

Supporting Information

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

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Calculation methods

The total turn-over frequency (TOF) reported in this work is based on the number of metal atoms (Pd + Ag) in catalysts, which is calculated from the equation as follows:

$$TOF = P_0V/(2RTn_{metal}t) \quad (\text{Eq. S1})$$

Where P_0 is the atmospheric pressure (101325 Pa), V is the volume of generated gas ($H_2 + CO_2$) at the time of half-completion of reaction, R is the universal gas constant ($8.3145 \text{ m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}$), T is the room temperature (298 K), n_{metal} is the total mole number of metal atoms (Pd+Ag) in catalyst and t is the time of half-completion of reaction in hour.

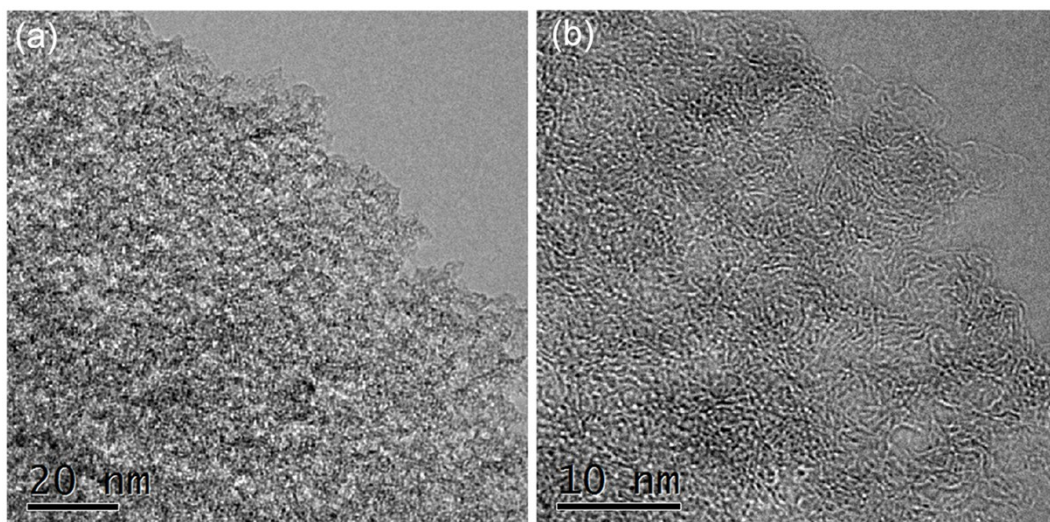


Fig. S1. Typical TEM images of the MC used for the catalysts synthesis.

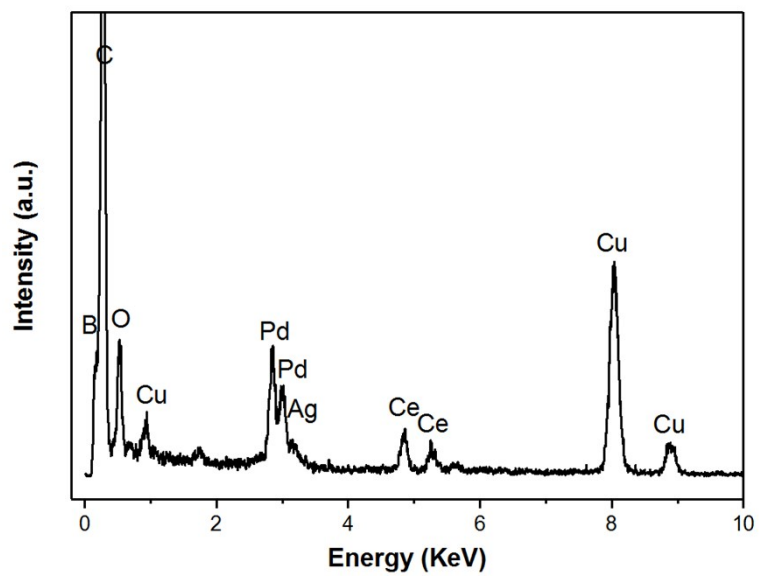


Fig. S2. The EDX spectra of the synthesized Pd_{0.8}Ag_{0.2}-CeO₂/MC catalyst.

