Supplementary Information

Single-atom Cu_1/ZrO_2 Coupled with SAPO-34 Enhances CO_2 Hydrogenation to Light Olefins

Linlong Hu[a,b], Chentao Wang [a], Huibin Wang[a], Hua Pan[c], Mi Yan[d], Ke Wang[a,b,] Pengfei Xie[a,b*]*

[a] Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310058, China

[b] Zhejiang Key Laboratory of Intelligent Manufacturing for Functional Chemicals, Zhejiang University, Hangzhou, 311215, China

[c] Zhejiang international Joint Laboratory on Low-Carbon Pollution Control and Resource utilization，College of Biological and Environmental Engineering, Zhejiang Shuren University, Hangzhou 310015, China

[d] Zhejiang Province Key Laboratory of Advanced Information Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310058, China

* Corresponding author, email address: pfxie@zju.edu.cn

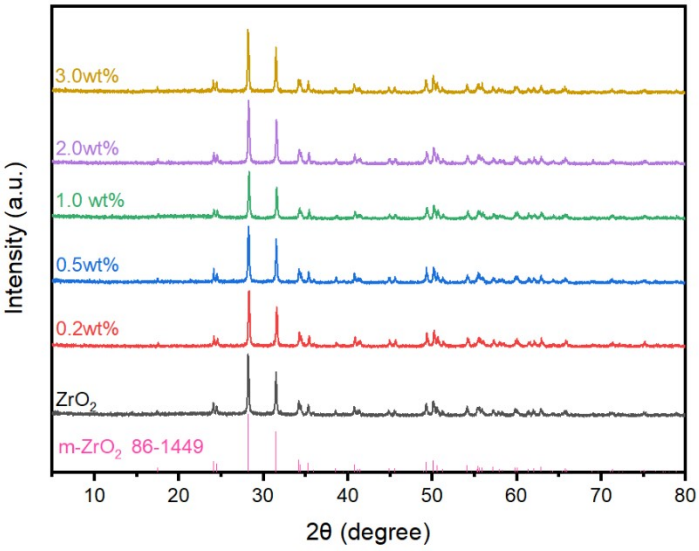

Fig. S1 XRD patterns of Cu_1/ZrO_2 catalysts with different single-atom contents.

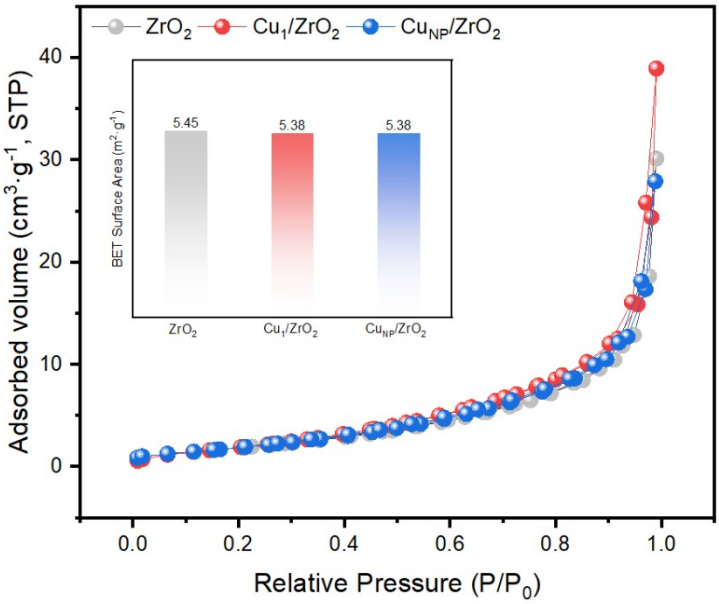

Fig. S2 N_2 adsorption-desorption isotherms of ZrO_2, Cu_1/ZrO_2 and Cu_{NP}/ZrO_2 catalysts; the inset shows the corresponding BET specific surface area.

