Supporting information

PdAu bimetallic nanoparticles anchored on amine-modified mesoporous ZrSBA-15 for dehydrogenation of formic acid at ambient conditions

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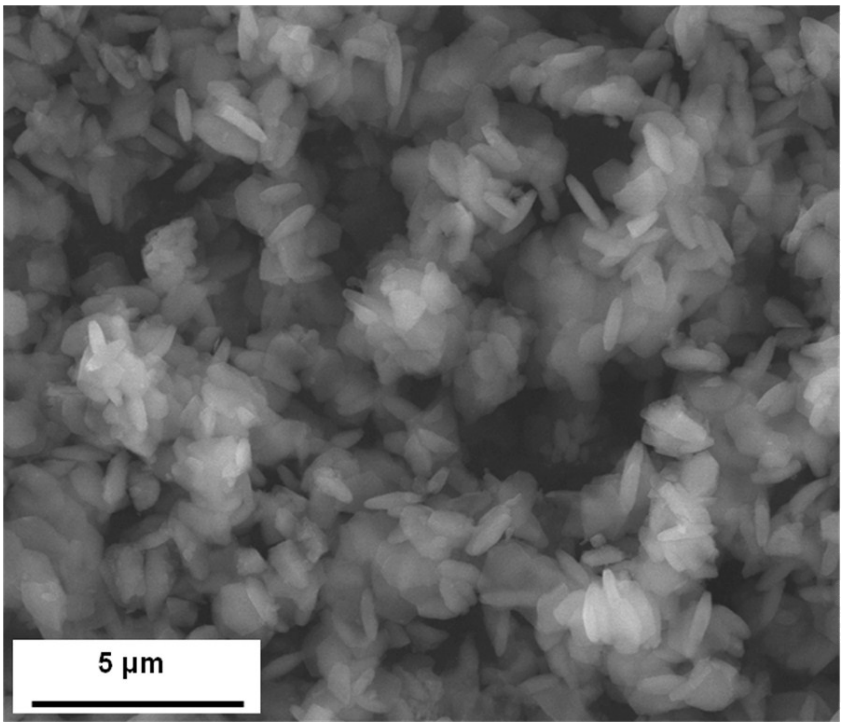

Fig. S1 SEM image of ZrSBA-15.

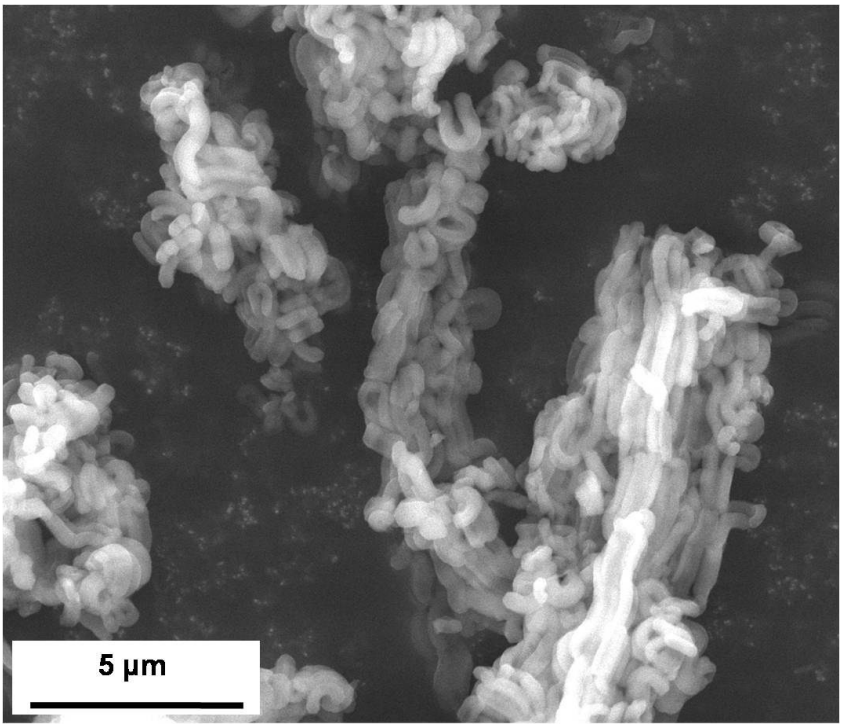

Fig. S2 SEM image of SBA-15.

