appearing at 1.6 and 2.6 Å, respectively (Fig. 3B), with no significant shift from the Pd–Pd distance in Pd foil. The first peak, at 1.6 Å, is believed to be partly due to Pd–N bonds originating from interactions with the amine-MSc support. The inverse FT of PdAgCr/amine-MSc was well fitted using Pd–O(N) and Pd–Pd shells with a coordination number (CN) and an interatomic distance (R) of CN = 4.7 and $R = 2.00 \text{ Å}$ and CN = 6.8 and $R = 2.74 \text{ Å}$, respectively (Table 1 and Fig. S5A, ESI[†]). Assuming that the contribution of Pd–N for all samples is almost the same since the mean diameter for all samples is comparable, the ratio of the contribution of Pd–O bonds to that

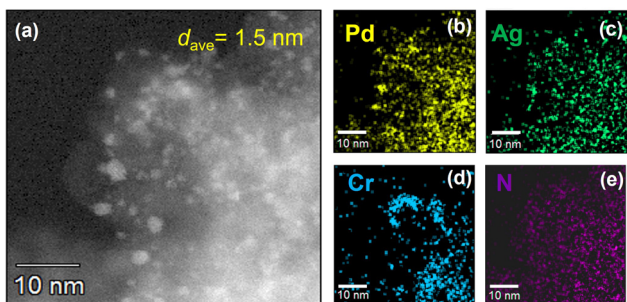


Fig. 1 (a) HAADF-STEM image of PdAgCr/amine-MSc. EDX mapping of (b) Pd, (c) Ag, (d) Cr, and (e) N over the region shown in (a).



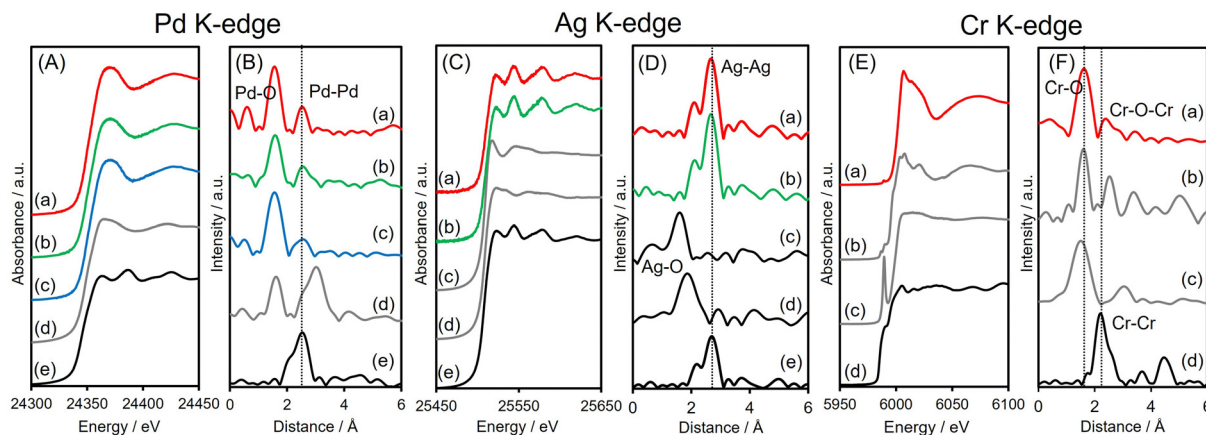


Fig. 3 (A) Pd K-edge XANES and (B) FT-EXAFS spectra of (a) PdAgCr/amine-MSC, (b) PdAg/amine-MSC, (c) Pd/amine-MSC, (d) PdO and (e) Pd foil; (C) Ag K-edge XANES and (D) FT-EXAFS spectra of (a) PdAgCr/amine-MSC, (b) PdAg/amine-MSC, (c) Ag₂O, (d) AgNO₃ and (e) Ag foil; and (E) Cr K-edge XANES and (F) FT-EXAFS spectra of (a) PdAgCr/amine-MSC, (b) Cr₂O₃, (c) CrO₃, and (d) Cr foil.

