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PdAg-CeO₂ nanocomposite anchored on mesoporous carbon: Highly efficient catalyst for hydrogen production from formic acid at room temperature

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Efficient and selective dehydrogenation of formic acid by a robust solid catalyst at room temperature is highly attractive for a fuel-cell-based hydrogen economy but still very challenging. Although great progress has been achieved in the development of heterogeneous catalysts, their catalytic performance remains inadequate. Here, we report a facile and surfactant-free method for the anchoring of PdAg-CeO₂ nanocomposite (3.6 nm in diameter) on mesoporous carbon (denoted as PdAg-CeO₂/MC). The optimized PdAg-CeO₂/MC catalyst exhibit exceedingly high catalytic activity (turnover frequency, 2272.8 h⁻¹ at 303 K and 5275.5 h⁻¹ at 333 K) with a 100% hydrogen selectivity, among the highest catalytic performance ever reported for all heterogeneous catalysts for formic acid dehydrogenation. Systematic studies implicated that strong synergistic interaction between PdAg-CeO₂ nanocomposites and MC host was realized due to the consist of amorphous CeO₂ with abundant oxygen vacancy for coordinations. The excellent catalytic results provide more possibilities for the effective application of formic acid as a promising hydrogen storage material.

Introduction

Due to the benefits of high energy capacity and efficiency without the environmental damage, hydrogen is generally considered as a promising energy carrier for satisfying the ever-increasing demand for clean and sustainable energy supply.¹⁻³ Storing hydrogen safely and efficiently is one of the most important issues for the emerging hydrogen-based economy but full of challenging.⁴⁻⁶ Liquid hydrogen storage materials have attracted considerable attention due to their convenience in recharge and transport.⁷⁻¹⁰ Formic acid (FA, HCOOH), a common liquid biomass product and contains gravimetric and volumetric H₂ capacities of 4.4 wt% and 53.4 g/L, respectively, can be recognized as a nontoxic and inexpensive liquid hydrogen storage material for fuel cell, specially designed for portable use. $^{\rm 11-15}$ FA can be catalytically decomposed to H₂ and CO₂ through dehydrogenation (Eq. 1) or CO and H₂O by dehydration (Eq. 2), which is largely dependent on the catalysts used and catalytic conditions.¹⁶⁻²⁰ Recently, selective dehydrogenation of FA for H₂ generation has been achieved via homogeneous catalysts with high activity.²¹ Nevertheless, the recycling of homogeneous catalysts requires the use of special additive and organic solvents and may restrict their practical application. Accordingly, heterogeneous catalysts, which can be easily recycled from reaction solutions, could effectively circumvent these problems. However, ideal heterogeneous catalysts

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with promising catalytic performance for FA dehydrogenation under ambient conditions is still urgently required.²²

$$\begin{array}{l} \mathsf{HCOOH}(\mathsf{I}) \rightarrow \mathsf{H}_2(\mathsf{g}) + \mathsf{CO}_2(\mathsf{g}) & (1) \\ \mathsf{HCOOH}(\mathsf{I}) \rightarrow \mathsf{H}_2\mathsf{O}(\mathsf{I}) + \mathsf{CO}(\mathsf{g}) & (2) \end{array}$$

FA dehydration is favored on acidic oxides while the FA dehydrogenation is preferred on basic metal oxides.^{23,24} As a typical basic metallic oxide, ceria (CeO₂) has attracted much attention as catalyst host for different catalytic processes, such as CO oxidation,²⁵ water-gas shift reactions,²⁶ as well as dehydrogenation reactions.²⁷ The catalytic performance improved by metal/CeO₂ is often assigned to interface properties optimization by the strong coordination between metal and CeO_2 host.²⁸⁻³⁰ However, the relatively low surface area of the CeO₂ host might limit the catalytic activity due to the poor mass transfer efficiency. To this end, mesoporous carbon (MC) materials with high surface area and pore structures would be an ideal candidate to stabilize active nanoparticles and improve the mass transfer processes.^{31,32} Based on the above consideration, PdAg alloy nanoparticles,^{22,33-37} one of the most active catalysts for FA dehydrogenation, modified by CeO₂ and supported on MC would be an effective way to realize optimized interface properties and mass transfer efficiency simultaneously.

