

Electronic Supplementary Information

**An effective amino acid-assisted growth of ultrafine palladium nanocatalysts
toward superior synergistic catalysis for hydrogen generation from formic acid**

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Table S1. Catalytic activities for hydrogen generation from formic acid catalyzed by various heterogeneous catalysts

Catalyst	Additive	Temp. (°C)	CO evolution	TOF (h ⁻¹)	Ref.
Arg-Pd/MS-30	HCOONa	60	No	5723	This work
	None	50	No	1365	This work
Pd/MS-30	HCOONa	50	No	2623	S1
Au/ZrO₂ NCs	NEt ₃	50	No	1593 ^a	S2
Ag@Pd/C	Aqueous	20	No	192	S3
Pd-S-SiO₂	Aqueous	85	No	719	S4
AuPd@ED-MIL-101	HCOONa	90	Yes	106	S5
PdAu/C-CeO₂	HCOONa	92	145 ppm	113.5	S6
Ag₄₂Pd₅₈	Aqueous	50	No	328 ^a	S7
Pd-B/C	HCOONa	30	No	1184	S8
PdAu@Au/C	HCOONa	92	30 ppm	21.4	S9
Co_{0.30}Au_{0.35}Pd_{0.35}	Aqueous	25	No	80 ^a	S10
Pd/APC	HCOONa	55	No	2999	S11
Pd/N-MS-30-two-175	HCOONa	60	No	8414	S12
Pd_{0.6}Ag_{0.4}@ZrO₂/C/rGO	HCOONa	60	No	4500	S13

^a Initial TOF values calculated at the initial stages of the catalytic reactions.

Table S2. ICP results of Pd content for Pd/MS-30 and Arg-Pd/MS-30

Sample	Pd content (wt%)
Pd/MS-30	7.92
Arg-Pd/MS-30	3.81
Recycled Arg-Pd/MS-30	3.75

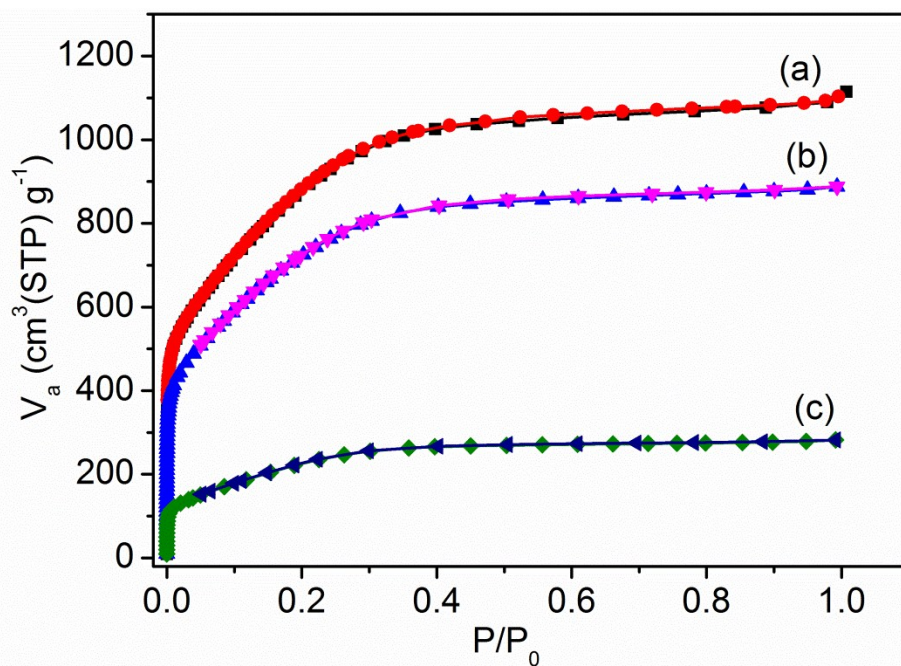


Figure S1. N_2 sorption isotherms of (a) MSC-30, (b) Pd/MSC-30, and (c) Arg-Pd/MSC-30 at 77K.