Table 1 Curve fitting results determined by Pd, Ag, and Cr K-edge FT-EXAFS data

	K-edge	Shell	CN	$R/\text{Å}$	σ^2
PdAgCr/amine-MSC	Pd	Pd-O(N)	4.7	2.00	0.0067
		Pd-Pd	6.8	2.74	0.0065
	Ag	Ag-Ag	11.3	2.89	0.0077
	Cr	Cr-O	4.6	2.01	0.0032
PdAg/amine-MSC	Pd	Pd-O(N)	4.8	2.02	0.0089
		Pd-Pd	9.3	2.76	0.015
	Ag	Ag-Ag	11.3	2.82	0.0073
Pd/amine-MSC	Pd	Pd-O(N)	5.0	2.01	0.0078
		Pd-Pd	9.6	2.73	0.015

of Pd-Pd bonds ($CN_{\text{Pd-O}}/CN_{\text{Pd-Pd}} = 0.69$) in the case of PdAgCr/amine-MSC was larger than those for PdAg/amine-MSC (0.52) and Pd/amine-MSC (0.52) (Table 1). These results are in good agreement with the Pd 3d XPS data and suggest that the Pd was partially oxidized following modification with CrO_x and/or Cr(OH)₃.

The Ag K-edge XANES spectra obtained from PdAgCr/amine-MSC and PdAg/amine-MSC were similar to that of Ag foil and their FT-EXAFS spectra showed a single intense peak ascribed to contiguous Ag-Ag bonds at approximately 2.6–2.8 Å without any noticeable evidence of Ag-O bonds (Fig. 3C and D). This peak is shifted to a slightly shorter interatomic distance compared with that for pure Ag foil, indicating the presence of Pd-Ag bonds. The inverse FT was well fitted using Ag-Ag shells with CN = 11.3 and $R = 2.89$ Å for PdAgCr/amine-MSC, and CN = 11.3 and $R = 2.82$ Å for PdAg/amine-MSC, indicating that Ag formed metallic NPs in both samples (Table 1 and Fig. S5B, ESI†). These results are in agreement with the Ag 3d XPS data.

The Cr K-edge XANES spectrum of CrO₃ displayed an intense pre-edge peak at 5992 eV which is characteristic of terminal Cr⁶⁺=O bonds in a tetrahedral coordination (Fig. 3E).^{44,45} The XANES spectrum obtained for PdAgCr/amine-MSC was different from that for CrO₃ but resembled that for Cr₂O₃, which

contains Cr³⁺. The edge energy for PdAgCr/amine-MSC was higher than that for Cr foil, confirming that the Cr in this sample was in the +3 oxidation state. The length of the first Cr-O bond in PdAgCr/amine-MSC as determined from its FT-EXAFS spectrum was comparable to that in Cr₂O₃ but longer than that in CrO₃. These data suggest the absence of Cr=O double bonds in PdAgCr/amine-MSC (Fig. 3F). A curve-fitting analysis also confirmed that the interatomic distance for the first Cr-O bond was 2.01 Å, in conjunction with a CN of 4.6 (Table 1 and Fig. S5C, ESI†). Moreover, the intensity of the peak associated with the second coordination sphere for PdAgCr/amine-MSC was significantly weaker than the intensity obtained for Cr₂O₃. In the case of the PdAgCr specimen, this peak was attributable to contiguous Cr-O-M (M: Cr or Pd) bonds because of the absence of evidence for Ag-O bonds in the Ag K-edge FT-EXAFS spectrum. The reduced intensity in this region was ascribed to the formation of small, structurally disordered nanoclusters. No evidence for metallic bonds, which were detectable at approximately 2.3 Å in the case of Cr foil, was observed. Because the reduction potentials for Cr³⁺ ions ($E^\circ(\text{Cr}^{3+}/\text{Cr}^{2+}) = -0.42$ V, $E^\circ(\text{Cr}^{2+}/\text{Cr}^0) = -0.90$ V vs. NHE) are more negative than those for Pd²⁺ and Ag⁺ ions ($E^\circ(\text{Pd}^{2+}/\text{Pt}^0) = +0.99$ V, $E^\circ(\text{Ag}^+/\text{Ag}^0) = +0.80$ V vs. NHE), the reduction of Cr³⁺ ions was inhibited to a greater extent than for Pd²⁺ and Ag⁺ ions, and Cr ions preferentially constitute extremely small clusters.