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Herein, we report a facile and surfactant-free method for prepare the amorphous CeO₂-modified PdAg alloy nanocomposites on mesoporous carbon (PdAg-CeO₂/MC) as a highly active catalyst for FA dehydrogenation. The PdAg-CeO₂ nanocomposites with a mean size of 3.6 nm were highly dispersed and well stabilized by the MC host. Further study indicates that the abundant and strong coordination sites provided by the small amount of amorphous CeO₂ would strongly improve the synergistic effect between MC and PdAg. As a result, the representative PdAg-CeO₂/MC catalyst exhibited exceedingly high activity for FA dehydrogenation with 100% hydrogen selectivity and high turnover frequency (TOF) value up to of 2272.8 h⁻¹ at 303 K and 5275.5 h⁻¹ at 333 K, respectively, which are among the state-of-art values ever reported for all heterogeneous catalysts.

Experimental

Materials

All chemicals were commercially available and used without need any further purification. Carbon powder (C, Strem Chemicals, 99+%), sodium borohydride (NaBH₄, J&KCHEMICAL[®], 98%), cerium (III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O, J&KCHEMICAL[®], 99.5%), formic acid (FA, HCOOH, Aladdin, 99%), sodium formate (SF, HCOONa, J&KCHEMICAL[®], 99%), hexadecyltrimethylammonium bromide-aided (CTAB, CH₃(CH₂)₁₅N(Br)(CH₃)₃, Fluka, \geq 96.0%), silver nitrate (AgNO₃, Xiya Reagent[®], 99%), and sodium tetrachloropalladate (Na₂PdCl₄, Aladdin, 98%) were used as obtained. We use ordinary distilled water as the reaction solvent.

Synthesis of catalysts

The PdAg-CeO2/MC catalysts were facilely synthesized via a surfactant-free co-reduction of well-dispersed carbon and the metal precursors using NaBH₄ as a reducing agent. Typically, 10 mg of carbon powder was dispersed in 3 mL H₂O and under sonicated at hot water for 1 h to fully exfoliate the carbon. Then, Na₂PdCl₄ (0.080 mmol), AgNO₃ (0.020 mmol), and Ce(NO₃)₃·6H₂O (0.025 mmol) were dissolved in the above suspension. After rapid magnetic stirred for 3 h, NaBH₄ (0.5 M, 2 mL) was quickly added and keep stirring for another 1 h, resulting in the generation of Pd_{0.8}Ag_{0.2}-CeO₂/MC catalyst as a black suspension. The catalyst was collected by centrifugation and washed by distilled water for three times. The monometallic Ag- and Pd-CeO2/MC were synthesized by changing the type of metal precursors. The PdAg-CeO2/MC with various bimetallic compositions (Pd_{0.9}Ag_{0.1}, Pd_{0.7}Ag_{0.3}, Pd_{0.4}Ag_{0.4}, and Pd_{0.5}Ag_{0.5}) were synthesized by adjusting the initial molar ratio of Pd and Ag precursors. The $Pd_{0.8}Ag_{0.2}$ -CeO₂/MC catalyst with different compositions of CeO₂ and carbon were also synthesized by changing the initial amounts of $Ce(NO_3)_3 \cdot 6H_2O$ and carbon. Besides, the referenced $Pd_{0.8}Ag_{0.2}/MC$ catalyst was synthesized without use Ce(NO₃)₃·6H₂O as metal precursors. The Pd_{0.8}Ag_{0.2} and Pd_{0.8}Ag_{0.2}-CeO₂ catalysts without carbon support were synthesized via a similar co-reduction method with the introduction of CTAB.

