Supporting Information

Au Species Supported on Nitrogen-rich Porous Organic Polymers for CO_2 Hydrogenation to Formic Acid

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Experimental Section

Synthesis of Pd/Trz-DETA, Ag/Trz-DETA and Ru/Trz-DETA

The Pd/Trz-DETA catalyst was prepared with a $NaBH_4$ wet chemical reduction method. Typically, 0.3 g of Trz-DETA was dispersed in 100 mL of ethanol and ultrasounded for 15 min. Then a solution of aqueous $PdCl_2$ (1.0 g/50 mL, 0.38 mL) in 100 mL of ethanol was added rapidly to the above mixture at 80 ℃, followed by stirring for 30 min. A 14-fold excess of $NaBH_4$ was added and the mixture was stirred continuously for 2 h at 80 ℃. After the reaction, the product was collected by filtration and washed several times with water and ethanol. Finally, Pd/Trz-DETA was obtained by vacuum drying at 60 ℃. Ag/Trz-DETA and Ru/Trz-TEPA were synthesized by a similar method as that of Pd/Trz-TETA, and were obtained using aqueous $AgNO_3$ solution (1.0 g/50 mL, 0.35 mL)and aqueous $RuCl_3$ solution (1.0 g/50 mL, 0.52 mL) , respectively.

Quantitative analysis

Formic acid yield calculation formula:

$$\text{mi (g)} = \frac{As \times Ii \times Mi}{Ai \times Is \times Ms} \times \text{ms} \qquad \text{TON} = \frac{N_{HCOOH}}{N_{Au}}$$

Where m_i is the yield of formic acid, m_s is the mass of DMSO, A_s and A_i are the H atoms numbers of DMSO and formic acid, I_s and I_i are the integral areas of DMSO and formic acid, M_s and M_i are the molar mass of DMSO and formic acid, and N_{HCOOH} and N_{Au} are the molar quantity formic acid and Au.

Characterization of the catalysts

Supporting Figures

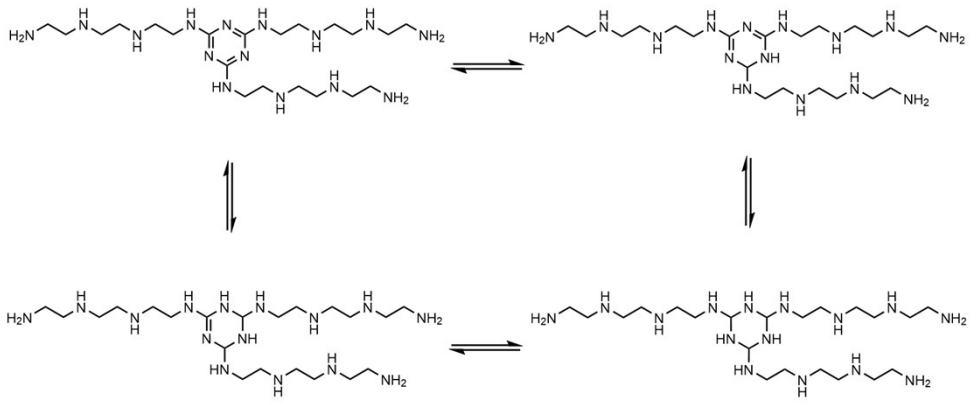
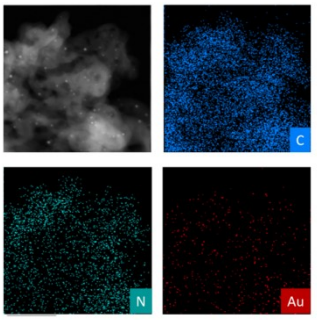
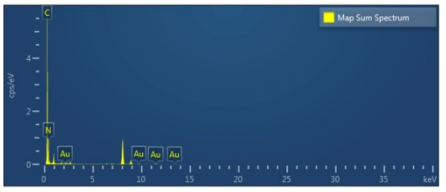


Fig. S1 Tautomeric forms of Trz-TETA.