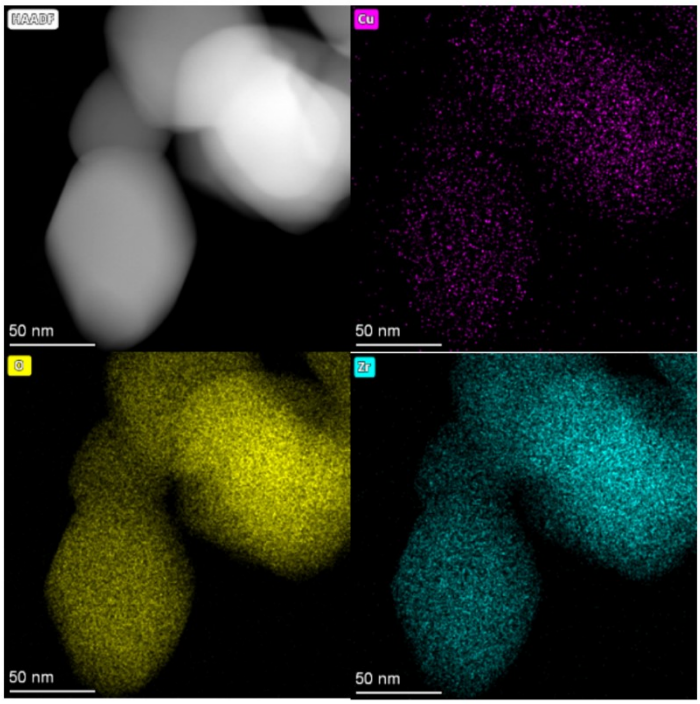

Fig. S3 Elemental mapping images showing the distribution of Cu, O and Zr in Cu_1/ZrO_2.

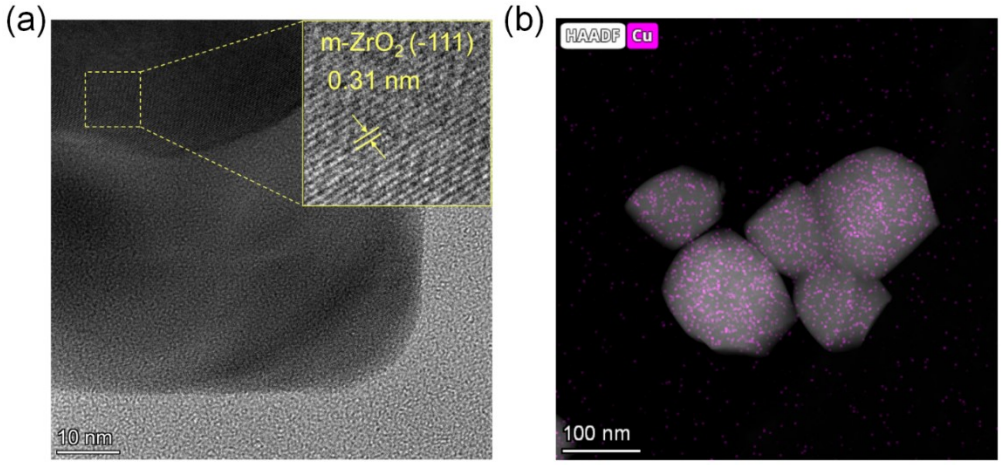

Fig. S4 HRTEM (a) and Cu EDS mapping (b) of 3.0wt% Cu_1/ZrO_2.