Characterization

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku RINT-2200 X-ray diffractometer using Cu-K α radiation at 40 kV and 40 mA. Raman spectra were analyzed on a confocal Raman

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microscope (LabRAM HR). N₂ adsorption/desorption isotherms at liquid nitrogen temperature (77 K) after degassing under vacuum at 180 °C for 8 h were measured by using BELSORP-mini II. The morphologies, as well as compositions of the samples, were determined by using a transmission electron microscope (TEM, Tecnai G2 F20) equipped with an energy dispersed X-ray detector (EDX) for elemental analysis. One or two droplets of the synthesized catalyst suspension were deposited on a carbon-coated copper grid for the TEM characterization. X-ray photoelectron spectra (XPS) were measured by a Thermo scientific ESCALAB 250 multifunctional imaging electron spectrometer calibrated by C_{1s} at 284.6 eV. Inductively coupled plasma atomic emission spectroscopic (ICP-AES, 725-ES, and Agilent 720ES) was adopted to detect the detail components of the samples. Fourier-transform infrared spectroscopy (FTIR) analysis of the samples was obtained by a Thermo Nicolet 870 instrument. The evolved gas from FA decomposition was analyzed by gas chromatography (Shimadzu, GC2014C) with thermal conductivity detector (TCD) and flame ionization detector (FID)-Methanator.

Catalytic decomposition of formic acid

The catalytic activity of all the synthesized catalysts toward dehydrogenation of FA for H_2 evolution was tested on a water-filled graduated burette system. In general, a two-necked round-bottomed flask reactor (25 mL) contains a mixture of as-synthesized catalyst and distilled water (6 mL) was placed in a water bath at a certain temperature (303-353 K) under ambient atmosphere. The released gas was measured by an exactly scaled gas burette filled with water and connected with the reaction flask. Before the catalytic reaction, SF was dissolved in the above solution. The catalytic reaction is started by the injection of FA (0.11 mL) into the above catalyst suspension. For comparison, all the catalytic reactions were performed with a fixed molar ratio of PdAg/FA (0.033). The volume of generated gas was measured through the gas burette and monitored by recording the volume of displaced water in the gas burette.

Reusability test

The reusability of the $Pd_{0.8}Ag_{0.2}$ -CeO₂/MC catalyst was tested. Typically, the catalyst was recollected via centrifugation and washed with distilled H₂O for three times after the first cycle of the catalytic reaction was completed. Then, the catalyst was reused for the same catalytic reactions. The reactions were repeated for five runs under the same conditions as the first cycle. Then, the catalyst was

Results and Discussion

around 3.6 nm are highly dispersed on the MC. The improvements structure is observed from the typical TEM images of the original MC (Fig. S1). The high-resolution TEM image shows that the metallic nanoclusters display a crystal lattice space of d = 0.238 nm (Fig. 1b), which is assigned to PdAg alloy nanostructure. Amorphous species

Fig. 1. (a) TEM (inset: the corresponding SAED image and particle size histogram); (b) HRTEM; (d) HADDF-STEM; and (e) the corresponding elemental mapping images of the optimized PdAg-CeO₂/MC catalyst. TEM (inset: the corresponding SAED image and particle size histogram) of the reference catalysts: (c) PdAg/MC; and (f) PdAg-CeO₂.

The novel PdAg-CeO₂/MC catalysts were synthesized via a facile and surfactant-free co-reduction process (Scheme 1), i.e. directly reducing the metal precursor salts, typically Na₂PdCl₄, AgNO₃, and Ce(NO₃)₃·6H₂O of various molar ratio, in an aqueous solution contains a well-dispersed catalyst host, MC, at room temperature. During magnetic stirring process, metal ions can be adsorbed on the defects of MC due to its high surface area and hydrophilic properties. After adding of NaBH₄ into the solution, the amorphous CeO₂ and PdAg alloy formed simultaneously and served as the in situ seeds for the growth of PdAg-CeO₂ nanocomposites on MC. Here, NaBH₄ was utilized as a reducing agent for the formation of PdAg alloy nanoparticles, and the hydrolysate (NaB(OH)₄) of NaBH₄ provide an alkaline environment for the in-situ formation of CeO₂.³⁰ Finally, a very small amount of the boron ions might react with the metallic alloy to form metal-B species (vide infra).^{38,39}

