

## Supporting Information

### Cu nanoparticles confined in siliceous MFI zeolite for methanol steam reforming

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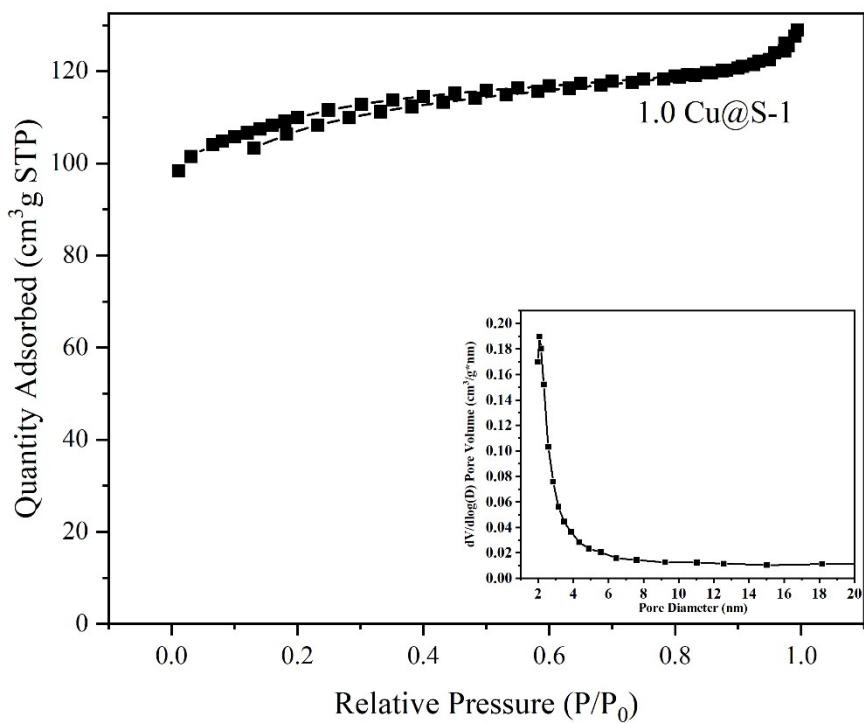


Fig. S1.  $N_2$  adsorption–desorption isotherms of 1.0 Cu@S-1

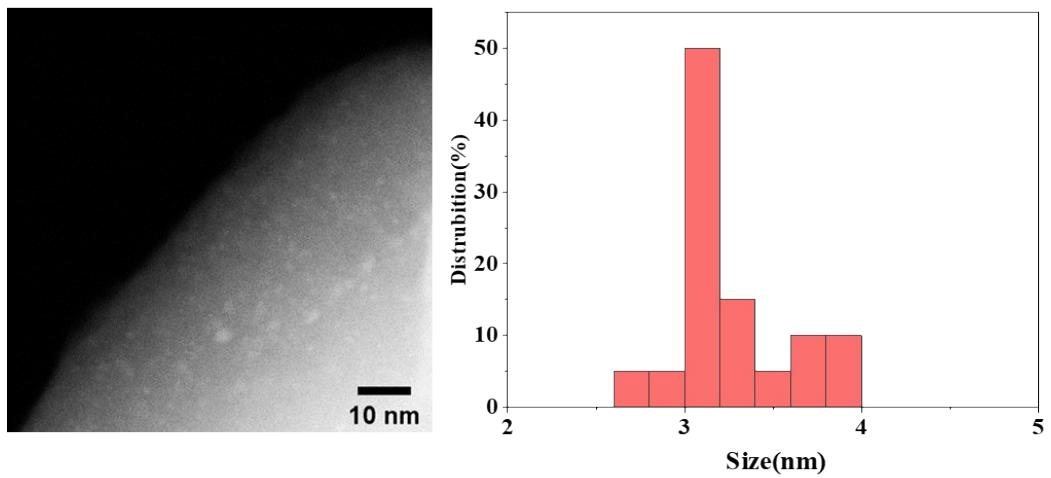


Fig. S2. HAADF-STEM image and corresponding Cu nanoparticles size distribution of the calcined 1.0 Cu/S-1