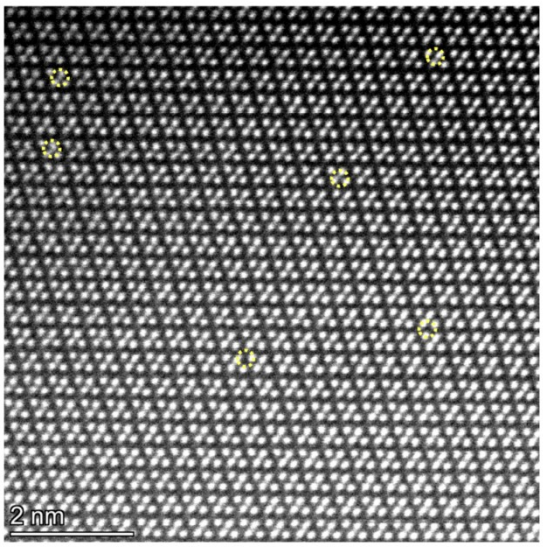

Fig. S5 AC-HADDF-STEM images of Cu_1/ZrO_2. Dark spots in the yellow circles represent single copper atoms.

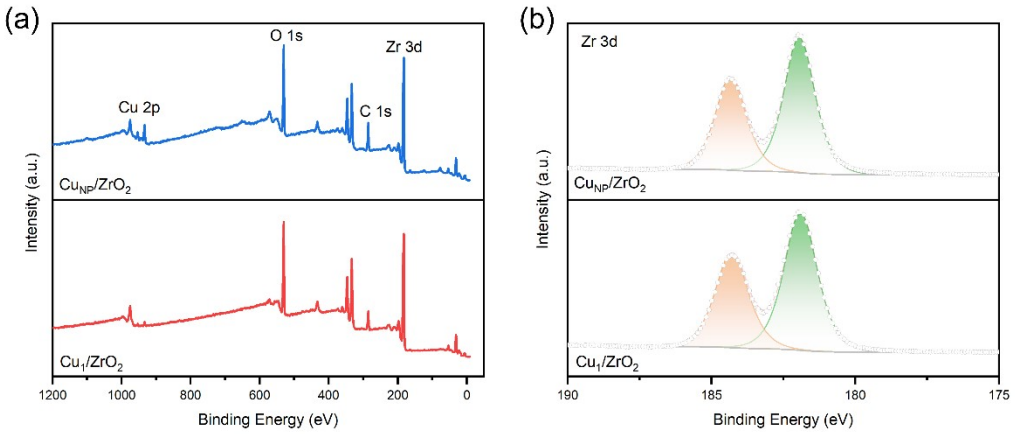

Fig. S6 XPS survey (a) and Zr 3d (b) spectrum of Cu_1/ZrO_2 and Cu_{NP}/ZrO_2.