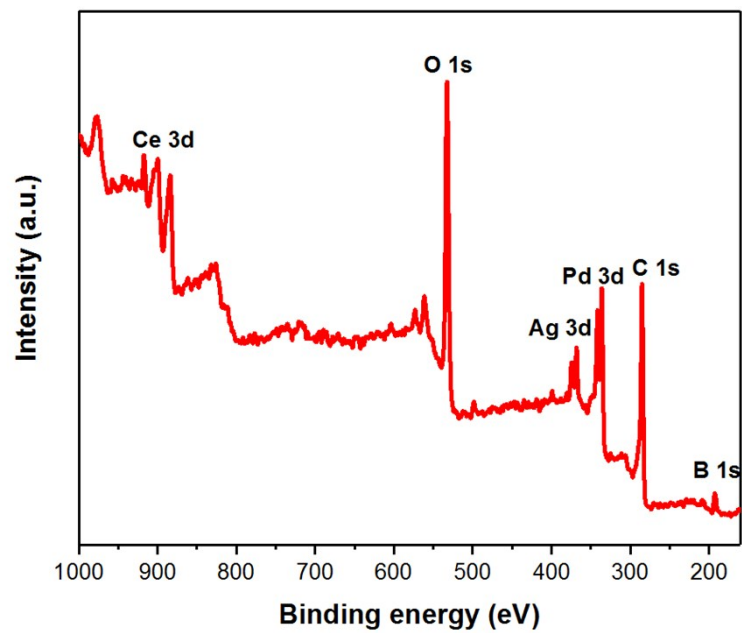


Fig. S3. XPS survey spectra of the synthesized Pd_{0.8}Ag_{0.2}-CeO₂/MC catalyst.

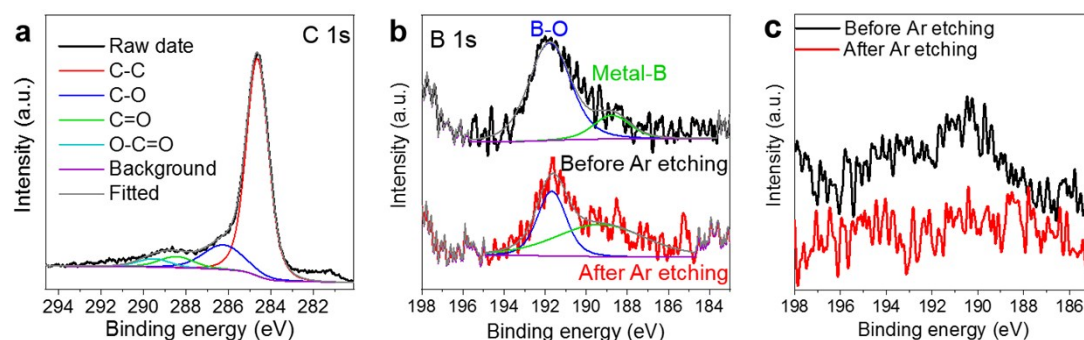


Fig. S4. XPS C 1s (a) and XPS B 1s depth profile (b) of the synthesized PdAg-CeO₂/MC. (c) XPS B 1s depth profile of MC(B) synthesized without using any metal precursors.

Boron-modified metal nanoparticle species synthesized by using NaBH₄ as a reducing agent in aqueous solution has been reported by Cai et al.³⁸ Since XPS mainly explores the surface of the material, the depth profiles obtained by Ar etching would effectively clear the surface residues and analyze the compositions inside the material. The XPS B 1s depth profiles show that the peak intensity of B-O decreases, while that of Metal-B remains unchanged after Ar etching for 50 s (Fig. S4b). The decrease of B-O concentration implies that the oxidized boron species were mostly deposits on the surface of MC (i.e. not bonded with carbon). This was further verified by the XPS B 1s depth profile of the MC(B) sample synthesized without using any metal precursors (Fig. S4c), which implies that the boron species can be effectively removed by Ar etching for the same time. According to ICP-AES result, the boron concentration of PdAg-CeO₂/MC decreased from 0.47 to 0.14 wt% after the catalytic reactions (Table S1), thus further prove that most of the boron species are oxidized boron deposits on the surface (which might be removed during catalytic and wash processes). The remaining small amount of boron should come from the metal-B (<0.1 wt% based on ICP-AES and XPS B 1s depth profile analysis) species in the catalyst.