The synthesized catalysts were collected by centrifugation, washed by water and dried in a vacuum oven for further characterization experiments. The microstructures and compositions of the PdAg-CeO₂/MC catalyst were determined by TEM measurements. As can be seen from the TEM and high angle annular dark-field scanning TEM (HAADF-STEM) images of PdAg-CeO₂/MC catalyst (Fig. 1a, b, and d), the metallic nanoclusters with size of

can be observed in the area adjacent to the crystal. HAADF-STEM image (Fig. 1d) shows that the surface amorphous species has a relatively low contrast as compared to that of the PdAg alloy particles. To determine their detail compositions, elemental mapping of the selected region from the green square in Fig. 1d was analyzed. As Fig. 1e shows, the entire catalyst surface is composed of carbon and boron (Fig. 1e). Most of the boron species are oxidized boron deposited on the surface of mesoporous carbon which can be removed during the catalytic and wash process, while only a small amount of metal-boron species (<0.1 wt%) was formed in the catalyst (vide infra). The Pd and Ag elements are strictly distributed in the regions where the two metallic particles are located, while the distribution and location of Ce ions are well-matched with the regions with low contrast on the surface of PdAg nanoparticles, thus implying the amorphous species is CeO₂. The EDX spectrum confirms the existence of Pd, Ag, Ce, O and B elements in the PdAg-CeO₂/MC catalyst (Fig. S2). The atomic ratio for Pd:Ag:Ce was further determined by ICP-AES analysis (Table S1), and the values are quite close to the concentrations of initial metal precursors. The growth of CeO₂ on the surface of PdAg alloy nanoclusters did not influence the particle size and distribution of PdAg nanoparticles on MC host. (Fig. 1a and c). The PdAg-CeO₂ nanocomposites synthesized without the

MC, however, were aggregated to larger clusters (Fig. 1f). Therefore, the MC host plays an important role in controlling the particle size and distribution of PdAg-CeO₂ nanocomposites. As determined by the corresponding selected area electron diffraction (SAED) images, the CeO₂-free sample (PdAg/MC) exhibits strong and bright crystal diffraction rings and spots, while the CeO₂ doped samples (PdAgPdAg/MC), further confirms the low crystallinity property of PdAg by the modification of amorphous CeO₂.

In the Raman spectrum (Fig. 2b), the peaks centered at 1334 and 1587 cm⁻¹ are attributed to the characteristic D- and G-band of carbonaceous materials. The D-band represents the vibration modes of carbon rings close to defects or edges. Thus, the higher intensity



Fig. 2. (a) Powder XRD patterns of the obtained MC, Pd-CeO₂/MC, PdAg, PdAg/MC, PdAg-CeO₂, PdAg-CeO₂/MC and Pd-CeO₂/MC catalysts; (b) Raman spectrum of the MC and PdAg-CeO₂/MC catalyst; (c) N₂ sorption isotherms and (d) the corresponding pore size distribution curves of the MC and PdAg-CeO₂/MC catalyst; (e) Structural illumination of the obtained PdAg-CeO₂/MC.

CeO₂/MC and PdAg-CeO₂) only exhibit weak and broad diffraction rings (Fig.1a and f), thus implying the amorphous CeO₂ modifier would effectively decrease the crystallinity of PdAg alloy nanoparticle (NPs). Due to the consists of abundant surface distortions and oxygen vacancies in the amorphous CeO₂,⁴⁰ the PdAg atoms can strongly bind with these defect sites and therefore disturb their long-range order by the ligand and strain effect around these sites.