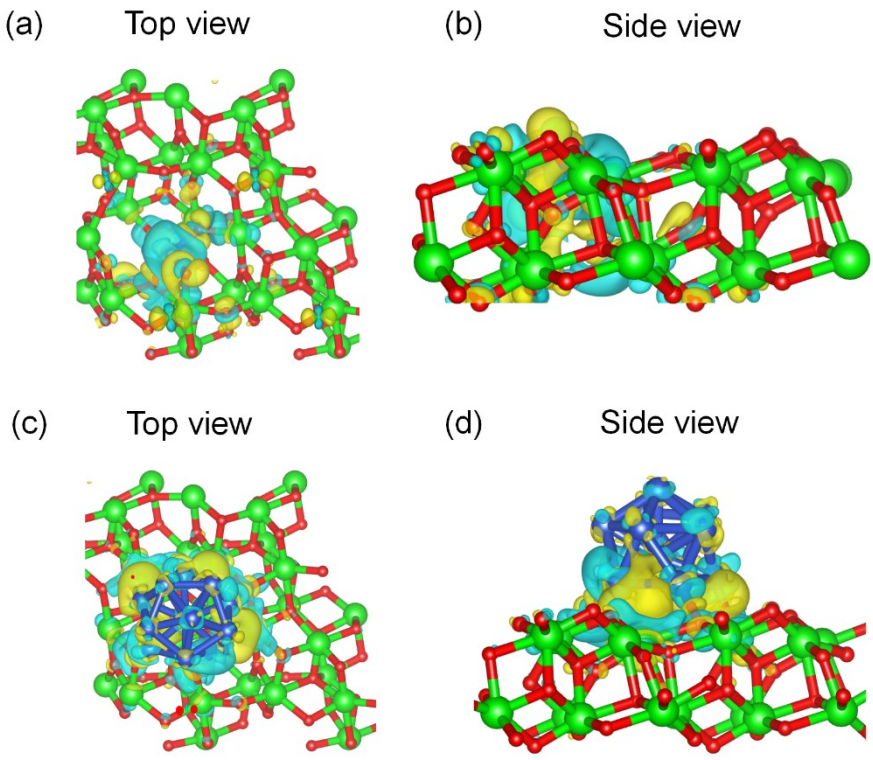

Fig. S7 The differential charge density map of Cu_1/ZrO_2 (a,b) and Cu_{NP}/ZrO_2 (c,d).

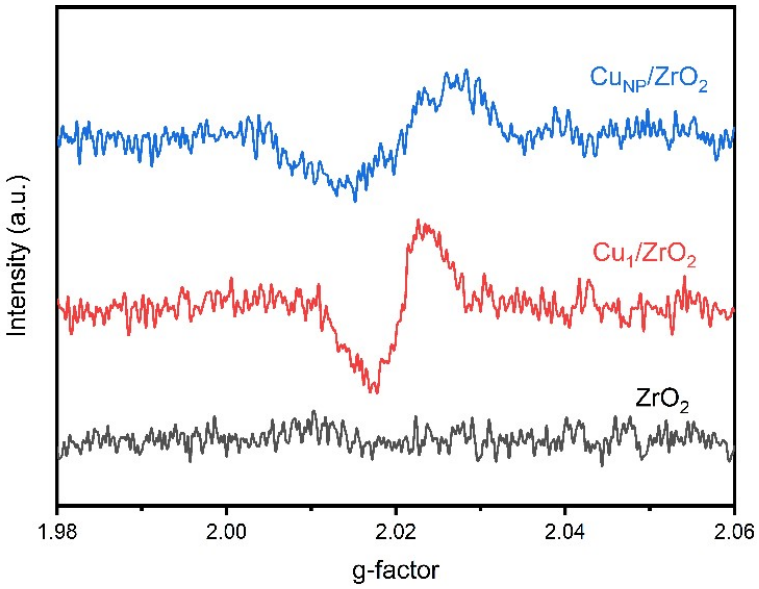

Fig. S8 The EPR results of ZrO_2, Cu_1/ZrO_2 and Cu_{NP}/ZrO_2.

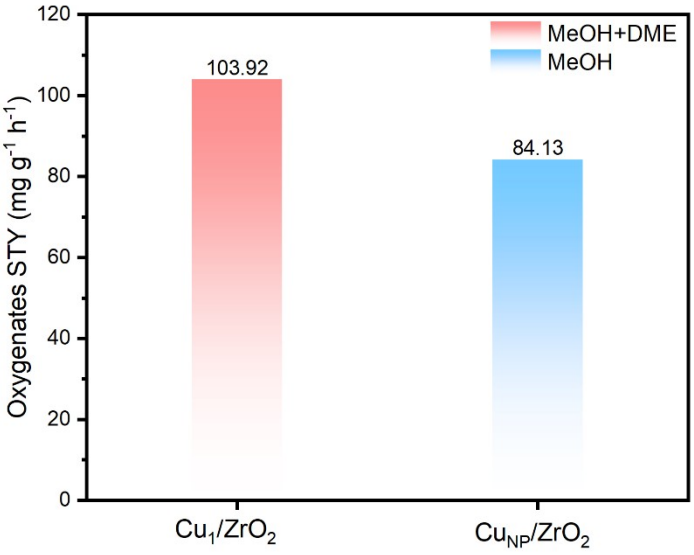

Fig. S9 Results of CO_2 hydrogenation over Cu_1/ZrO_2 and Cu_{NP}/ZrO_2 catalysts.