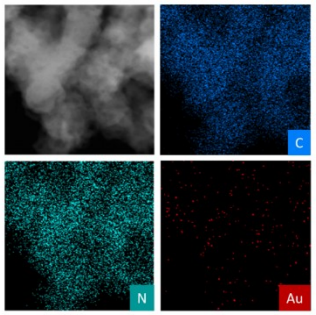
(a)

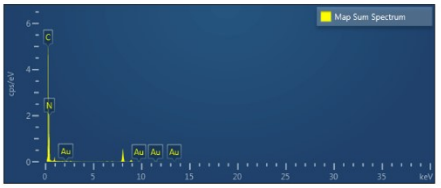




Element	Line Type	k factor	Absorption Correction	Wt%	Wt% Sigma
C	K series	2.47155	1	83.71	0.46
N	K series	3.10261	1	15.31	0.43
Au	L series	2.81409	1	0.98	0.18
Total:				100	

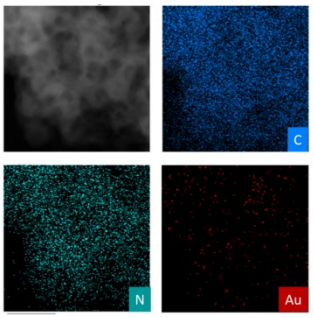
(b)

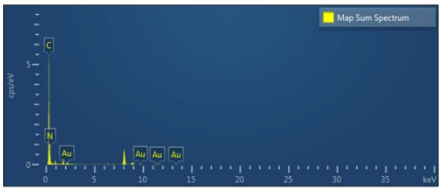




Element	Line Type	k factor	Absorption Correction	Wt%	Wt% Sigma
C	K series	2.47155	1	65.17	0.43
N	K series	3.10261	1	33.88	0.43
Au	L series	2.81409	1	0.96	0.13
Total:				100	

(c)





Element	Line Type	k factor	Absorption Correction	Wt%	Wt% Sigma
C	K series	2.47155	1	81.97	0.43
N	K series	3.10261	1	16.99	0.4
Au	L series	2.81409	1	1.04	0.2
Total:				100	

Fig. S2 EDX spectra analysis and images of (a) Au/Trz-DETA and (b) Au/Trz-TEPA with the corresponding element mapping signals of C, N and Au.

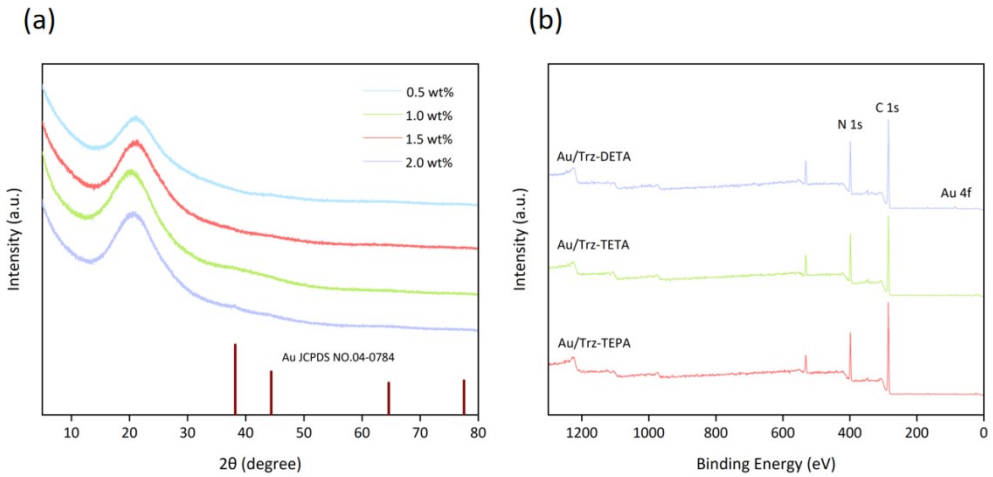


Fig. S3 (a) XRD patterns of Au/Trz-DETA catalyst with different Au loading amounts. (b) XPS survey spectra of Au/Trz-DETA, Au/Trz-TETA and Au/Trz-TEPA.