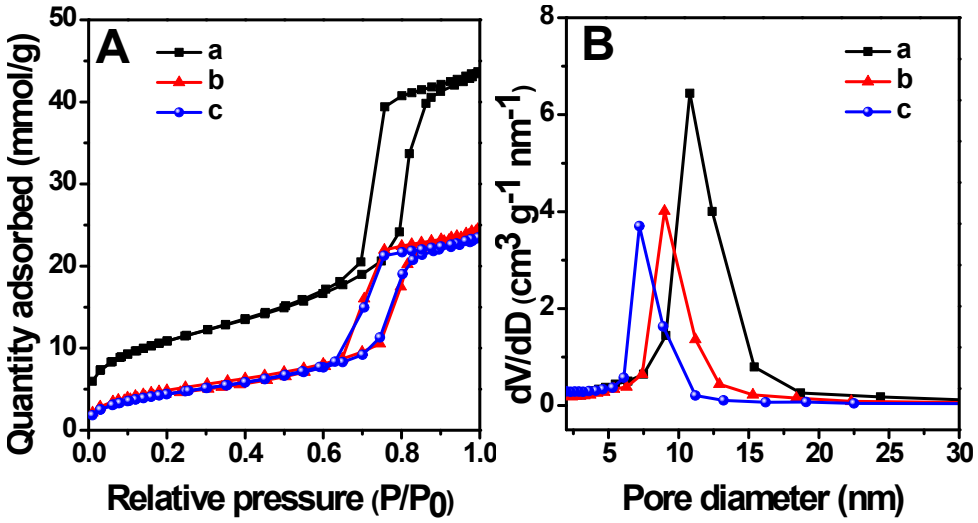

Fig. S3 The N_2 adsorption-desorption isotherms (A) and the pore size distributions (B) of ZrSBA-15 (a), ZrSBA-15-AP (b) and $Pd_{60}Au_{40}$/ ZrSBA-15-AP (c).

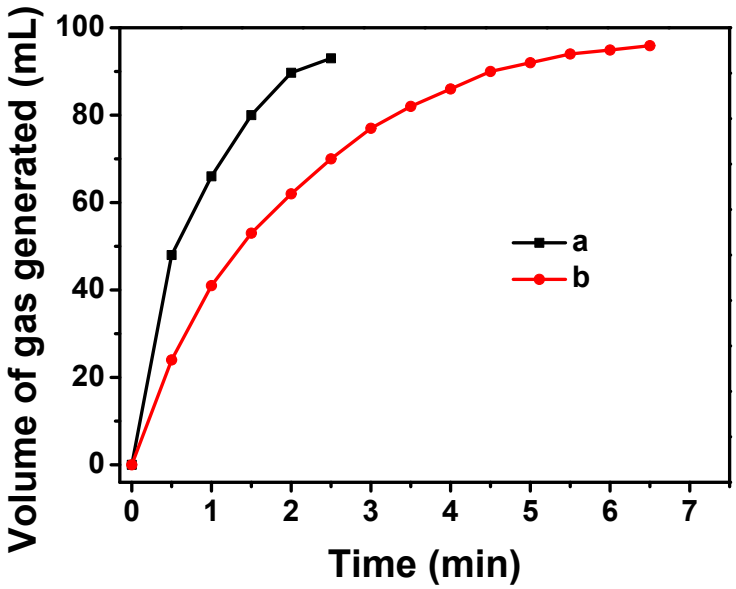

Fig. S4 The volume of generated gas versus time for the additive-free dehydrogenation of FA (0.2 M, 10 mL) at 298 K in the presence of $Pd_{60}Au_{40}$/ZrSBA-15-AP (a) and $Pd_{60}Au_{40}$/SBA-15-AP (b) , respectively.