The XRD patterns of all the synthesized catalysts and the MC host are shown in Fig. 2a. The original MC has a broad and weak peak at approximately $2\theta = 24^{\circ}$, which is associated with amorphous carbon.³¹ The characteristic diffraction peaks observed from the monometallic Ag- and Pd-CeO₂/MC reference samples are assigned to the (111), (200) and (220) face of metal Ag (PDF#65-8428) and Pd (PDF#65-6174), respectively. All the bimetallic samples exhibit crystalline peaks centered between the diffraction peaks of Ag and Pd, thus further confirms the formation of PdAg alloy nanostructure. The cerium component was not detected in all the CeO₂-modified samples due to the amorphous state as verified by TEM images (Fig. 1b and f). In particular, the diffraction peaks of PdAg alloy for the CeO₂-modified samples (PdAg-CeO₂ and PdAg-CeO₂/MC) are weak and broad as compared to the CeO₂-free samples (PdAg and of D band of both MC and PdAg-CeO₂/MC indicates the high degree of disorder or high concentration of defect sites.⁴¹ The abundant surface defects can effectively stabilize the PdAg-CeO₂ nanocomposites as revealed by TEM results (Fig. 1). Besides the carbon signatures (D and G band), a new band at around 446 cm⁻¹ was detected for the PdAg-CeO₂/MC sample, which is originated from CeO₂.⁴² The band value of the amorphous CeO₂ is shifted to lower energy than that of the typical first-order F2g peak of CeO₂ (464 cm⁻¹), suggesting the existence of electron transfer from MC host to the CeO₂ dopant.⁴² Owing to the consist of abundant coordination sits in the amorphous CeO₂, it can strongly coordinate with PdAg alloy NPs and the defects of MC to form intimate interfaces between them as observed from the HRTEM image (Fig.1 c). Such intimate interfaces might further contribute to the electronic interaction between the MC host and PdAg alloy NPs.

Both MC and PdAg-CeO₂/MC exhibit combined type I and type IV N_2 sorption isotherms with parallel and horizontal branch loops of H4-type (Fig. 2c), indicating that they possess similar well-developed small pores with open slit-shaped pore structure. The pore size distribution curve (Fig. 2d) further demonstrated that the MC and PdAg-CeO₂/MC catalyst both contain pores with similar pore sizes of approximately 1.1 and 4.0 nm. The surface area (486 m²/g) and pore

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volume (0.48 cm³/g) of the PdAg-CeO₂/MC catalyst are lower than that of the MC (1651 m²/g and 1.26 cm³/g), revealing that a part of the defects or pores were occupied by the PdAg-CeO₂ nanocomposites as shown in the schematic diagram (Fig. 2e). This PdAg-CeO₂/MC catalyst with high surface area and abundant mesopores are typically beneficial for mass transfer processes, which can largely increase the reaction dynamics.



Fig.3. XPS spectrum of (a) Pd 3d, (b) Ag 3d for the synthesized PdAg-CeO₂/MC, PdAg/MC, and PdAg-CeO₂ catalysts. XPS spectrum of (c) Ce 3d, and (d) O 1s of the synthesized PdAg-CeO₂/MC catalyst.

Surface compositions and electronic valance states of the catalysts were determined by XPS analyses (Fig. 3). The XPS survey spectrum shows the co-existence of Pd, Ag, Ce, C, O and B in PdAg-CeO2/MC (Fig. S3), and their atomic contents calculated according to the XPS peak areas are 7.40, 2.70, 7.48, 19.03, 50.99 and 12.41 At.%, respectively. Peaks with binding energies (BEs) of 335.7 and 340.8 eV for Pd 3d_{5/2} and 3d_{3/2} of PdAg-CeO₂/MC, respectively (Fig. 3a), can be attributed to Pd⁰ state. And peaks centered at BEs of 367.9 and 373.9 eV in Ag $3d_{5/2}$ and $3d_{3/2}$ orbits, respectively, were assigned to Ag⁰ state (Fig. 3b). The XPS spectrum of PdAg-CeO₂/MC catalyst shows that there is a negative shift in BEs of Pd 3d and Ag 3d as compared to those of PdAg/MC and PdAg-CeO₂, thus implying the electron transfer from the MC host and CeO₂ to PdAg surface in the PdAg-CeO₂/MC catalyst. As the key step of the C-H bond cleavage in the FA dehydrogenation reaction can be easier catalyzed by the modulated Pd NPs with surface electron-rich properties.^{43,44} Such strong interaction will effectively optimize the surface electronic state of PdAg and improve its catalytic activity for FA dehydrogenation.^{18,45} The valance state of Ce was analyzed by XPS Ce 3d sand O 1s spectrum (Fig. 3c,d). The peaks centered at 883.1, 901.6, and 917.0 eV are attributed to Ce⁴⁺, and the peaks at 885.5 eV, 898.7 eV, and 904.2 eV are originated from Ce³⁺, indicating the existence of a mixed Ce valence state in CeO₂. The consist of Ce³⁺ ions indicates the formation of oxygen vacancies (O_V) in CeO₂ lattice, which can serve as defects to coordinate with metal atoms as well as the MC host.⁴⁶ In the XPS O 1s spectrum (Fig. 3d), the peaks centered at the BE of 532.0 and 529.9 eV are assigned to the O_V and lattice oxygen (O_L), respectively. The higher peak intensity of O_V further proves the existence of abundant surface defects in CeO₂ dopant.⁴⁷ Such a high concentration of defects in CeO₂ would highly improve the coordination with PdAg and MC, and finally, increase the electronic interaction between them. The C1s XPS spectrum (Fig. S4a) can be well-fitted with four peaks of the dominant carbon species based on the Shirley algorithm. The main peak with BE of approximately 192.3 eV in the XPS B1s spectra is assigned to oxidized boron (B-O),⁴⁸ while another peak with BE of approximately 188.9 eV was attributed to the metal-B species (Fig. S4B).^{48,49} According to XPS B 1s depth profile (Fig. S4c), ICP-AES (TableS1), and FTIR analysis result,⁵⁰ the oxidized boron species at surface can be removed during the catalytic and wash processes, while a very small amount of metal-B (<0.1 wt%) remains in the catalyst, which can be neglected in contribution of the catalytic activity.

