

Supporting Information for

Core–Shell Cu@(CuCo-alloy)/Al₂O₃ Catalysts for the Synthesis of Higher Alcohols from Syngas

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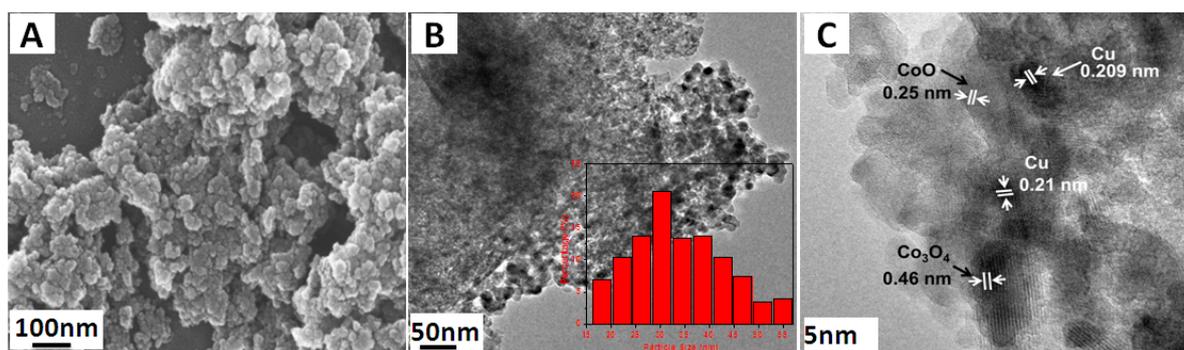


Fig. S1 (A) SEM image and (B, C) HRTEM images of the as-synthesized powdered-CuCo/Al₂O₃ (Cu/Co=1/2) sample. The inset in (B) shows the corresponding particle size distribution.

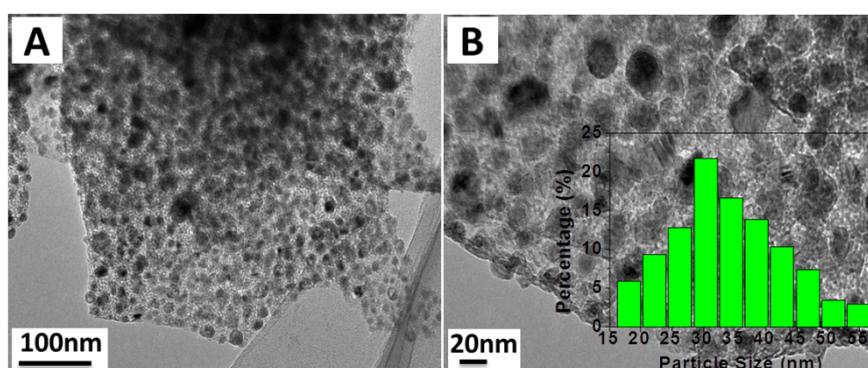


Fig. S2 HRTEM images of the used Cu@(CuCo-alloy)/Al₂O₃ (Cu/Co=1/2) catalyst. The inset shows the corresponding particle size distribution.

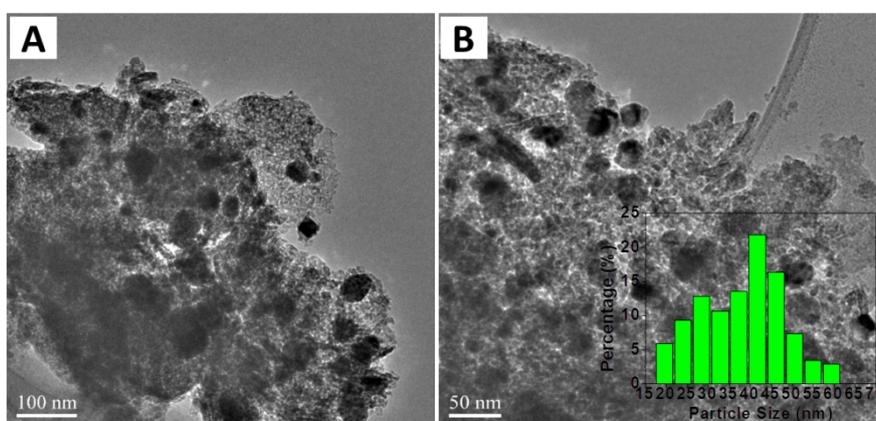


Fig. S3 HRTEM images of the used powdered-CuCo/Al₂O₃ (Cu/Co=1/2) catalyst. The inset shows the corresponding particle size distribution.