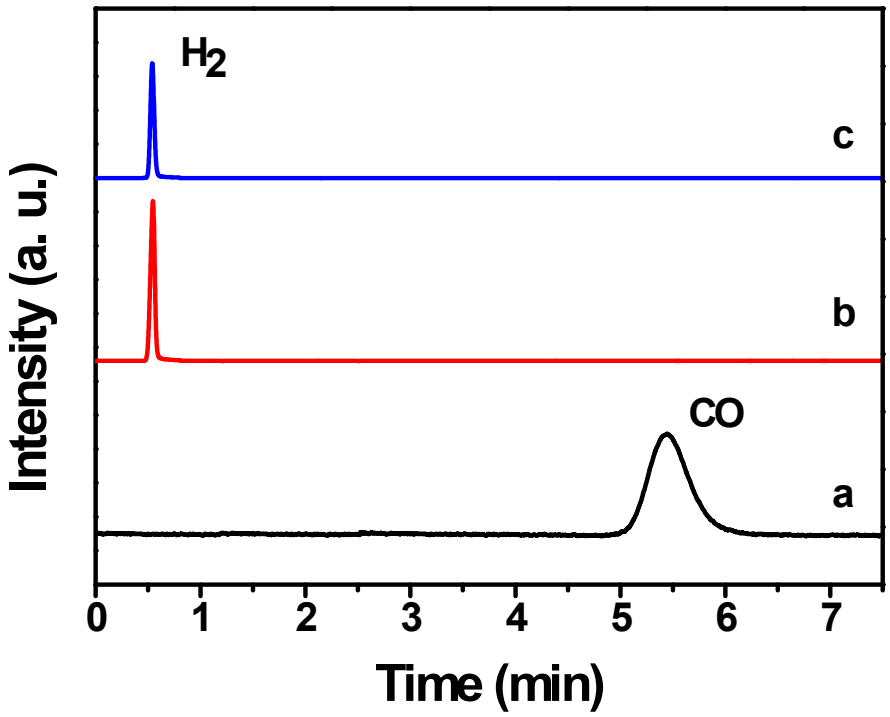

Fig. S5 Gas chromatography analysis results of pure CO (a), pure H_2 (b) and generated gas for $Pd_{60}Au_{40}$/ZrSBA-15-AP catalyzed additive-free dehydrogenation of FA (0.2 M, 10 mL) (c).

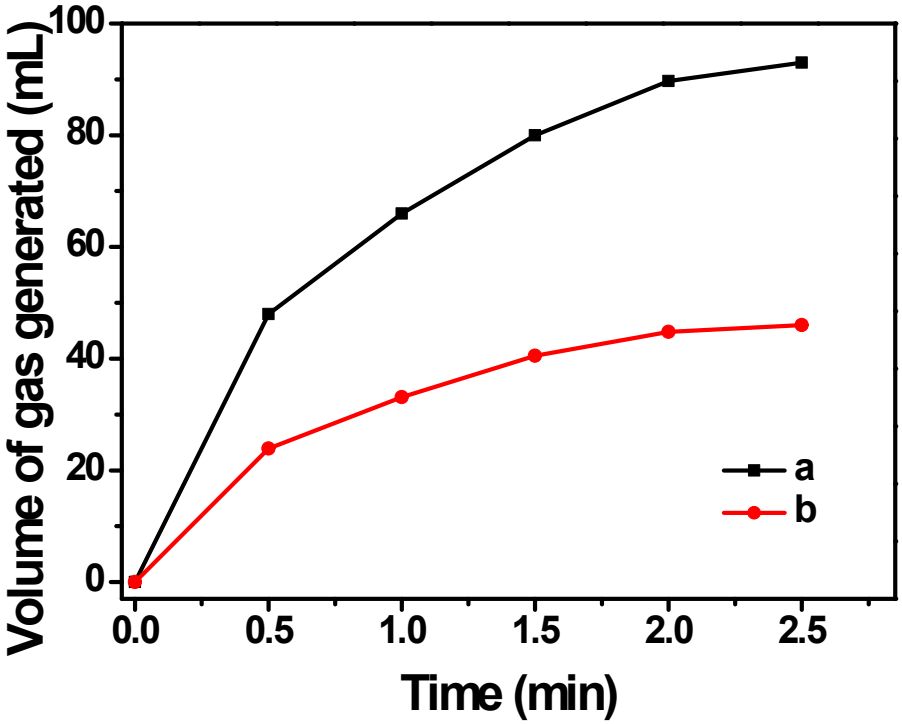

Fig. S6 The volume of generated gas versus time for $Pd_{60}Au_{40}$/ZrSBA-15-AP catalyzed additive-free dehydrogenation of FA (0.2 M, 10 mL) at 298 K in the absence (a) or presence (b) of NaOH trap.