Hydrogen generation from FA dehydrogenation over the assynthesized catalysts was evaluated based on volumetric measurements of the gases released during the reaction. Fig. 4a shows the catalytic performance of PdAg, PdAg-CeO₂, PdAg/MC and PdAg-CeO₂/MC catalysts for H₂ generation from an FA-SF mixture aqueous solution (n_{FA} : n_{SF} = 1:6, $n_{(Pd + Ag)}/n_{FA}$ =0.033) at room temperature (303 K). The PdAg alloy NPs exhibited a relative poor catalytic activity with 87 mL gas (H₂+CO₂) released in 45 min and a TOF value of 274.4 h⁻¹ (Fig. 4b). The PdAg-CeO₂ shows an improved activity with 105 mL gas (H₂ + CO₂) released in 43 min, and reach a TOF value of 322.0 h⁻¹, which is 1.18 times that of pristine PdAg (Fig. 4b). As revealed by TEM and XRD results (Fig. 1 and Fig. 2a), the crystallinity of PdAg alloy NPs can be decreased by the amorphous CeO₂ modifying, which implies that more active sites can be exposed to improve the catalytic activity. The PdAg/MC catalyst without CeO₂

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doping shows largely enhanced catalytic activity with 141 mL gas (H₂ + CO₂) generated in 18.0 min (Fig. 4a) and the corresponding TOF value is 593 h⁻¹, which is 2.16 times that of the pristine PdAg catalyst (Fig. 4b). This enhanced catalytic is typically due to the synergistic effect between MC and PdAg.⁵¹⁻⁵³ In addition, the electron transfer from MC and CeO₂ to PdAg as revealed by XPS results (Fig. 3) would effectively increase the catalytic activity for FA dehydrogenation. After introducing a small amount of CeO₂, the optimized PdAg- \mbox{CeO}_2/\mbox{MC} catalyst exhibited greatly enhanced catalytic activity for FA dehydrogenation (Fig. 4a and b). The reaction was completed in only 4.0 min with 142 mL of gas $(H_2 + CO_2)$ generated. The TOF for H_2 evolution is calculated to be 2272.8 h⁻¹, which to our knowledge, is one of the state-of-art values among all the reported heterogeneous catalysts for FA dehydrogenation at 303 K (Table S2).9,11,15,18,38,43,54-63 Interesting, the TOF value is 8.30 times that of the pristine PdAg (Fig. 4b), and much higher than that the sum of PdAg-CeO₂ (1.17 times) and PdAg/MC (2.16 times). The generated gas was only the mixture of H₂ and CO₂ according to the gas chromatography (GC) analysis results (Fig. S6 and Fig. S7), indicating the 100% H₂ selectivity of the PdAg-CeO₂/MC for FA dehydrogenation. Based on the above TEM, XRD, Raman, and XPS analysis results, the much improved catalytic activity would be contributed by the strongly increased synergistic effect between MC and PdAg via the modification of amorphous CeO₂.