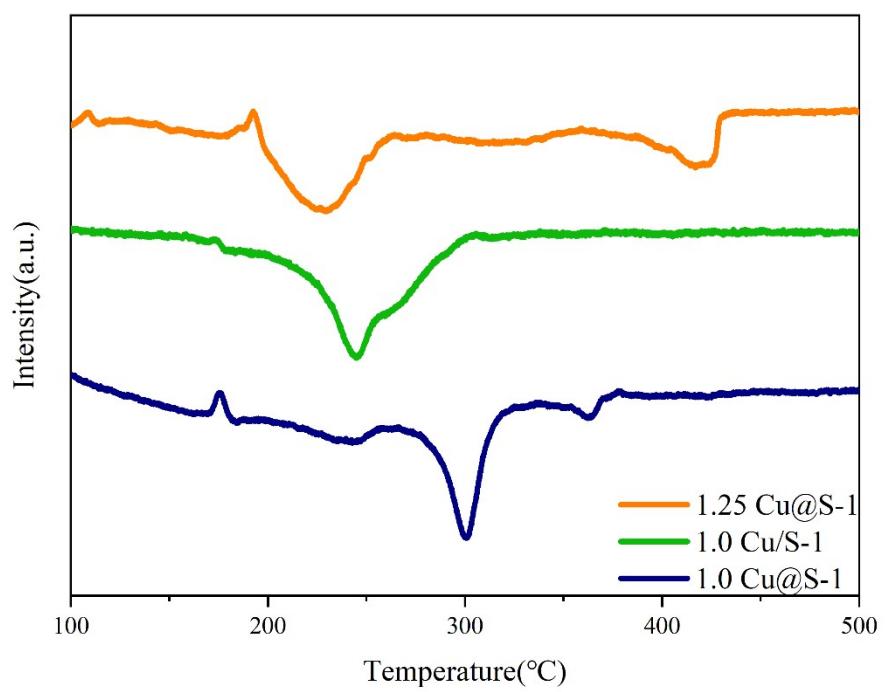


Fig. S3. H<sub>2</sub>-TPR profile of 1.0 Cu@S-1, 1.0 Cu/S-1 and 1.25 Cu@S-1

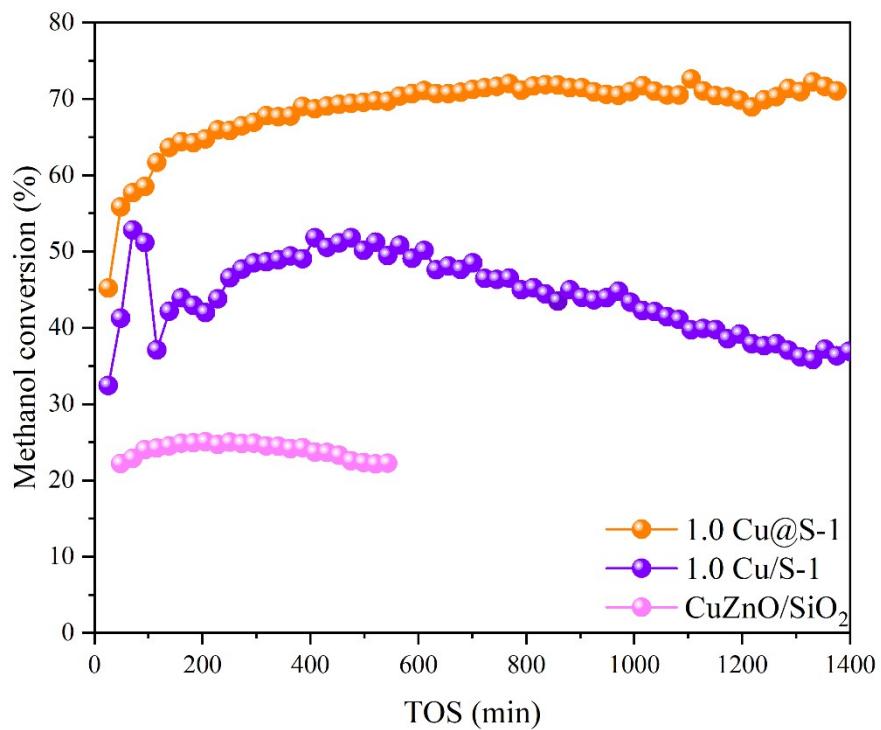


Fig. S4. Stability of 1.0 Cu@S-1, 1.0 Cu/S-1 and CuZnO/SiO<sub>2</sub> at 300°C (Reaction condition: 44% methanol, N<sub>2</sub> at a rate of 34 ml/min, WHSV = 4.55h<sup>-1</sup>, 1 atm.)