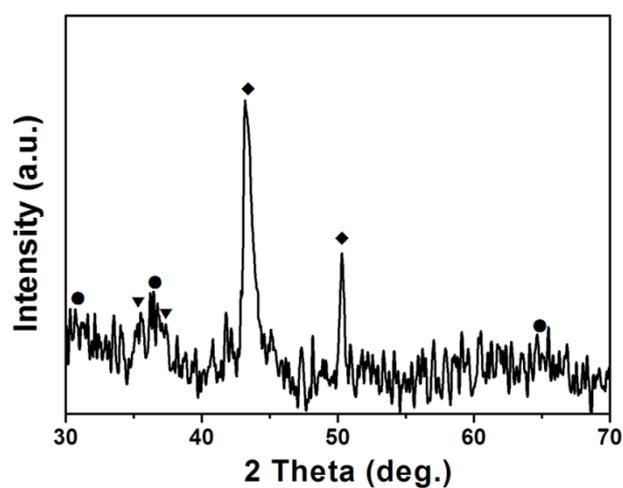


Fig. S4 XRD pattern of the used Cu@(CuCo-alloy)/Al₂O₃ (Co/Cu=1/2) catalyst. Crystalline phase: (◆) CuCo alloy, (▼) CuO, (●) Co₃O₄.

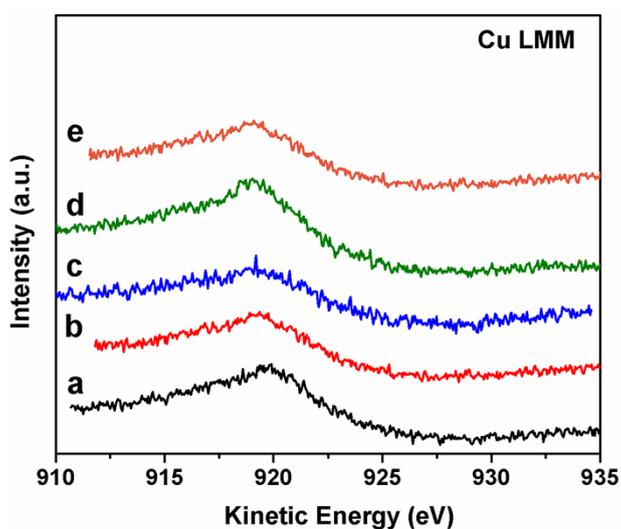


Fig. S5 Cu LMM XAES spectra of Cu/Al₂O₃ and Cu@(CuCo-alloy)/Al₂O₃ samples with various Cu/Co ratios: (a) Cu/Al₂O₃, (b) Cu/Co=5/1, (c) Cu/Co=2/1, (d) Cu/Co=1/2, (e) Cu/Co=1/5.