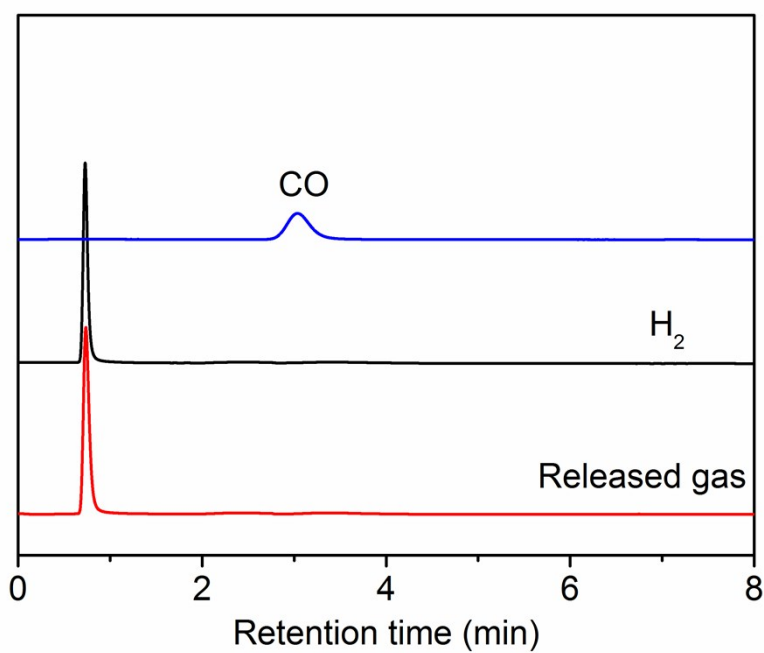


Figure S2. Gas chromatograms of CO and H_2 as reference gases and the released gas from the dehydrogenation of FA over Arg-Pd/MSC-30 ($n_{\text{Pd}}/n_{\text{FA}} = 0.01$, FA/SF = 1:1, 323 K).

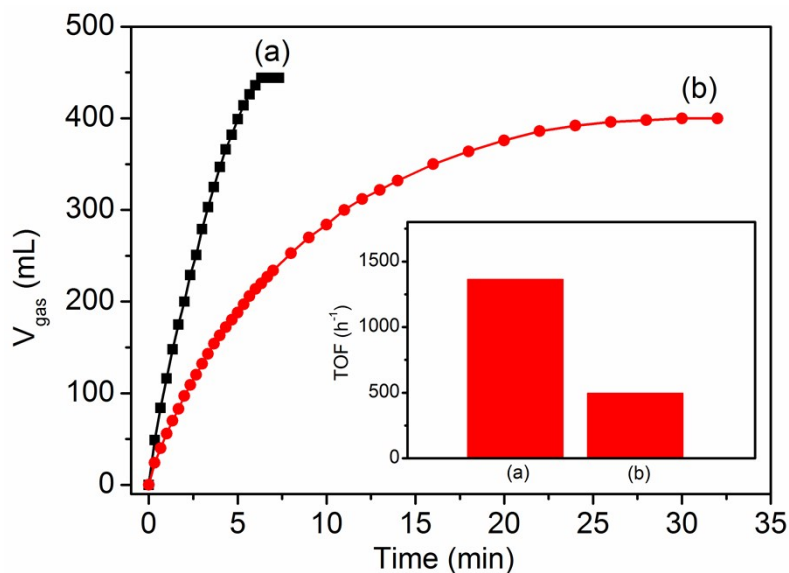


Figure S3. Volume of the generated gas ($\text{CO}_2 + \text{H}_2$) versus time for the dehydrogenation of pure FA over the as-prepared (a) Arg-Pd/MSC-30 and (b) Pd/MSC-30 ($n_{\text{Pd}}/n_{\text{FA}} = 0.01$, 323 K, $n_{\text{FA}} = 9.0$ mmol). Insert: corresponding TOF values for dehydrogenation of pure FA over the Arg-Pd/MSC-30 and Pd/MSC-30 catalysts.