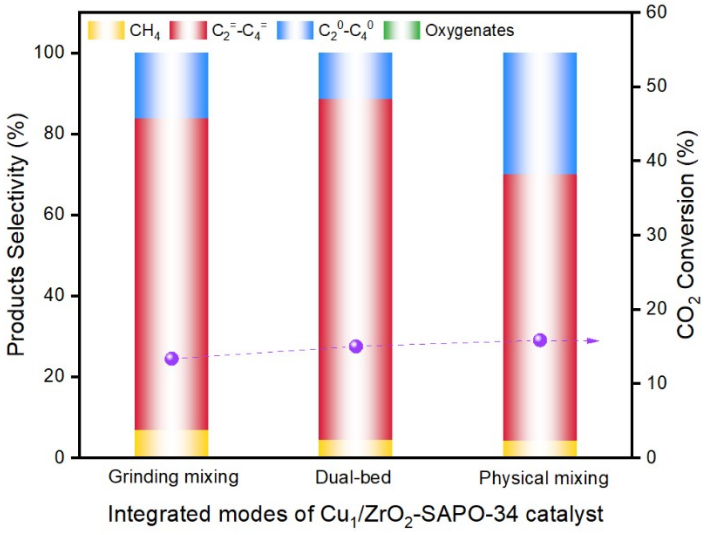

Fig. S10 Results of CO_2 hydrogenation over Cu_1/ZrO_2-SAPO-34catalysts with different integrated modes (Reaction conditions: 380ºC, 3.0 MPa and WHSV = 15000 mL g^{-1} h^{-1}).

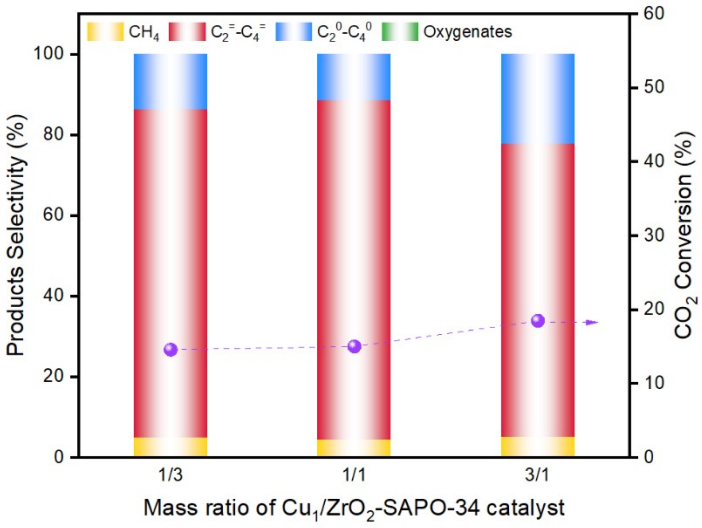

Fig. S11 Results of CO_2 hydrogenation over Cu_1/ZrO_2-SAPO-34 catalysts with different mass ratio (Reaction conditions: 380ºC, 3.0 MPa and WHSV = 15000 mL g^{-1} h^{-1}).

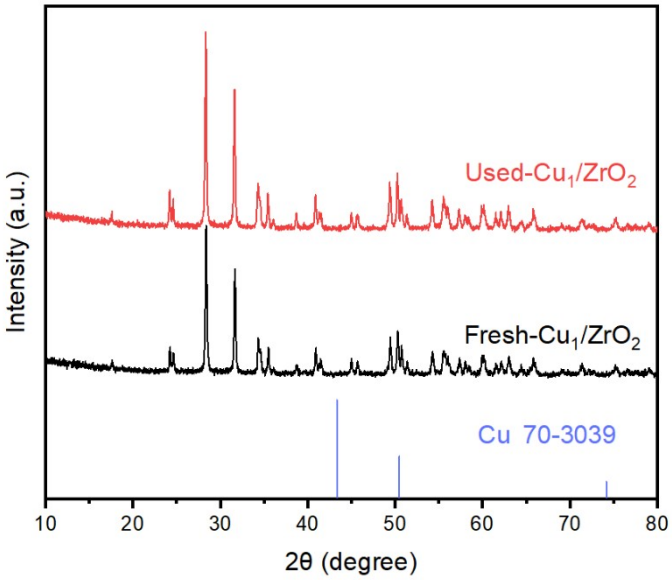

Fig. S12 XRD patterns of the fresh and used Cu_1/ZrO_2 catalysts.