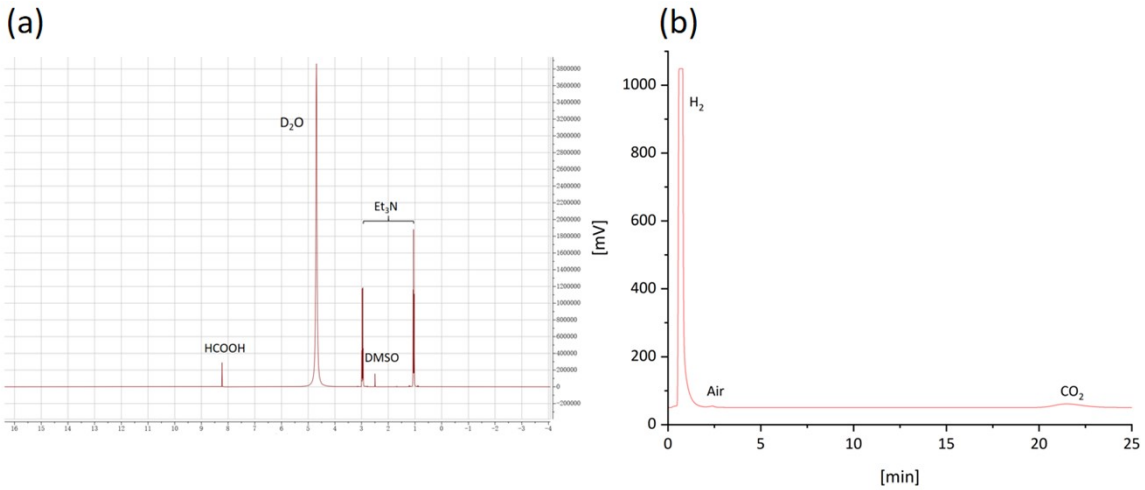


Fig. S4 (a) ^{1}H NMR spectra of the reaction solution (b) GC spectra of gas after reaction

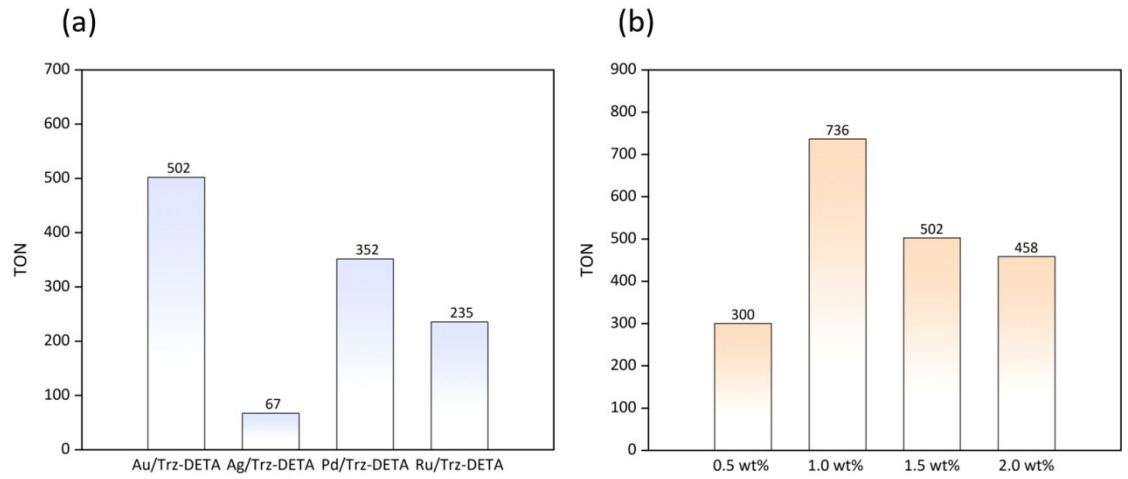


Fig. S5 (a)Reactivity comparison of Trz-DETA loading with different metals.(1.5 wt% metal loadings) (b) Catalytic activity of Au/Trz-DETA catalyst with different Au loadings.