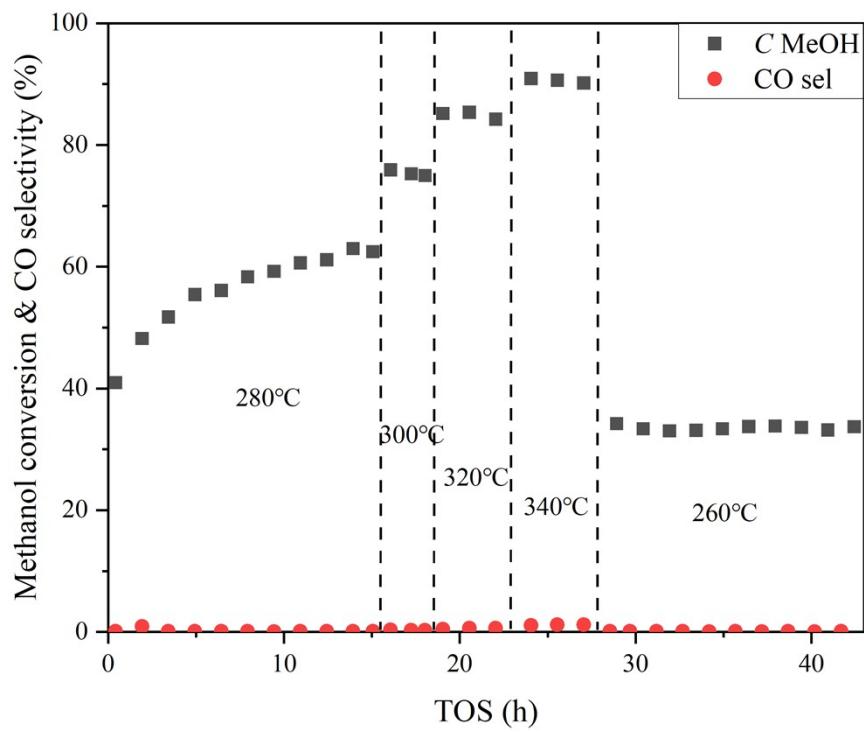


Fig. S5. TOS-dependent MSR performance of 1.0 Cu@S-1 catalyst under different temperature. (Reaction condition: 44% methanol, N<sub>2</sub> at a rate of 34 ml/min, WHSV = 4.55h<sup>-1</sup>, 1 atm.)

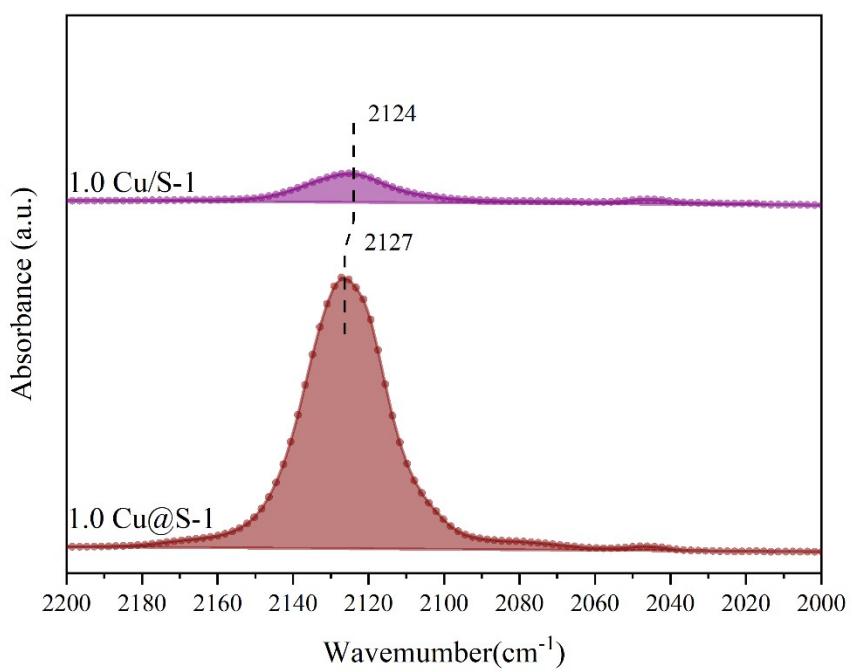


Fig. S6. *In-situ* CO-FTIR spectra of the reduced 1.0 Cu@S-1 and 1.0 Cu/S-1.