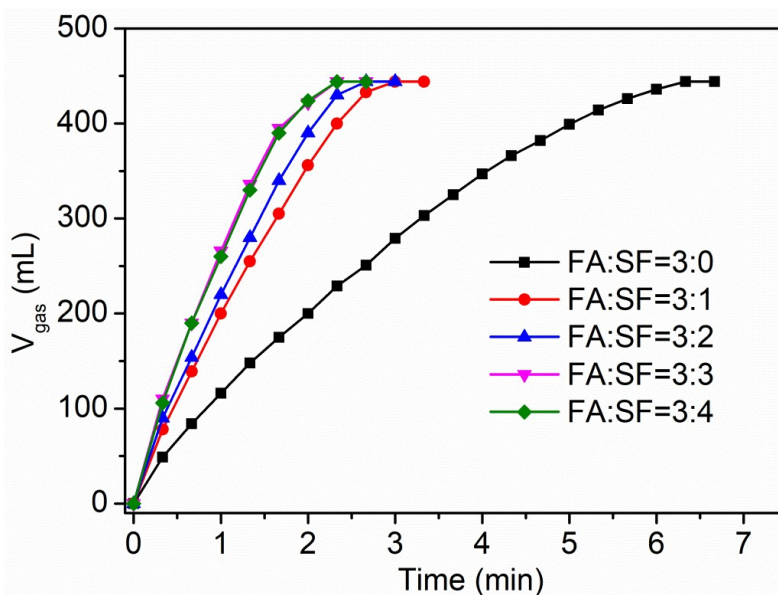


Figure S4. Volume of the generated gas ($\text{CO}_2 + \text{H}_2$) versus time for the dehydrogenation of FA with different FA/SF molar ratios over the as-prepared Arg-Pd/MSC-30 catalyst ($n_{\text{Pd}}/n_{\text{FA}} = 0.01$, 323 K).

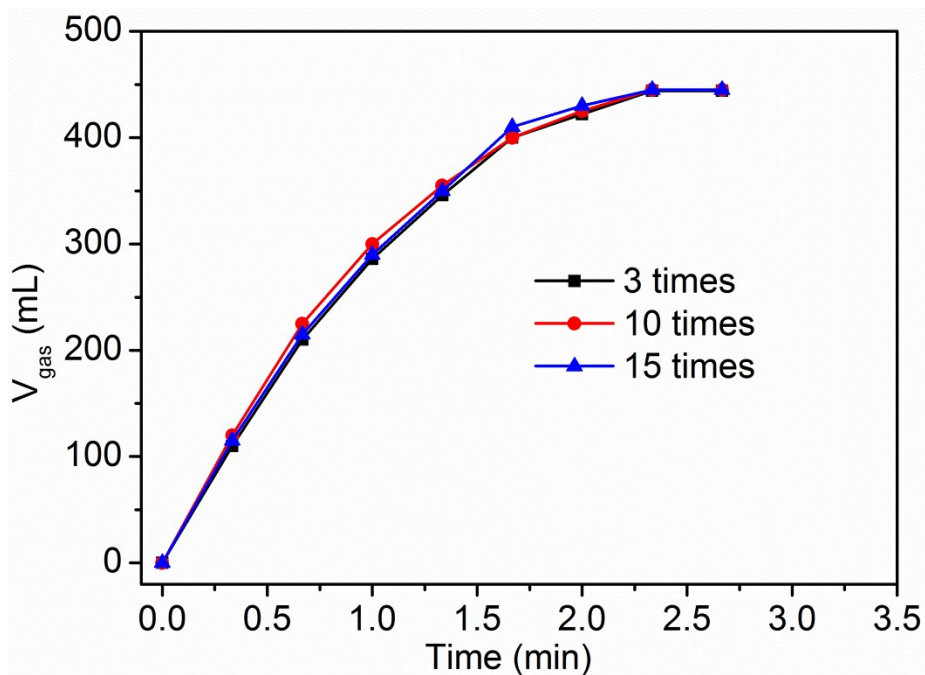


Figure S5. Volume of the generated gas ($\text{CO}_2 + \text{H}_2$) versus time for the dehydrogenation of FA with over the as-prepared Arg-Pd/MSC-30 catalyst washed with different times after reduction ($n_{\text{Pd}}/n_{\text{FA}} = 0.01$, 323 K).

