Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Greener and facile synthesis of Cu/ZnO catalysts for CO_2 hydrogenation to methanol by urea hydrolysis of acetates

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Estimation of wastewater production

According to the study of Prieto et al. (Catal. Today, 2013, 215, 142–151.), the influence of washing on physical properties and catalytic performance has been thoroughly studied. The as-precipitated precursors were submitted up to 7 washing steps by resuspending the solid in deionized water, vigorously stirring the suspension for 5 min, and following by filtration of the solid. Each washing step required 50 mL/g dried solid and 7 steps are required to remove nitrate and sodium from precipitate and achieve highest catalytic performance. From that information, the amount of wastewater produced per amount of catalyst can be calculated as following (assuming 70% weight loss from calcination).

$$\text{Volume of wastewater} = 7\ \text{steps} \times \frac{50\ \text{L}}{\text{kg}_{\text{precipitate}} \cdot \text{step}} \times \frac{100\ \text{kg}_{\text{precipitated}}}{70\ \text{kg}_{\text{catalyst}}} = 500\ {}^{\text{L}}\!/_{\text{kg}_{\text{catalyst}}}$$

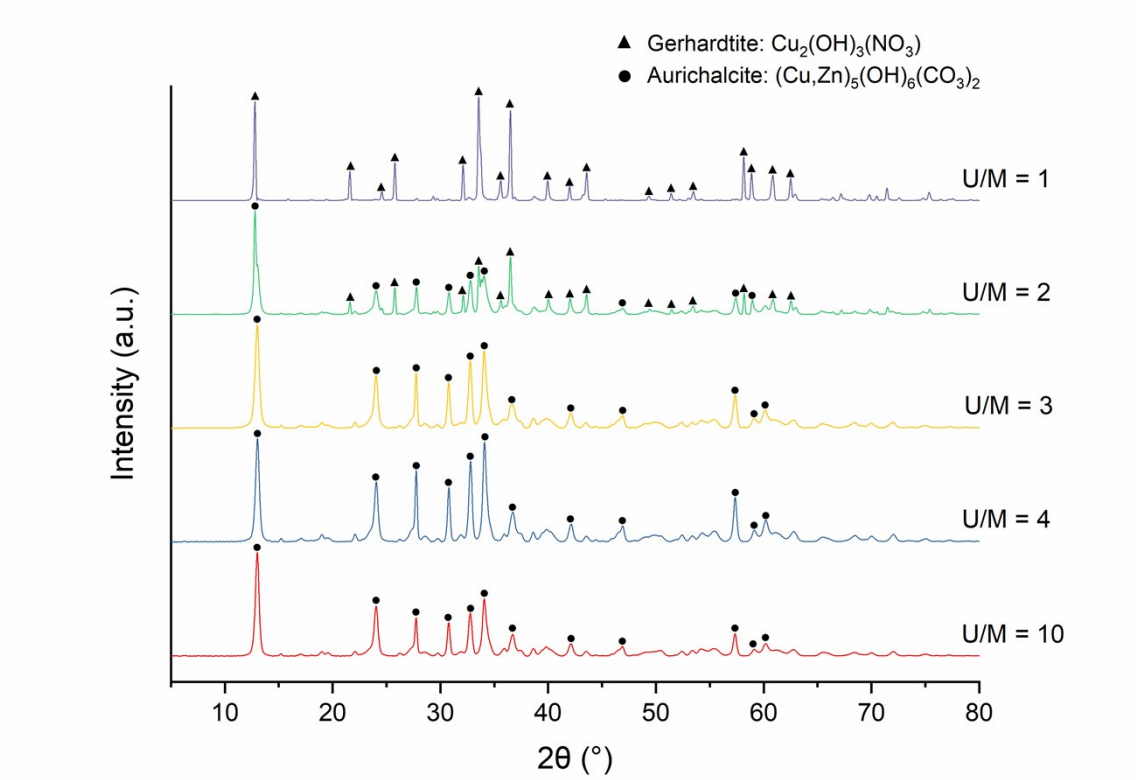

Figure S1. XRD patterns of the as-precipitated precursors and calcined Cu/ZnO catalysts (Cu:Zn = 1:1) prepared by urea hydrolysis of nitrate salts with various urea to metal molar ratios (U/M) of 1-10 and washing step at 95 °C