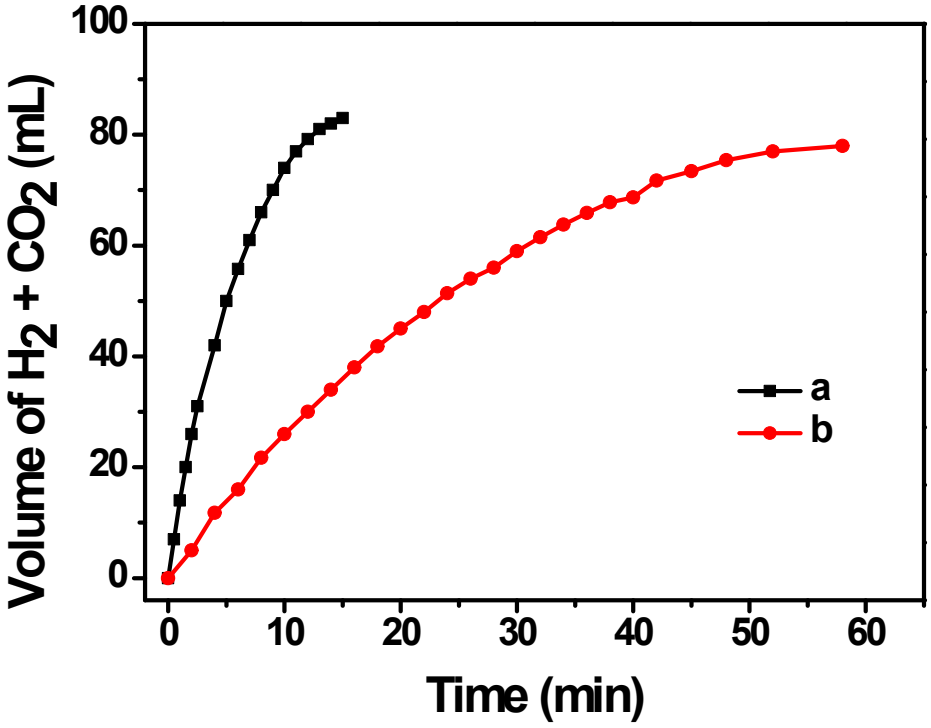

Fig. S7 The volume of generated gas mixture versus time for the dehydrogenation of FA (0.2 M, 10 mL) over $Pd_{60}Au_{40}$/ZrSBA-15-AP catalyst at 288 K (a) and 275 K (b).

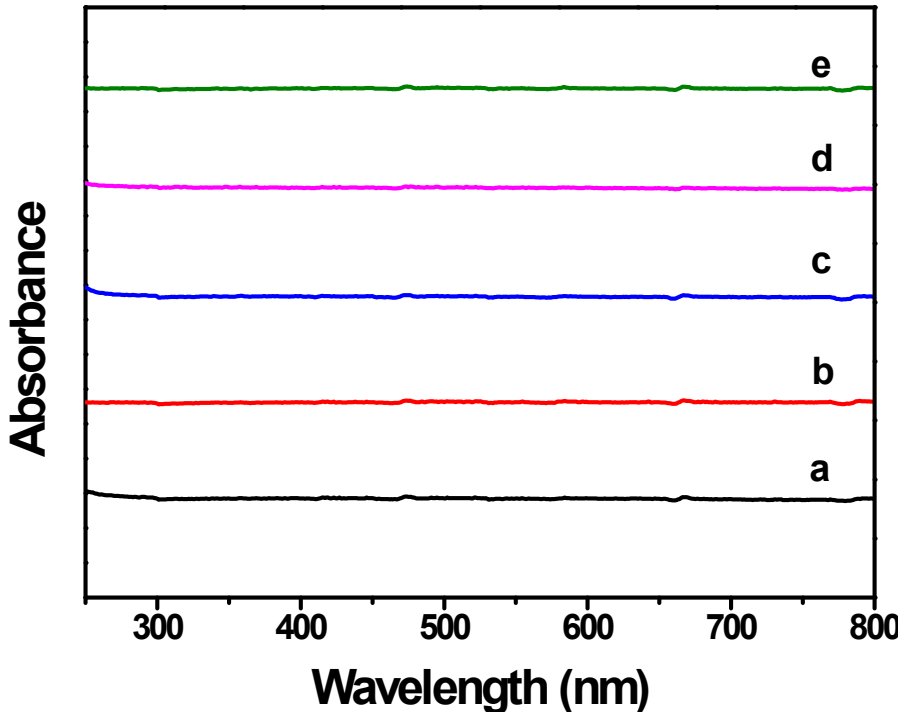

Fig. S8 UV-Vis spectra of the aqueous solution containing different organic amines: (a) AP, (b) AEAP, (c) AEAEAP, (d) MAP, and (e) DMAP.