Based on these data, a reasonable structural model for PdAgCr/amine-MSC was devised. In this model, Ag atoms are preferentially located in the core regions of the NPs, while Pd atoms tend to be situated in the shells. In addition, the amorphous CrO_x phase including Cr(OH)₃ is partially located on the surfaces of these Pd-rich shells as a result of the formation of Pd-O-Cr bonds, as illustrated in Scheme 1. This configuration is based on the EXAFS analysis showing that the Pd atoms in PdAgCr/amine-MSC were partially oxidized, either because of the interaction with Cr atoms or the coordination with N atoms in the surface amine groups by the exposure to the surface.



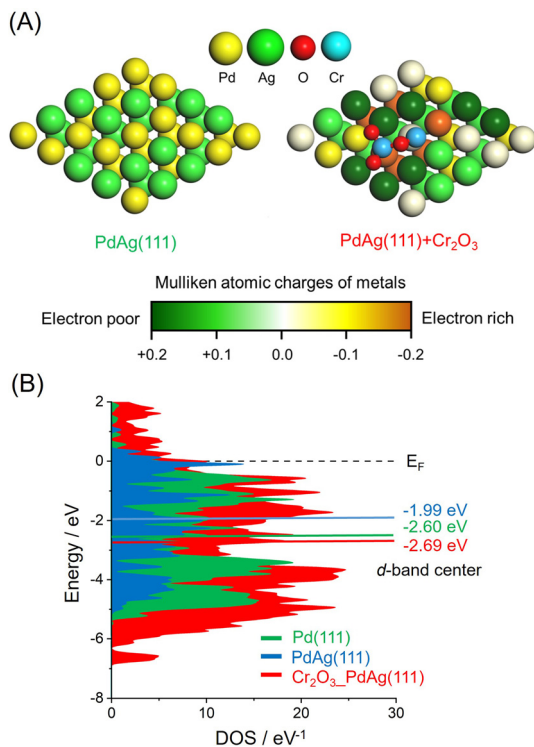


Fig. 4 (A) The optimized structure of pristine PdAg(111) and PdAg(111) associated with one stoichiometric Cr₂O₃ cluster with a color overlay of representative Mulliken atomic charge determined using density functional theory calculations. (B) Calculated DOS plots.

The effect of the CrO_x phase on the electronic state of the Pd and Ag atoms was assessed by calculating atomic charges using DFT. These calculations were based on supercell slab models consisting of 5 × 5 surface unit cells including PdAg(111) interacting with Cr₂O₃ clusters together with pristine PdAg(111). The optimized structures are shown in Fig. 4A, in which the colors of Pd atoms indicate the calculated Mulliken atomic charges. These investigations indicated that the integration of Pd with Ag induced charge transfer from Ag atoms to Pd atoms to produce electron-rich Pd^{δ-} and electron-deficient Ag^{δ+}. In addition, Pd atoms in the vicinity of the Cr atoms in Cr₂O₃ were determined to have a large negative charge as a consequence of electron transfer from the Cr atoms. In contrast, Ag atoms bound to the O atoms of Cr₂O₃ were highly positive, suggesting electron transfer from the Ag atoms to the O atoms. These electronic interactions generated unique ensemble sites and a significant electronic gap based on the adjacent electron-deficient Ag^{δ+} and electron-rich Pd^{δ-}. Density of states (DOS) calculations showed that the d-band center of PdAg(111) associated with Cr₂O₃ was located at -2.69 eV and so had a similar energy to that of -2.60 eV for PdAg(111). However, this value was more negative than that of -1.99 eV for Pd(111) (Fig. 4B). These findings confirmed that modification with CrO_x did not change the electronic structure of the catalyst in the bulk but rather caused uneven charge distribution on the surface of the material.