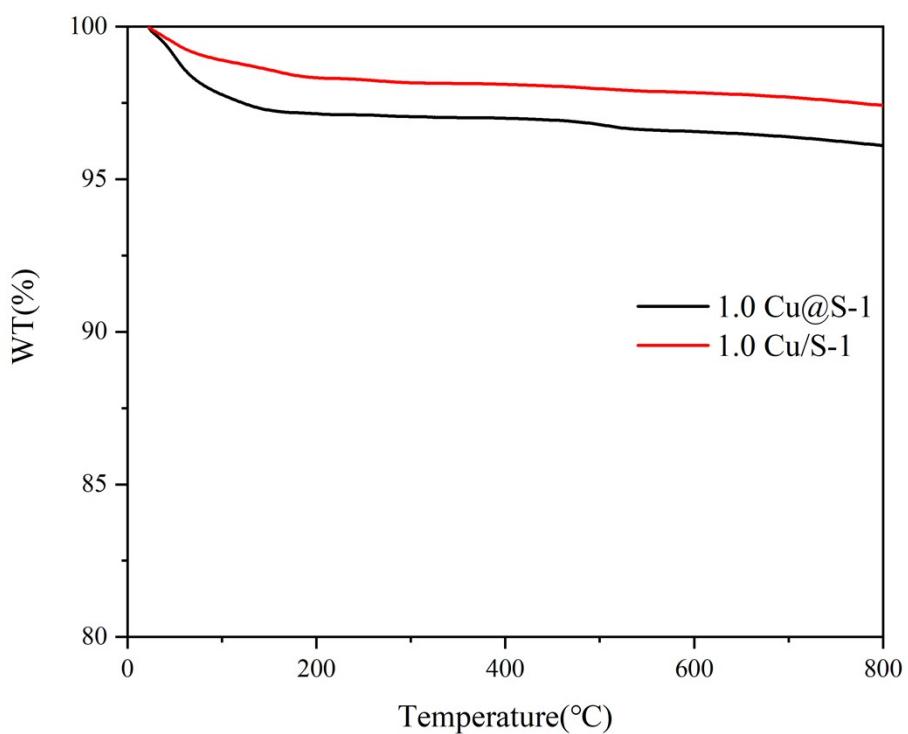


Fig. S7. TGA results of the spent 1.0 Cu@S-1 and 1.0 Cu/S-1

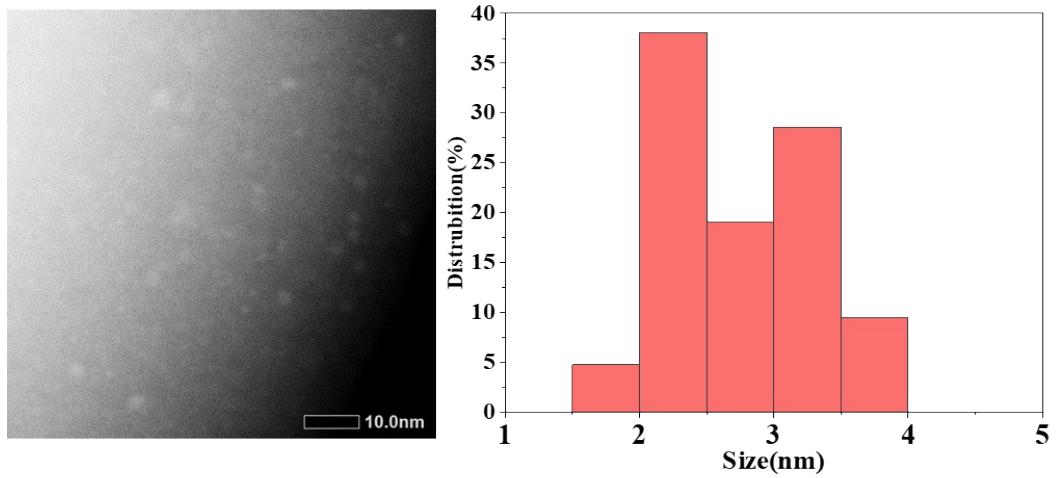


Fig. S8. HAADF-STEM image and corresponding Cu nanoparticles size distribution of the spent 1.0 Cu@S-1