The catalytic performance of PdAg-CeO2/MC catalysticformEA dehydrogenation is also influenced by the Molatoratio/6PPd/Ageas shown in Fig. 4c and Fig. S8. The monometallic Pd-CeO₂/MC catalyst exhibited 100% hydrogen conversion for FA dehydrogenation in 11.4 min with a TOF value of 852 h⁻¹, while the monometallic Ag-CeO₂/MC catalyst was almost inactive. After alloyed with a small amount of Ag, the catalytic activity of PdAg-CeO2/MC catalysts can be greatly improved. With a decrease of the Pd/Ag molar ratio from 9/1 to 8/2, the catalytic activity of the PdAg-CeO2/MC catalysts was increased with TOF from 1694.0 to 2272.8 h⁻¹, and a further decrease of Pd/Ag molar ratio from 8/2 to 5/5 resulting the decrease of activity with TOF value from 2272.8 to 681 h⁻¹. This synergistic effect between the different components of Pd and Ag is ascribed to the strain and ligand effects induced surface electronic structure and catalytic performance modification in alloy nanostructures.¹⁵ Additionally, the contents of Ce dopant and the MC host also affect the catalytic activity of the PdAg-CeO2/MC catalysts. When the PdAg-CeO2/MC catalyst with a Ce content of 25.2 wt% and a PdAg-CeO2 loading amount of 31.0 wt%, the optimized catalytic activity for FA dehydrogenation can be realized (Fig. S9 and Fig. S10).

Furthermore, dehydrogenation of FA by adding SF has been typically served as an effective strategy to increase H_2 evolution kinetics. In this study, we have thoroughly studied the effects of SF concentration on catalytic activity. Fig. 4d and Fig. S11 shows the



Fig. 4. (a) Volume of the generated gas ($H_2 + CO_2$) versus time and (b) the corresponding TOF values for FA dehydrogenation in a FA-SF solution at 303 K over PdAg, PdAg-CeO₂, PdAg/MC and PdAg-CeO₂/MC catalysts, respectively ($n_{FA}/n_{SF} = 1/6$; $n_{(Pd+Ag)}:n_{FA} = 0.033$); (c) Catalytic performance of the PdAg-CeO₂/MC catalysts with different Pd/Ag molar ratios for FA dehydrogenation at 303 K in a FA-SF solution ($n_{FA}/n_{SF} = 1/6$; $n_{(Pd+Ag)}:n_{FA} = 0.033$); (d) Catalytic performance of the optimized Pd_{0.8}Ag_{0.2}-CeO₂/MC catalyst for FA dehydrogenation at 303 K in FA-SF solutions with different FA/SF molar ratios.

catalytic performance of the optimized PdAg-CeO2/MC for FA

dehydrogenation with different FA/SF molar ratio at 303 K. Without adding SF in the system, the catalyst realized a TOF value of 431.3 h⁻ ¹ with 105 mL gas (H_2+CO_2) generated in 12.8 min. After the introduction of SF in the system, the catalytic activity was largely improved. The optimized FA/SF molar ratio was found to be 1/6 in the present conditions (Fig. 4d). The high surface area, abundant defects and mesopores provided by the MC can promote the adsorption of HCOO⁻ on the surface of the catalyst. It was reported that the adsorbed HCOO⁻ on catalyst can induce a favourable adsorption orientation of FA (H-down) on the active sites to boost the FA dehydrogenation process or act as the FA dehydrogenation intermediate.55 Therefore, a relative high SF concentration is beneficial for the FA dehydrogenation over the PdAg-CeO2/MC catalyst. The H₂ generation from a relatively high or low concentration of pure SF solution was compared with that from an FA and SF mixture solution over the same catalyst (Fig. S12). Although a slightly higher volume of H₂ generated in a high SF concentration (3 M) than in a low SF concentration (1 M), the total volume of H₂ generated from SF only accounts for a very small proportion of that from mixture solution during the recorded reaction time (4 min).