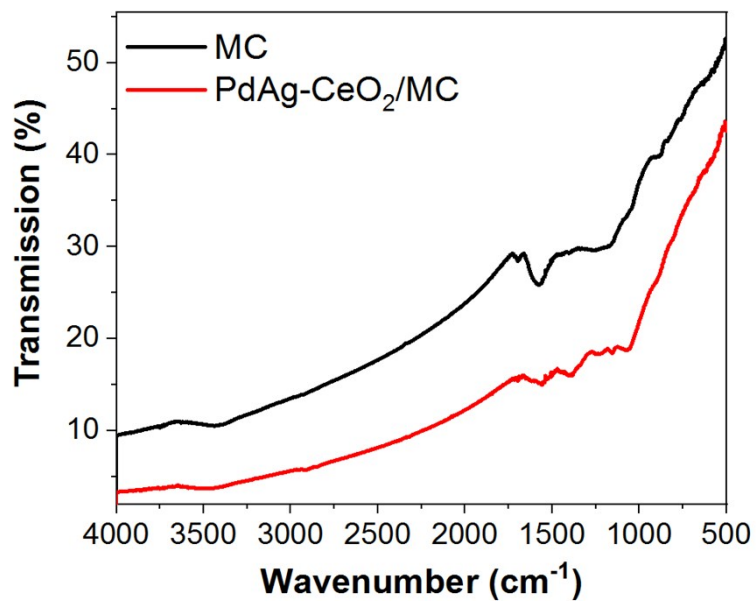


Fig. S5. FTIR spectra of the MC host and PdAg-CeO₂/MC samples.

The typical B-C stretching vibration with absorption band at around 1020 cm⁻¹ was not observed from the FTIR spectra of PdAg-CeO₂/MC,⁵⁰ again indicates the boron species might not bond with carbon.

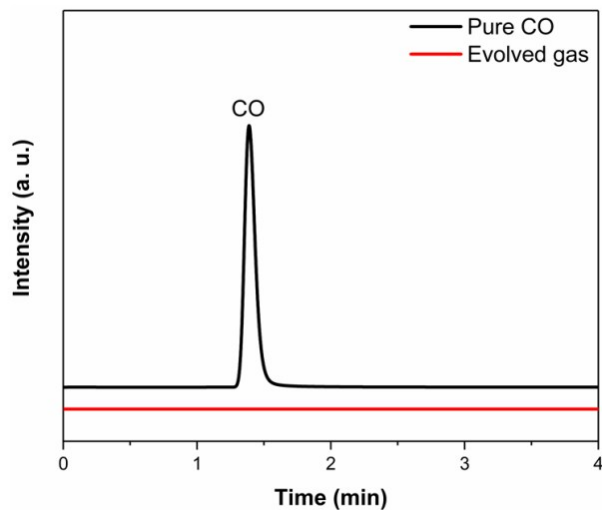


Fig. S6. GC spectrum using FID-Methanator for the commercial obtained pure CO gas and evolved gas from FA/SF aqueous solution over the optimized PdAg-CeO₂/MC catalyst ($n_{\text{FA}}:n_{\text{SF}} = 1:6$; $n_{(\text{Pd+Ag})}:n_{\text{FA}} = 0.033$).