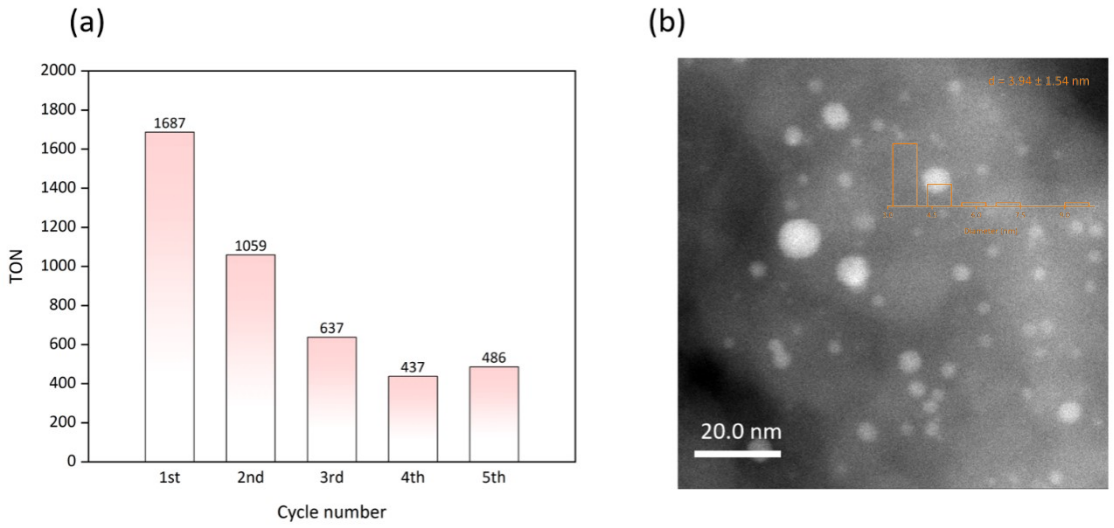


Fig. S6 (a) Catalyst recycling of Au/Trz-TETA. (b) HAADF-STEM image of Au/Trz-DETA after cycling five times.

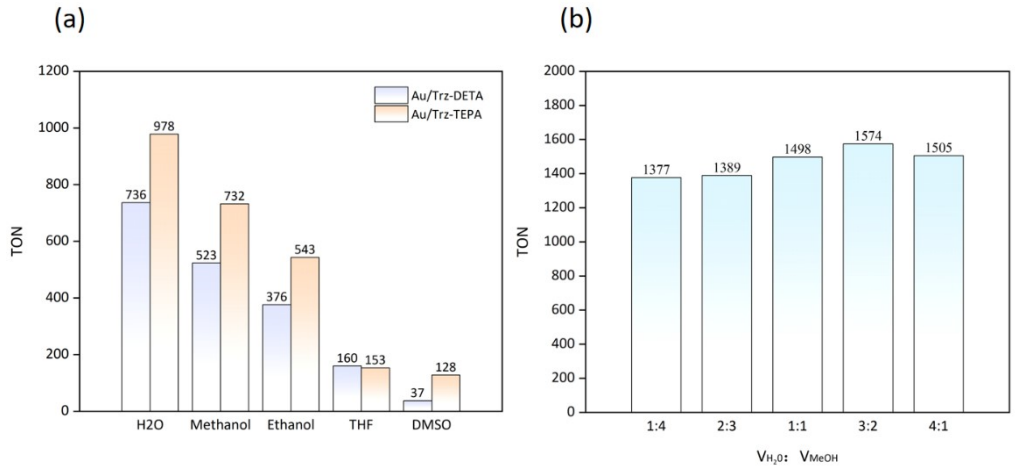


Fig. S7 (a) Reactivity comparison of various solvents of Au/Trz-DETA and Au/Trz-TEPA. (b) Catalytic activity of Au/Trz-TETA at different volume ratios of H_2O and methanol (Vtotal = 5 mL).

$$RR'NH + CO_2 \longrightarrow RR'N^+H\cdots COO^-$$

$$RR'N^+H\cdots COO^- + \begin{matrix} OH^- \longrightarrow RR'NCOO^- + H_2O \\ RR'NH \longrightarrow RR'NCOO^-\,N^+H_2RR' \end{matrix}$$

Fig. S8 CO_2 adsorption and activation on Au/Trz-TETA catalysts

Supporting Tables

Table S1 The actual Au loadings of various catalysts determined by ICP-AES

Catalyst	Theory (wt. %)	Actual (wt. %)
Au/Trz-DETA	0.50	0.53
	1.00	1.02
	1.50	1.47
	2.00	2.08
Au/Trz-TETA	1.00	0.98
Au/Trz-TEPA	1.00	0.96

Table S2 Textural parameters of Trz-DETA, Trz-TETA, Trz-TEPA and Au/Trz-TETA

	S_{BET}/m·g^{-1}	D_{AVG}/nm	D_{MODE}/nm	V_{TOTAl}/cm^3·g^{-1}
Trz-DETA	52	24.40	3.714	0.30
Trz-TETA	47	26.96	4.448	0.33
Trz-TEPA	43	35.68	32.26	0.37
Au/Trz-TETA	52	34.06	3.308	0.43

References

1 M. Niksefat, J. Rahimi, A. Maleki and A. S. Nia, *Algal Res.*, 2023, **70**, 103003.

2 W. Zhan, Y. Shu, Y. Sheng, H. Zhu, Y. Guo, L. Wang, Y. Guo, J. Zhang, G. Lu and S. Dai, *Angewandte Chemie-International Edition*, 2017, **56**, 4494-4498.