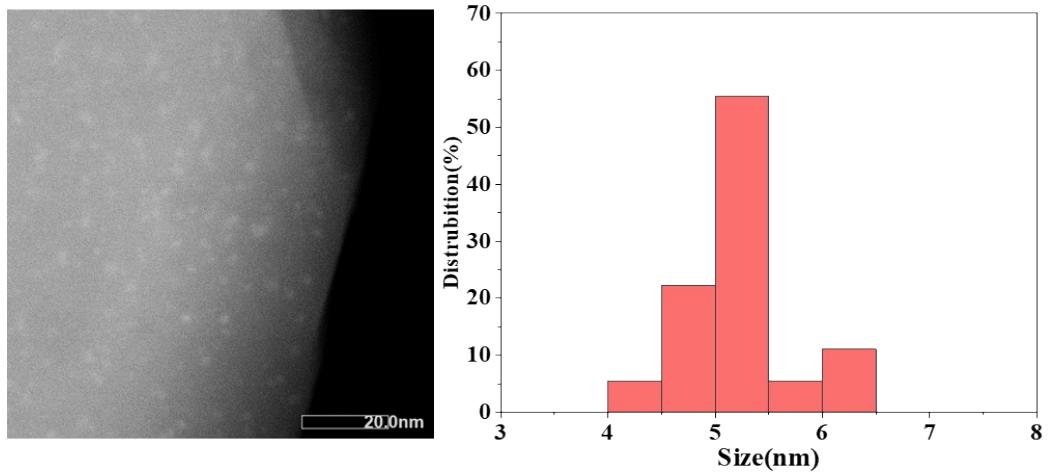


Fig. S9. HAADF-STEM image and corresponding Cu nanoparticles size distribution of the spent 1.0 Cu/S-1

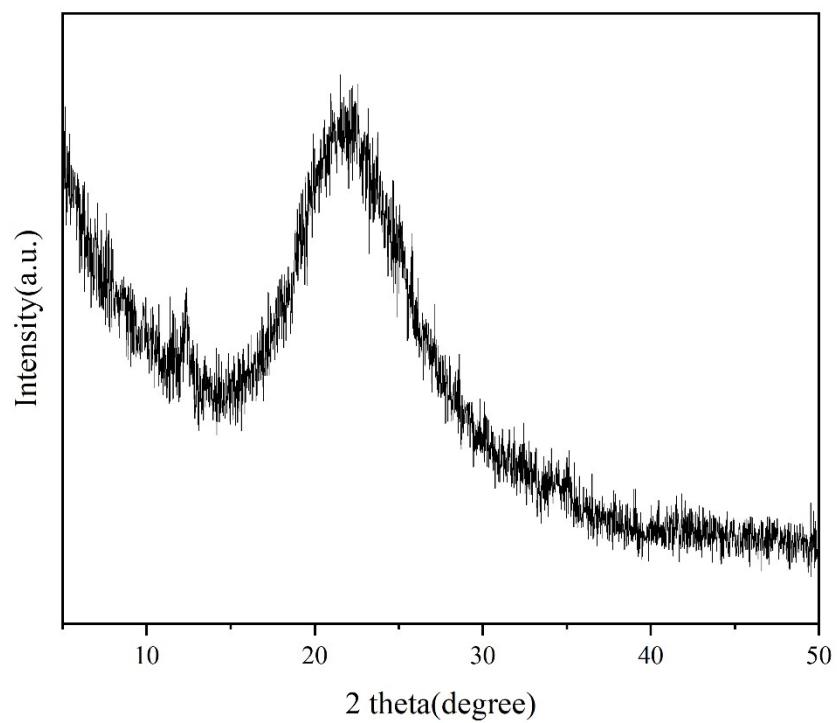


Fig. S10. The XRD pattern of the CuZnO/SiO<sub>2</sub>.

Table S1 Cu loading and BET surface of the as-synthesized catalyst

Sample	Cu loading wt% <sup>a</sup>	Surface area <sup>b</sup>		Pore volume		D <sub>Cu</sub> (%)
		S <sub>BET</sub>	S <sub>micro</sub>	V <sub>micro</sub>	V <sub>ext</sub>	
0.25 Cu@S-1	0.26	324	227	0.11	0.08	-
0.50 Cu@S-1	0.53	350	228	0.12	0.08	-
0.75 Cu@S-1	0.73	368	246	0.11	0.08	-
1.0 Cu@S-1	1.05/1.05 <sup>c</sup>	356	265	0.13	0.06	62.1
1.25 Cu@S-1	1.21	365	243	0.12	0.08	48.9
1.0 Cu/S-1	1.03	358	198	0.10	0.10	39.4
CuZnO/SiO <sub>2</sub>	1.18/1.18 <sup>d</sup>					

<sup>a</sup> Determined by XRF. <sup>b</sup> S<sub>BET</sub>: BET surface area, S<sub>micro</sub>: t-plot microporous surface area.

<sup>c</sup> Determined by ICP-OES analysis.

<sup>d</sup> the loading of Zn, determined by XRF