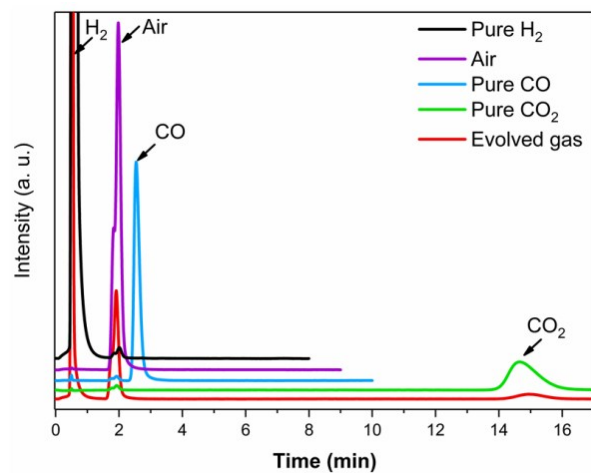


Fig. S7. GC spectrum using TCD for the commercial obtained pure H₂, Air, CO, CO₂ gas and evolved gas from FA/SF aqueous solution over the optimized PdAg-CeO₂/MC catalyst ($n_{\text{FA}}:n_{\text{SF}} = 1:6$; $n_{(\text{Pd}+\text{Ag})}:n_{\text{FA}} = 0.033$).

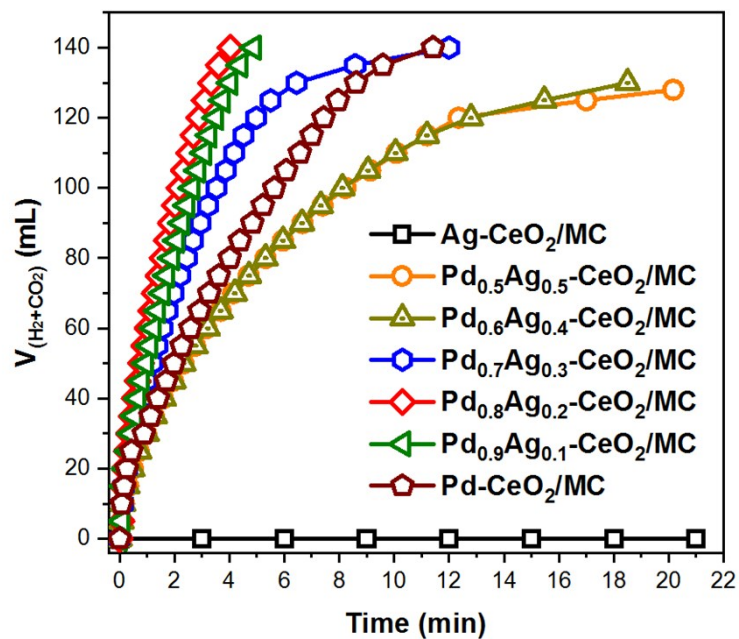


Fig. S8. Volume of the generated gas ($\text{H}_2 + \text{CO}_2$) versus time for FA dehydrogenation in a FA-SF solution at 303 K over PdAg-CeO₂/MC catalysts with different Pd contents ($n_{\text{FA}}:n_{\text{SF}} = 1:6$; $n_{(\text{Pd}+\text{Ag})}:n_{\text{FA}} = 0.033$).

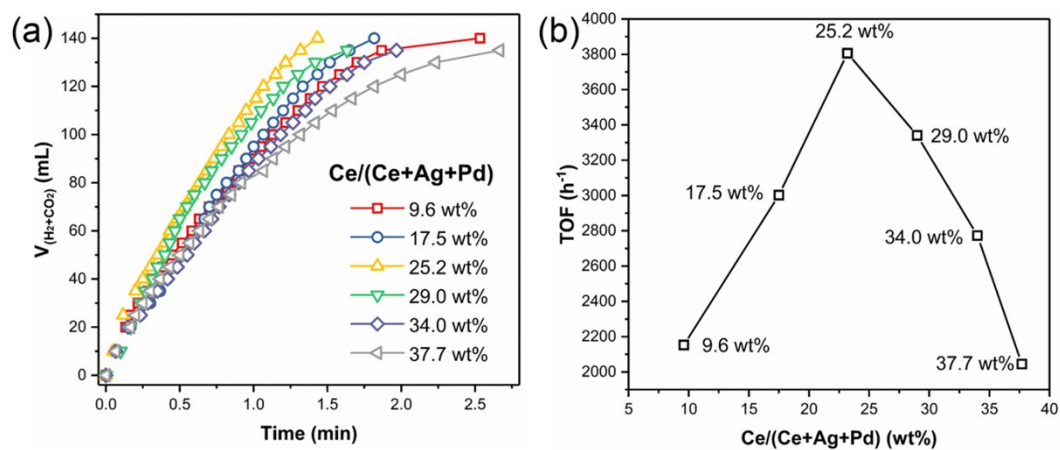


Fig. S9. (a) Volume of the generated gas ($H_2 + CO_2$) versus time and (b) TOF for FA dehydrogenation in a FA-SF solution at 303 K over PdAg-CeO₂/MC catalysts synthesized with different Ce contents ($n_{FA}:n_{SF} = 1:6$; $n_{(Pd+Ag)}:n_{FA} = 0.033$).