Fig. 5. The correlation between activation energy, FA/SF molar ratio and TOF value.

To understand the influence of SF concentration on the FA dehydrogenation kinetics, the experiment of temperatures depended FA dehydrogenation in different FA/SF molar ratios were carried out. Fig. S13a shows the catalytic performance of the PdAg-CeO₂/MC catalyst in FA dehydrogenation without adding SF at temperatures ranging from 303 K to 353 K. The results show that the H₂ generation rate and production are increased with the increase of reaction temperature. The $PdAg-CeO_2/MC$ catalyst exhibited the highest catalytic activity with a TOF value as high as 5244.8 h⁻¹ in the absence of SF at 353 K (Table S2). The corresponding activation energy (E_{a1}) calculated based on the Arrhenius plot fitted by H₂ release rates at different reaction temperatures is 40.2 kJ/mol (Fig. S13d). Fig. S13b shows the catalytic performance of the same catalyst with a FA/SF molar ratio of 1/3 at temperatures range from 303 K to 343 K. The rates for H₂ generation are increased with the increase of reaction temperatures and the corresponding activation energy (E_{a2}) is calculated to be 35.1 kJ/mol (Fig. S13e), which is lower than that in the case without adding additive (Fig. S13a). The catalytic activity can be further increased under all the measured temperatures after further increase the SF concentration (FA/SF molar ratio = 1/6) (Fig.

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S13c). The corresponding activation energy can be further, decreased to E_{a3} =23.9 kJ/mol (Fig. S13f), which is the lowest value among affective reported heterogeneous catalysts (Table S2). The correlation between the activation energy, FA/SF molar ratio, and TOF is summarized in Fig. 5. It is clear that the activation energy based on reaction temperature can be successfully decreased by the increase of SF concentration, and thus the kinetics for FA dehydrogenation over PdAg-CeO₂/MC catalyst can be largely improved by a relative higher SF concentration as revealed by the increased TOF values. It should be noted that the optimized SF/FA molar ratio (6/1) is relatively lower than reported catalytic systems (3/1), which might due to the abundant mesoporous structure of MC can effective adsorb of the SF molecules and thus further improve the FA dehydrogenation kinetics.

The reusability test of PdAg-CeO₂/MC catalyst for FA dehydrogenation at 303 K is shown in Fig. S14. The H₂ generation rate and production are well maintained during the test, indicating the excellent stability of PdAg-CeO₂/MC catalyst. The slightly prolonged reaction time after 5 cycles is mostly due to the loss of catalyst during the recycling process. The recovered catalyst after the reusability test was characterized by TEM (Fig. S15) and XRD (Fig. S14), showing that there is no obvious variation in the particle size, distributions, and crystal structure, further confirming the excellent stability of PdAg-CeO₂/MC catalyst for FA dehydrogenation under the present conditions.

Conclusions

In summary, a facile surfactant-free co-reduction method has been successfully applied for the synthesis of novel PdAg-CeO₂/MC catalysts with exceedingly high catalytic activity for H₂ production from FA dehydrogenation. According to TEM, XRD, Raman, and XPS results, amorphous CeO₂ modifier with abundant surface defects can strongly coordinate with PdAg and MC host, and thus create intimate interfaces between PdAg and MC to improve the electron transfer from MC and CeO₂ to PdAg alloy nanoparticles. As a result, the synthesized PdAg-CeO₂/MC catalyst exhibited exceedingly high catalytic activity for FA dehydrogenation with 100% hydrogen selectivity and TOF of 2272.8 h⁻¹ (FA/SF = 1/6) at 303 K and 5275.5 h⁻¹ (SF-free) at 333 K, respectively, which are among the highest values ever reported for all heterogeneous catalysts for FA dehydrogenation. The strategy of introducing a metal oxide modifier to improve the synergistic effect between active metallic nanoparticles and host is expected to improve the catalytic activity of other supported catalysts.

Conflicts of interest

There are no conflicts to declare.

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CeO₂-modified PdAg alloy nanocomposites are anchored on mesoporous carbon, showing exceedingly high catalytic activity for HCOOH dehydrogenation at room temperature.