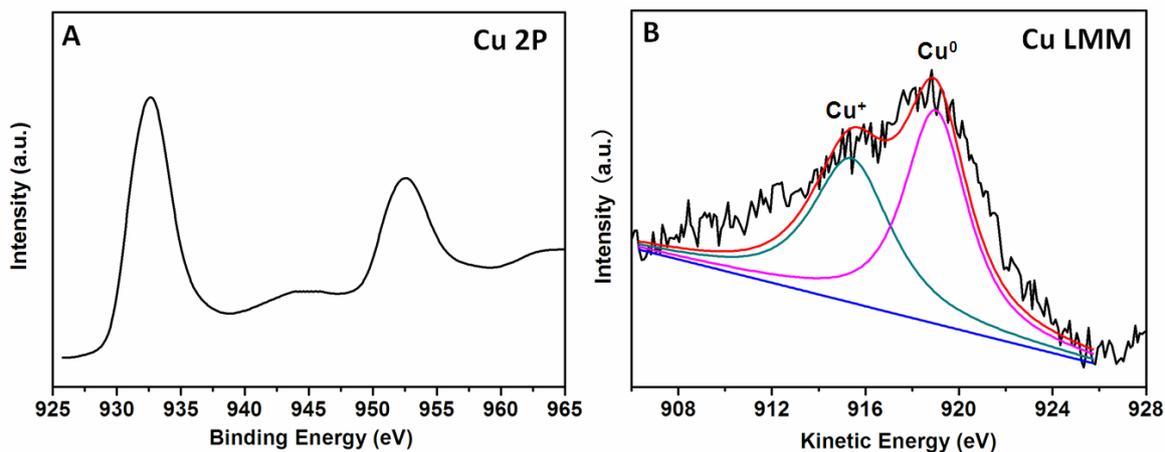


Fig. S6 Cu XPS spectra of the used Cu@(CuCo-alloy)/Al₂O₃ (Co/Cu=1/2) catalyst.

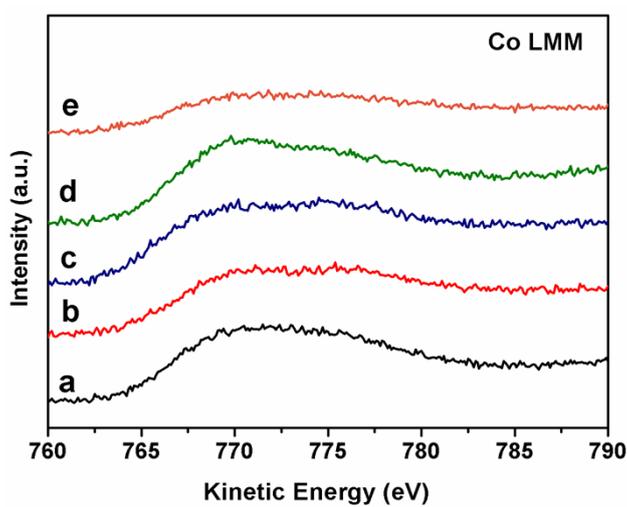


Fig. S7 Co LMM XAES spectra of Co/Al₂O₃ and Cu@(CuCo-alloy)/Al₂O₃ samples with various Cu/Co ratios: (a) Co/Al₂O₃, (b) Cu/Co=1/5, (c) Cu/Co=1/2, (d) Cu/Co=2/1, (e) Cu/Co=5/1.

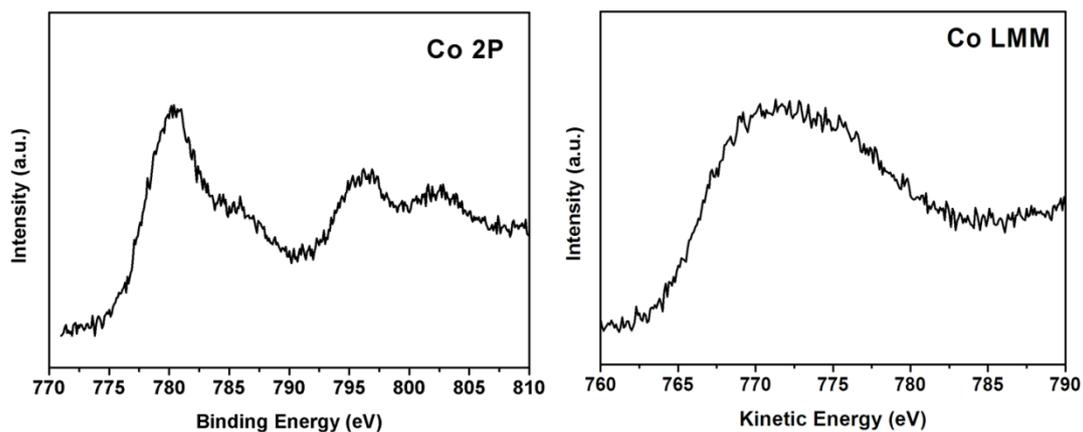


Fig. S8 Co XPS spectrum of the used Cu@(CuCo-alloy)/Al₂O₃ (Co/Cu=1/2) catalyst.