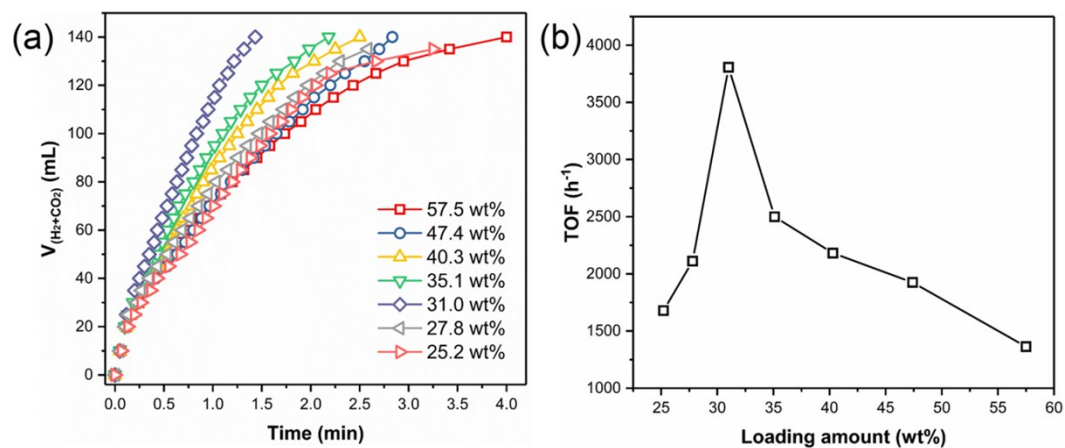


Fig. S10. (a) Volume of the generated gas ($H_2 + CO_2$) versus time and (b) TOF for FA dehydrogenation in a FA-SF solution at 303 K over PdAg-CeO₂/MC catalysts synthesized with different PdAg-CeO₂ contents ($n_{FA}:n_{SF} = 1:6$; $n_{(Pd+Ag)}:n_{FA} = 0.033$).

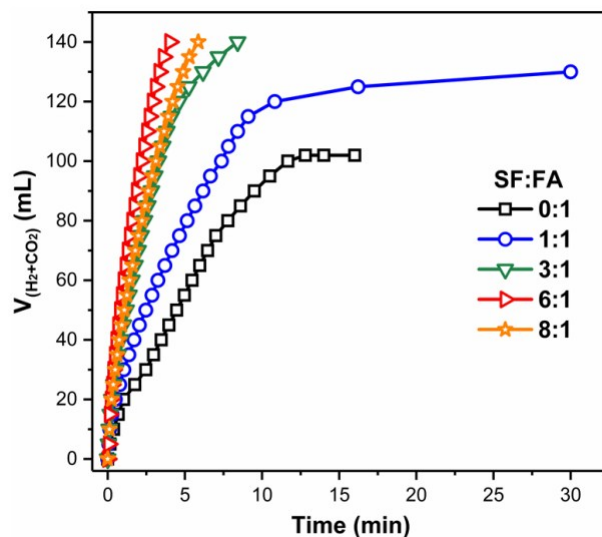


Fig. S11. Volume of the generated gas ($\text{H}_2 + \text{CO}_2$) versus time for FA dehydrogenation in a FA-SF solution at 303 K over the optimized $\text{Pd}_{0.8}\text{Ag}_{0.2}\text{-CeO}_2/\text{MC}$ catalyst in the presence of different SF:FA molar ratio ($n_{(\text{Pd}+\text{Ag})}:n_{\text{FA}} = 0.033$).