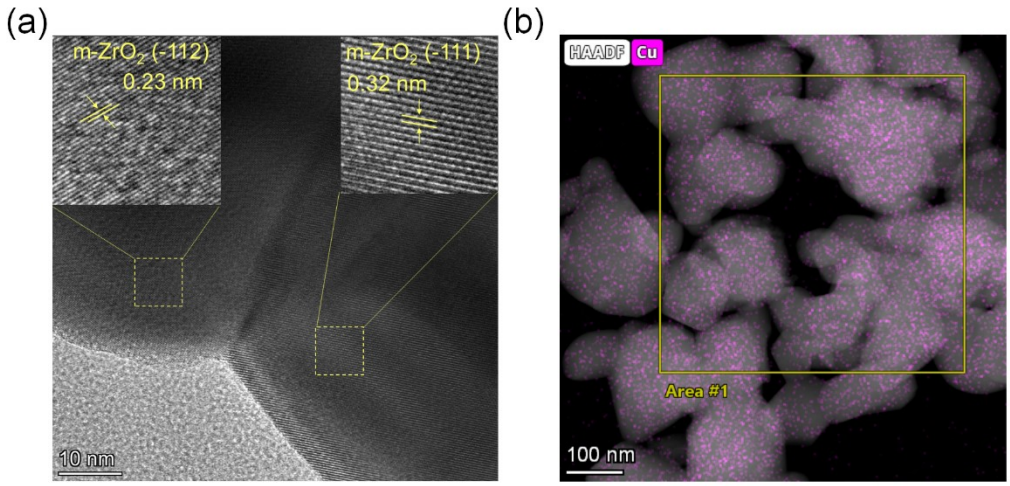

Fig. S13 HRTEM image (a) and EDS mapping image of Cu element (b) of spent 1.0wt% Cu_1/ZrO_2.

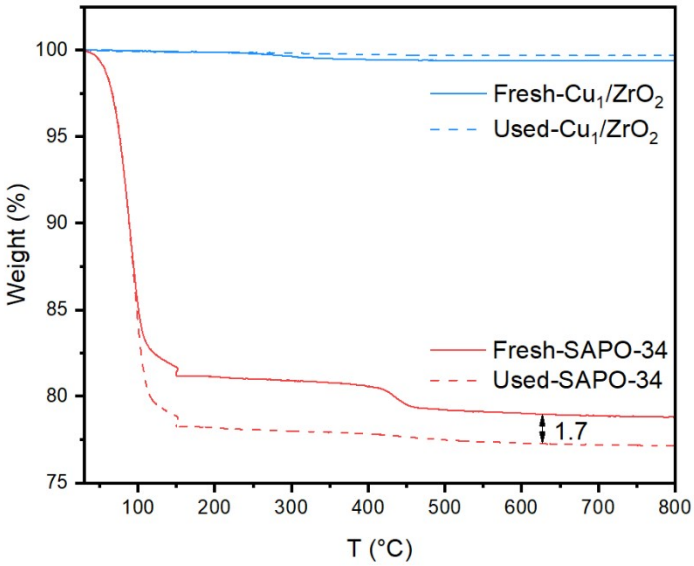

Fig. S14 TGA of fresh and used Cu_1/ZrO_2 as well as fresh and used SAPO-34 catalysts.