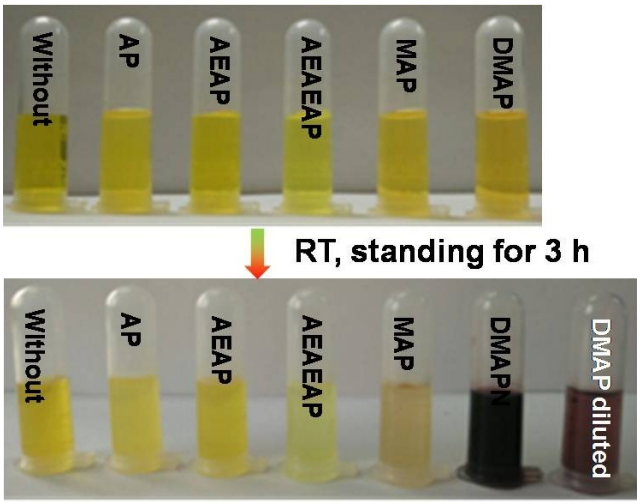

Fig. S9 The photos of the mixed solution containing different organic amines and the metal precursors ($PdCl_4^{2-}$, $AuCl_4^-$) at room temperature.

Table S1 Comparison of the catalytic performance of $Pd_{60}Au_{40}$/ZrSBA-15-AP presented in this work with the recently reported heterogeneous catalyst systems for the FA dehydrogenation in the absence of any additives at room temperature.

Catalyst	T (K)	$TOF_{initial}$ (h^{-1})[a]	Con. (%)	Ea kJ mol^{-1}	Ref.
$Pd_{60}Au_{40}$/ZrSBA-15-AP	298	1185	95	42.5	This work
Pd/CN_x	298	639	98	48.8	S1
Ag@Pd/C	298	157	43	-	S2
AgPd/C	298	274	46	22.0	S3
AuPd/C	298	41	24	28.0	S4
CoAuPd/C	298	54	91	-	S5
NiAuPd/C	298	20	73	-	S6
AgAuPd/rGO	298	95	100	-	S7
CoAuPd/r-GO	298	63	51	-	S8
CoAuPd/DNA-rGO	298	130	96	-	S8
AuPd/N-mrGO	298	39	93	-	S9
Au@Pd/N-mrGO	298	111	98	-	S9
AuPd/N-rGO	298	17	57	-	S10
AuPd-CeO_2/N-rGO	298	68	98	-	S10
AuPd/ZIF-8-rGO	298	532	83	-	S11
AuPd-MnO_x/ZIF-8-rGO	298	764	94	-	S11
PdAg-MnO_x/N-SiO_2	298	482	99	72.4	S12
CrAuPd/N-SiO_2	298	707	87	49.8	S13
PdAu/N-SiO_2	298	164	76	26.2	S14
PdAu-MnO_x/N-SiO_2	298	981	92	26.2	S14
AgPd@MIL-100(Fe)	298	58	37	-	S15
Pd/SBA-15-NH_2	298	127	28	-	S16

[a] The initial TOF values of some literature reported catalysts have been recalculated on the basis of the conversion of formic acid after reacting 20 min in order to make comparison.

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Calculation method of initial TOF value:

The initial TOF value was calculated based on the molar amount of noble metal Pd and Au atoms according to the following equation:

$$\mathbf{TOF} = \frac{\mathbf{P_0 V / 2RT}}{\mathbf{n_{metal}}\, \boldsymbol{t}}$$

wherein P_0 is the atmospheric pressure (101325 Pa), V is the volume of (H_2 + CO_2) released at 20% conversion of FA (m^3), R is the universal gas constant (8.3145 m^3 Pa mol^{-1} K^{-1}), T is the room temperature (298 K), n_{metal} is the total mole number of noble metal atoms in catalyst, and *t* is the reaction time (h) when a 20% conversion of FA is reached.