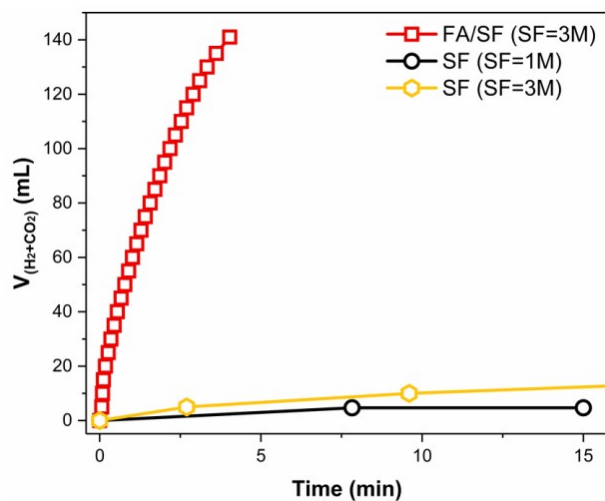


Fig. S12. Pd_{0.8}Ag_{0.2}-CeO₂/MC catalyst catalyzed H₂ generation from a FA/SF mixture solution (SF=3M); a low concentration of SF solution (1M); and a high concentration of SF solution (3M) at 303 K ($n_{(Pd+Ag)}:n_{FA} = 0.033$).

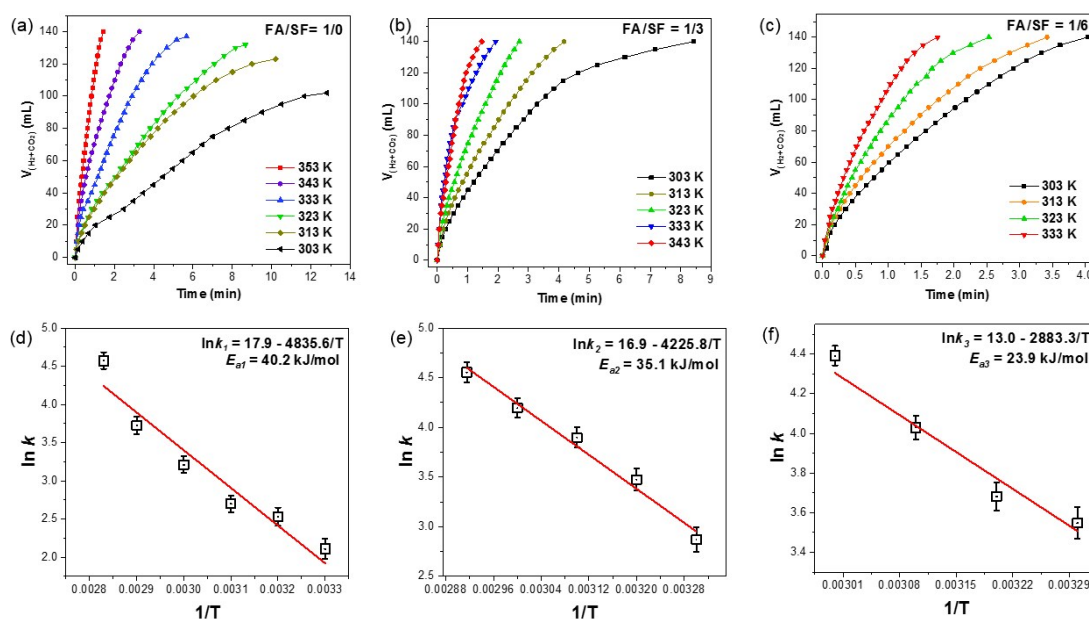


Fig. S13. Volume of the generated gas ($H_2 + CO_2$) versus time for the FA dehydrogenation over $Pd_{0.8}Ag_{0.2}-CeO_2/MC$ catalyst at different temperatures in solutions containing different SF:FA molar ratios: (a) 0:1; (b) 3:1; and (c) 6:1 ($n(Pd+Ag):nFA = 0.033$). Inset: Arrhenius plot of FA dehydrogenation over $Pd_{0.8}Ag_{0.2}-CeO_2/MC$ catalyst in solutions containing different FA/SF molar ratios: (d) 1/0; (e) 1/3; and (f) 1/6 ($n(Pd+Ag):nFA = 0.033$).