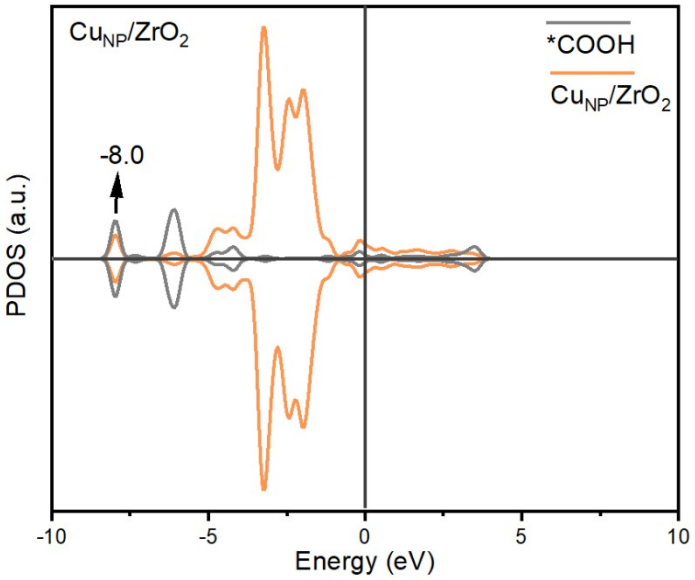

Fig. S15 DOS of *COOH adsorbed on Cu_{NP}/ZrO_2.

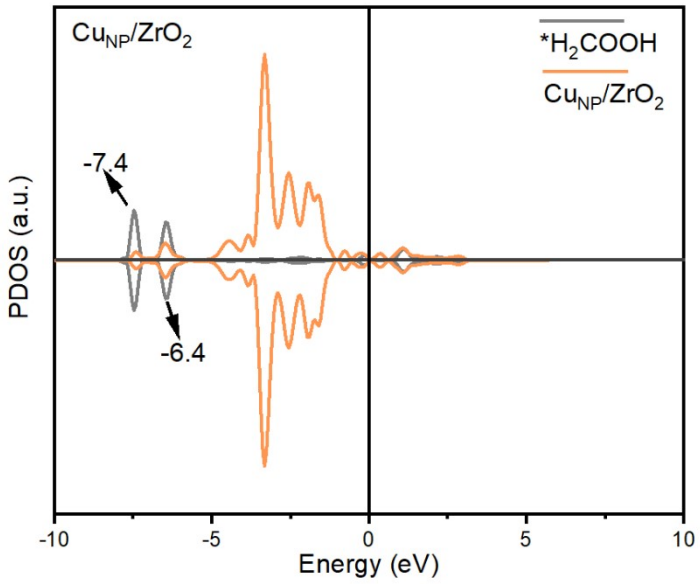

Fig. S16 DOS of *CH_3O adsorbed on Cu_{NP}/ZrO_2.

Table S1. Cu content of Cu/ZrO_2 catalyst.

Sample	Theoretical content (wt%)	Measured content (wt%)
1.0wt% Cu_1/ZrO_2	1.3	1.1
Cu_{NP}/ZrO_2	1.3	1.5

Table S2. Cu Dispersion of Cu_1/ZrO_2 and Cu_{NP}/ZrO_2 by N_2O Titration.

Sample	Cu dispersion (%)
1.0wt% Cu_1/ZrO_2	N.D.
Cu_{NP}/ZrO_2	53.8

N.D. represents not detected.

Table S3. Carbon balance (exclude carbon deposition) of the 1.0 wt% Cu/ZrO_2-SAPO-34 catalysts during reaction. Reaction conditions: 380ºC, 3.0 MPa and WHSV = 15000 mL g^{-1} h^{-1}.

Sample	Integrated mode	Total amount of carbon generated (mmol)	Total amount of carbon consumed (mmol)	Carbon balance (%)
Cu_1/ZrO_2-SAPO-34	Physical mixing	0.0300	0.0319	94.6
	Grinding mixing	0.0249	0.0267	93.4
	Dual-bed	0.0286	0.0300	95.3
Cu_{NP}/ZrO_2-SAPO-34	Dual-bed	0.0439	0.0466	94.2