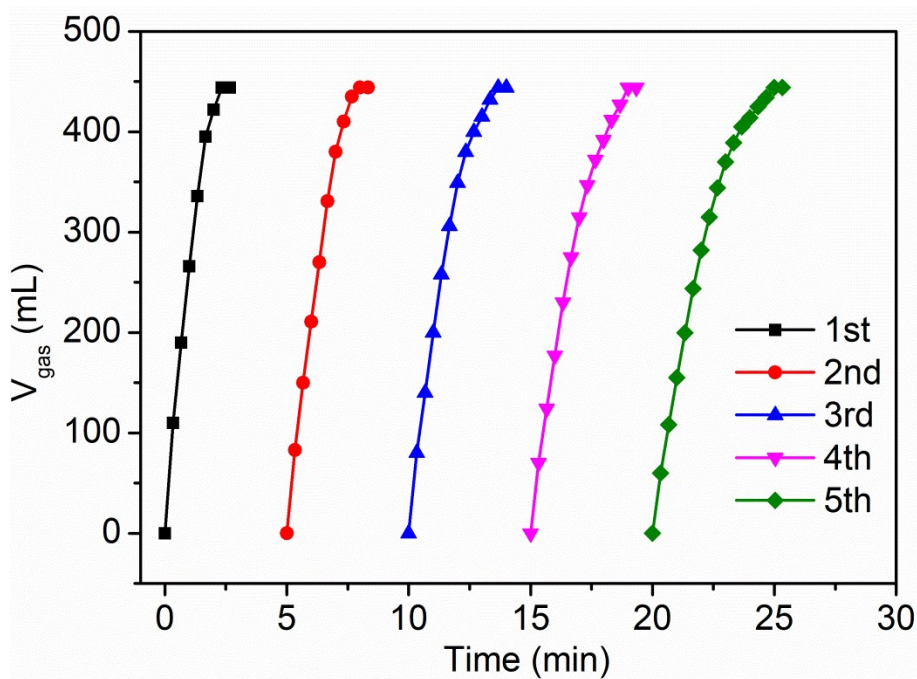


Figure S6. Durability test for the dehydrogenation of FA over Arg-Pd/MSC-30 ($n_{\text{Pd}}/n_{\text{FA}} = 0.01$, FA/SF = 1:1, 323 K).

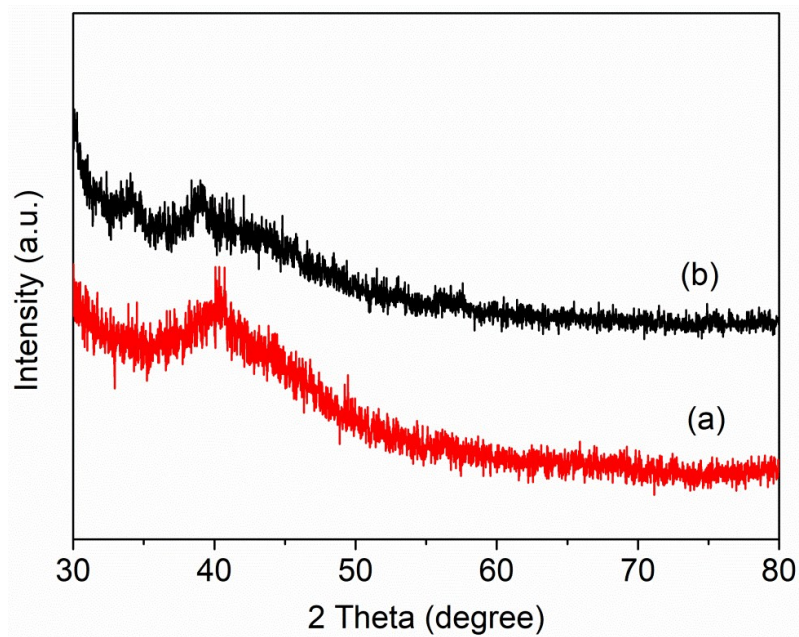


Figure S7. PXRD patterns of Arg-Pd/MSC-30 (a) before and (b) after catalysis.

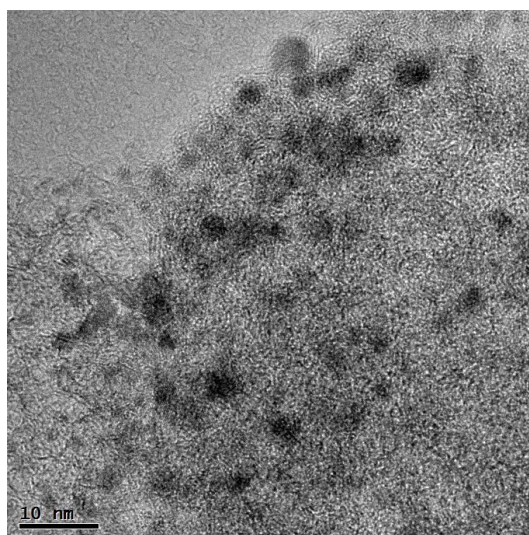


Figure S8. TEM image of Arg-Pd/MSC-30 after catalysis

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