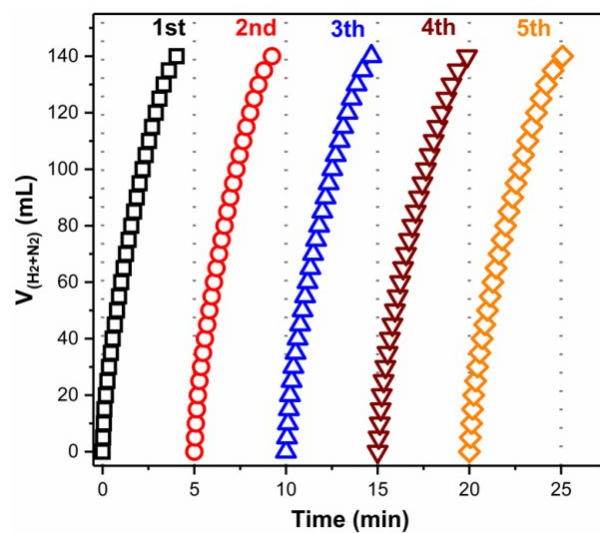


Fig. S14. Stability of the optimized $\text{Pd}_{0.8}\text{Ag}_{0.2}\text{-CeO}_2/\text{MC}$ catalyst for FA dehydrogenation in a FA-SF solution at 303 K.

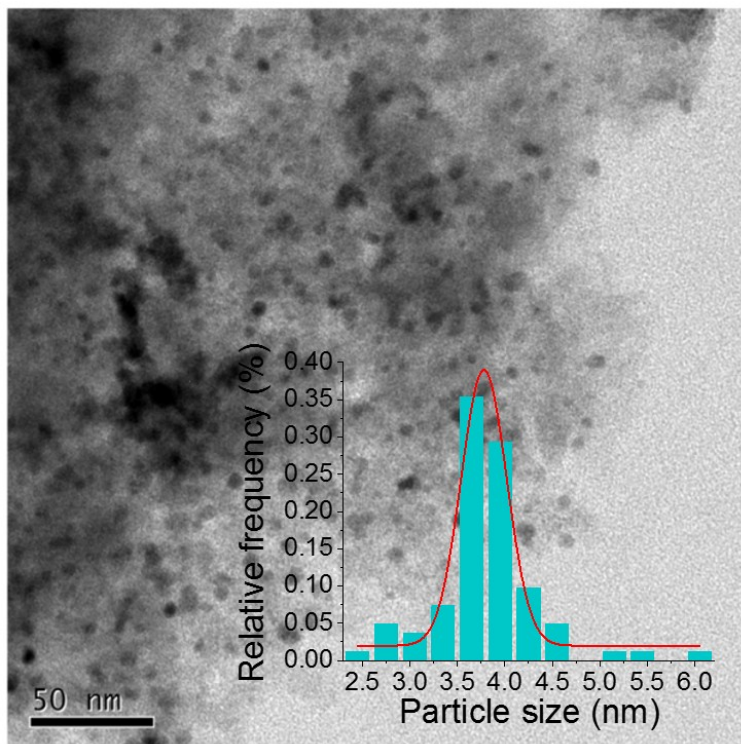


Fig. S15. TEM image and the corresponding particle size histogram (inset) of the $\text{Pd}_{0.8}\text{Ag}_{0.2}\text{-CeO}_2/\text{MC}$ catalyst after the reusability test.