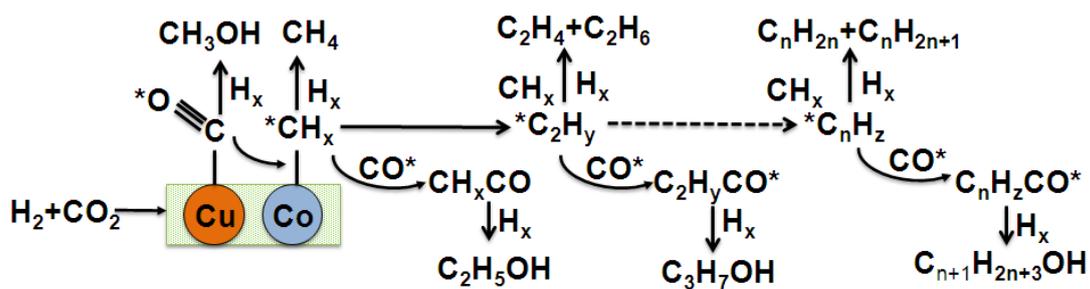


Fig. S9 Reaction pathway for CO hydrogenation over CuCo-based catalyst.¹⁻³

Table S1. The nominal and determined metal contents in the Cu@(CuCo-alloy)/Al₂O₃ samples with various Cu/Co ratios and the powdered-CuCo/Al₂O₃ (Cu/Co=1/2) sample

| Catalyst | Nominal ratio (Cu/Co) | Determined ratio (Cu/Co) | Metal content (wt.%) | |
|--|--------------------------|-----------------------------|----------------------|------|
| | | | Cu | Co |
| Co/Al ₂ O ₃ | – | – | – | 29.6 |
| Cu/Co (5/1) | 5/1 | 4.81/1.00 | 52.8 | 7.7 |
| Cu/Co (2/1) | 2/1 | 1.96/1.00 | 49.7 | 23.6 |
| Cu/Co (1/2) | 1/2 | 1.00/2.63 | 24.1 | 39.8 |
| Cu/Co (1/5) | 1/5 | 1.00/4.63 | 11.3 | 49.5 |
| Cu/Al ₂ O ₃ | – | – | 30.9 | – |
| powdered- CuCo/Al ₂ O ₃ (1/2) | 1/2 | 1.00/2.28 | 20.6 | 42.8 |

Table S2. Cu, Co 2p_{3/2} and Cu, Co LMM peak maximum and Modified Auger parameter (α')

| | Cu/Al ₂ O ₃ | Cu/Co (5/1) | Cu/Co (2/1) | Cu/Co (1/2) | Cu/Co (1/5) | Co/Al ₂ O ₃ | Used Cu/Co (1/2) |
|--|-----------------------------------|----------------|----------------|----------------|----------------|-----------------------------------|---------------------|
| Cu 2p _{3/2} peak Maximum E_b /eV | 931.9 | 932 | 932.1 | 932.2 | 932.4 | – | 932.3 |
| Cu LMM Auger peak Maximum E_k /eV | 919.4 | 919.3 | 919.18 | 919.03 | 918.8 | – | 918.9 |
| Modified Auger parameter (α')/eV | 1851.3 | 1851.3 | 1851.28 | 1851.23 | 1851.2 | – | 1851.2 |
| Co 2p _{3/2} peak Maximum E_b /eV | – | 781.2 | 780.0 | 780.1 | 780.3 | 780.9 | 780.5 |
| Co LMM Auger peak Maximum E_k /eV | – | 770.9 | 770.8 | 771.0 | 771.1 | 771.3 | 771.1 |
| Modified Auger parameter (α')/eV | – | 1552.1 | 1550.9 | 1551.0 | 1551.3 | 1552.2 | 1551.6 |

References:

- 1 J. J. Spivey and A. Egbibi, *Chem. Soc. Rev.*, 2007, **36**, 1514.
- 2 V. Subramani and S. K. Gangwal, *Energy Fuels*, 2008, **22**, 814.
- 3 K. Fang, D. Li, M. Lin, M. Xiang, W. Wei and Y. Sun, *Catal. Today*, 2009, **147**, 133.