2.2. Catalytic activity during FA dehydrogenation

Dehydrogenation of FA was conducted in an aqueous solution containing HCOOH and HCOONa at a molar ratio of 9/1. No induction period was observed during periodic monitoring of the reaction (Fig. 5A), and H₂ and CO₂ were generated in a molar ratio of almost 1, indicating complete dehydrogenation of the FA. PdAgCr/amine-MSC displayed the highest activity among the various catalysts and exhibited substantially higher performance than the monometallic Pd and binary PdAg materials.⁴⁶ Using the optimal FA concentration (Fig. S6, ESI[†]), a turnover frequency (TOF) of 6898 h⁻¹ (based on the mass of Pd employed) was achieved, which was 1.6 times larger than the value for the PdAg catalyst. The catalytic activity attained by PdAgCr/MSC without amine modification was quite low, confirming that the amine functional group plays a crucial role in determining the elementary steps in the catalytic dehydrogenation of FA, especially in the O–H bond dissociation step, as discussed elsewhere.^{29,31,46} In addition, the reaction essentially did not occur when using pure Ag or Cr. The addition of Mn, Ni or Co was found to slightly increase the catalytic activity, while the presence of Fe, Zn, Ga or Cu reduced the dehydrogenation performance (Fig. 5B). These results indicate that a significant synergistic effect was obtained from the ternary NPs. The effect of the composition of the PdAgCr catalyst was investigated by simply varying the initial molar ratio of the metal precursors. Fig. 5C shows the effect of the Cr mole fraction relative to the combined moles of Pd and Ag on the Pd-based TOF and indicates that the activity was maximized at a Cr mole fraction of 0.5. This volcano type activity relationship verified that the unusual synergistic effect observed in the present work originated from the combination of the three metals and also



Fig. 5 (A) Time course of the reaction in the dehydrogenation of FA using various amine-MSC supported catalysts. (B) Effect of the addition of third metals to the Pd-based catalysts. (C) TOF versus mole fraction of Cr for the PdAg/amine-MSC catalyst. (D) Arrhenius plots in the dehydrogenation of FA.



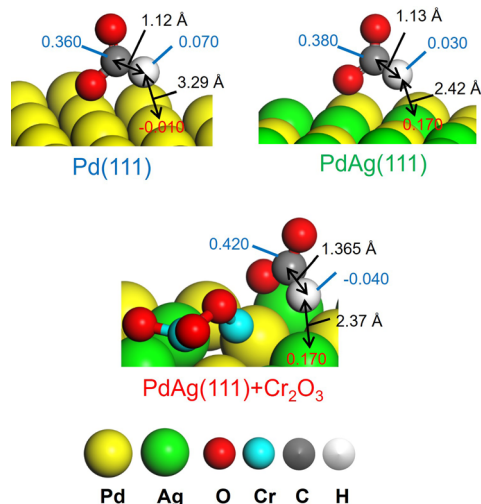


Fig. 7 Representative Mulliken atomic charges as determined by DFT calculations in reaction intermediate III for Pd(111), PdAg(111), and PdAg(111) associated with the Cr_2O_3 cluster.

that the formation rate for HD increased in the order of monometallic Pd < binary PdAg < ternary PdAgCr (Fig. S12, ESI[†]), in agreement with the lower reaction barriers for the H_2 desorption step calculated using DFT (Table 2). It has been suggested that the energy of an adsorbed atom is related to the intrinsic electronic properties of the metallic particles on the catalyst. Specifically, a greater downward shift of the d-band center from the Fermi level of a metal increases the possibility that anti-bonding states will be formed, leading to weaker binding of the adsorbed atom.⁶⁰ Thus, the binary PdAg catalyst exhibited a lower activation energy for H_2 desorption than the monometallic Pd catalyst because the d-band center of PdAg(111) is deeper than that of Pd(111) (Fig. 4B). The participation of multiple interactions induced by the modification with CrO_x in this process was also apparent. The dissociated hydride species at electron-rich $\text{Pd}^{\delta-}$ sites were determined to be negatively charged, while those at electron-deficient $\text{Ag}^{\delta+}$ sites were found to be positive. These hydrides having different charges generated at sites provided by CrO_x modification are believed to have increased the production of hydrogen molecules.