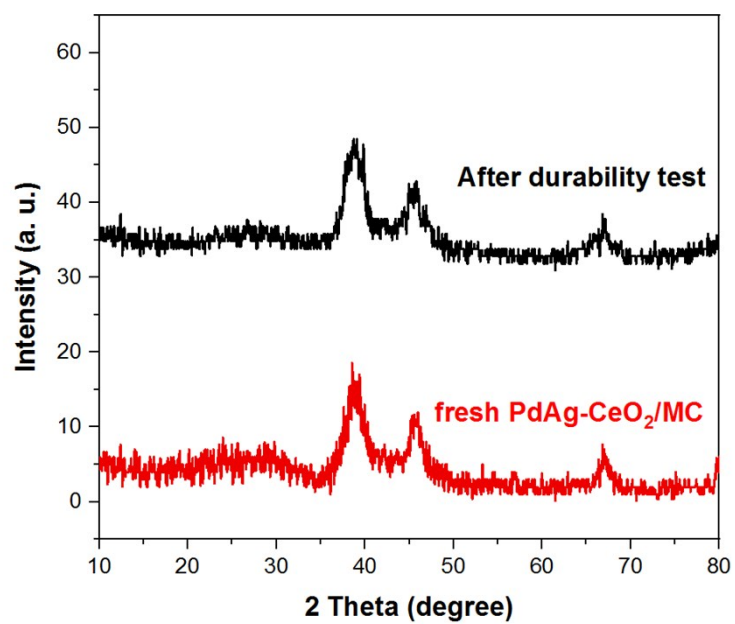


Fig. S16. XRD patterns of the freshly synthesized Pd_{0.8}Ag_{0.2}-CeO₂ catalyst and the sample after the reusability test.

Table S1. Catalysts composition determined by inductively coupled plasma atomic emission spectroscopic (ICP-AES).

Catalysts	Pd (wt%)	Ag (wt%)	Ce (wt%)	B (wt%)	B (wt%) (after catalysis)
Pd-CeO ₂ /MC	42.6	~	14.1	~	~
Ag-CeO ₂ /MC	~	43.0	13.9	~	~
PdAg-CeO ₂ /MC	34.0	8.6	14	0.47	0.14
PdAg/MC	41.1	10.4	~	~	~
PdAg-CeO ₂	56.7	14.4	23.3	~	~

Table S2 Catalytic activities for the dehydrogenation of formic acid catalyzed by different heterogeneous catalysts.

Catalyst	Temp. (K)	Additive	E_a (kJ/mol)	TOF (h^{-1})	Ref.
AuPd@ED-MIL-101	363	HCOONa	-	430.6 ^a	11
PdAu/C-CeO ₂	365	HCOONa	115	113.5 ^a	54
Ag ₁₈ Pd ₈₂ @ZIF-8	353	HCOONa	51.38	580 ^a	20
PdAg-CeO ₂ /MC	353	None	40.2	5244.8	This work
In situ-Pd@MSC	333	HCOONa	31.7	9110 ^b	55
PdAg@ZrO ₂ /C/GO	333	HCOONa	50.1	4500 ^a	56
PdAg-CeO ₂ /MC	333	HCOONa	23.9	5275.2	This work
PdAg-CeO ₂ /MC	333	None	40.2	1529.6	This work
Ag ₄₂ Pd ₅₈ /C	323	HCOONa	22	382 ^b	15
Au ₄₁ Pd ₅₉ /C	323	HCOONa	28	230 ^b	57
Au@Schiff-SiO ₂	323	None	-	4368 ^a	58
(Co ₃)EPd _{0.4} Au _{0.6} /rGO	323	HCOONa	39.8	4840 ^a	59
(Co ₆)Ag _{0.1} Pd _{0.9} /rGO	323	HCOONa	43.1	3512.6 ^a	18
Pd/MSC-30	323	HCOONa	38.6	2623 ^a	60
PdAg-CeO ₂ /MC	323	HCOONa	23.9	3720.7	This work
Pd-B/C	303	HCOONa	-	1009.5 ^a	38
Au ₂ Pd ₃ @(P)N-C	303	None	-	358.3 ^b	61
PdAg-CeO ₂ /MC	313	HCOONa	23.9	2272.8	This work
Pd/CN _{0.25}	298	None	48.8	664.5 ^a	43
Au _{0.5} Pd _{0.5} /NH ₂ -N-rGO	298	None	-	4445.6 ^a	62
CoAuPd/C	298	None	-	80.0 ^a	16
NiPd/NH ₂ -N-rGO	298	None	-	954.3 ^a	45
Pd _{0.5} Au _{0.3} Mn _{0.2} /N-SiO ₂	298	None	26.2	785 ^a	63
AuPd-MnO _x /ZIF-80-rGO	298	None	-	382.1 ^a	9

^aThe initial TOF values calculated on initial time or initial conversion of FA;

^bThe TOF values calculated on the completion time of gas releasing.