3. Conclusions

This work increased the activity of a binary PdAg catalyst during dehydrogenation of FA based on interfacial modification with a highly dispersed amorphous CrO_x phase. The combined effects of the weakly basic amine groups on the material surface and the synergistic catalysis provided by PdAgCr NPs explain the improved activity of this catalyst. The basic amine groups on the surface of the support promoted the dissociation of O–H bonds in FA molecules, while the CrO_x phase enhanced the rate-determining C–H bond dissociation step of the metal-formate intermediate as well as the H_2 desorption step. These effects resulted from the formation of unique ensemble sites

involving adjacent electron-deficient $\text{Ag}^{\delta+}$ and electron-rich $\text{Pd}^{\delta-}$ atoms. These findings provide vital information that will assist in the future design of catalytically active centers for dehydrogenation of FA. They also emphasize the importance of interface design for further improvement of catalytic performance as a means of realizing environmentally-friendly hydrogen release systems.

4. Experimental section

4.1. Materials

Acetone, nitric acid (HNO_3), *p*-phenylenediamine, AgNO_3 , $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, sodium hydroxide (NaOH), sodium borohydride (NaBH_4), formic acid (FA) and sodium formate (SF) were purchased from Nakalai Tesque, Inc. Pd(II) nitrate solution was obtained from Wako Pure Chemical Ind. Co., Ltd. Mesoporous carbon (MSC, average pore diameter: $100 \pm 10 \text{ \AA}$) was obtained from Aldrich Chemical Co. All commercially available compounds were used as received. Distilled water was employed as the reaction solvent.

4.2. Synthesis of amine functionalized MSC (amine-MSC)

The detailed procedure is described elsewhere.⁴⁶ Briefly, the MSC (1.0 g) was mixed with aqueous nitric acid solution (60%, 50 mL) at $80 \text{ }^\circ\text{C}$ for 5 h. The sample was collected by filtration, washed with distilled water, and dried under vacuum overnight. The acid treated MSC (1.0 g) was added into 500 mL of distilled water and sonicated for 2 h. The aqueous dispersion solution was mixed with acetone (50 mL) containing *p*-phenylenediamine (PDA, 3.24 g) and stirred at room temperature for 48 h. The resultant sample was separated by filtration and washed with acetone and distilled water until no color was confirmed in the filtrate, followed by drying under vacuum overnight.

4.3. Synthesis of the PdAgCr supported amine-MSC catalyst (PdAgCr/amine-MSC)

The amine-MSC (0.3 g) was mixed with an aqueous solution (80 mL) containing $\text{Pd}(\text{NO}_3)_2$ (0.606 mL, Pd 47 mM), AgNO_3 (2.85 mL, 10 mM), and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1.425 mL, 10 mM). After mixing, NaOH aqueous solution (4.2 mL, 1M) was added to adjust the pH around 10 and stirred for 30 min. Subsequently, the sample was reduced by NaBH_4 under an Ar atmosphere, collected by filtration, and dried under vacuum overnight, giving PdAgCr/amine-MSC (Pd 1 wt%, Pd:Ag:Cr = 1:1:0.5). Monometallic Pd, binary PdAg, and ternary PdAgM (M = Mn, Co, Ga, Ni, Zn, Fe, and Cu) supported on amine-MSC catalysts were also prepared by the same method. Metal loadings were determined using inductively coupled plasma (ICP) analysis.

4.4. Characterization

Powder XRD patterns, BET surface area, ICM-ES, XPS spectra, and TEM images were acquired according to the procedure described previously.⁴⁶ Quantification of the loading amount of amine functionality in samples was performed by two methods.



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