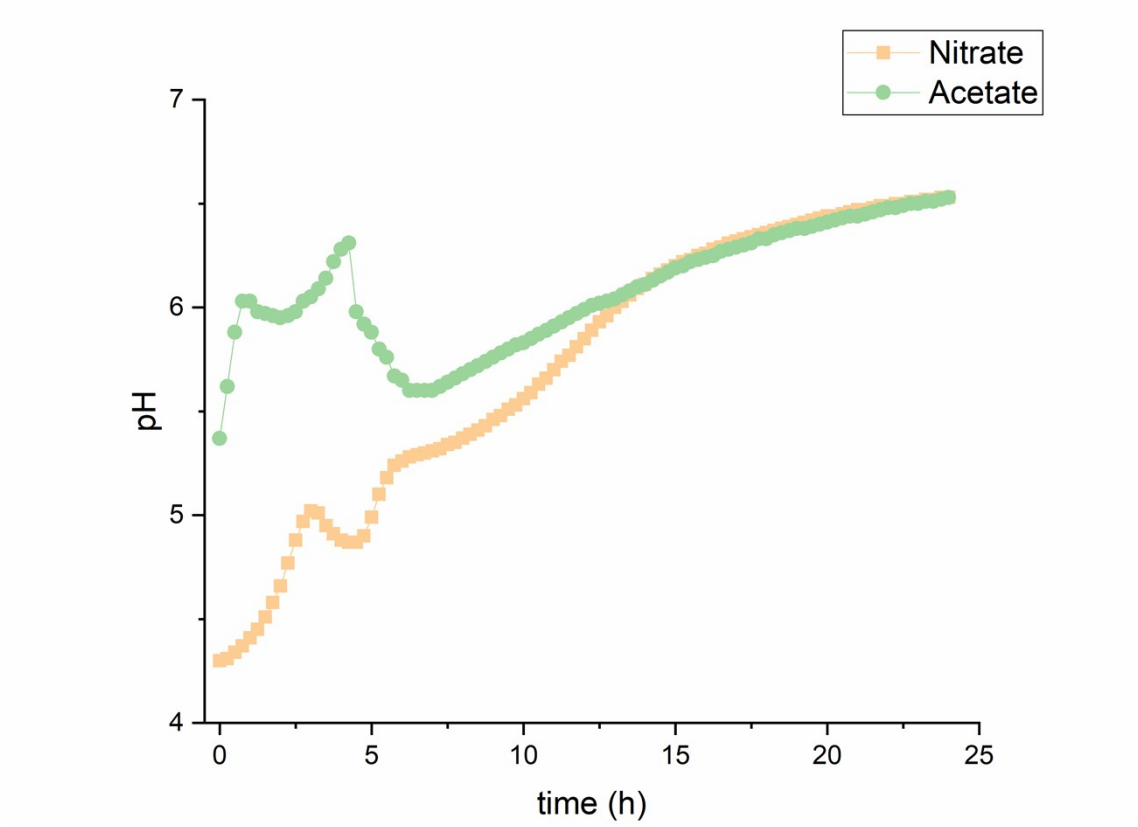

Figure S2. Evolution of the pH of the solution during synthesis of Cu/ZnO catalysts (Cu:Zn = 1:1) through urea hydrolysis of nitrate or acetate salts with urea to metal molar ratio (U/M) of 10 at 80 °C.

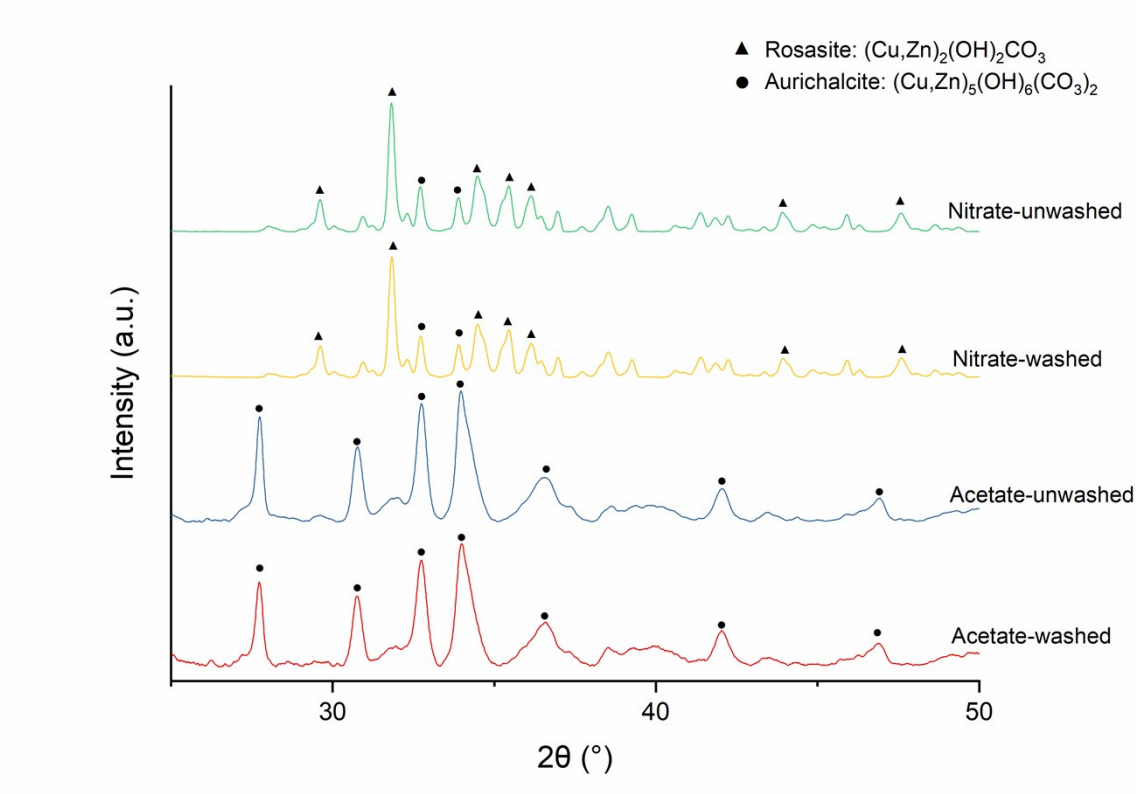

Figure S3. XRD patterns of as-precipitated precursors for Cu/ZnO (Cu:Zn = 1:1) prepared by urea hydrolysis of nitrate and acetate salts with urea to metal molar ratio (U/M) of 10 at 80 °C.

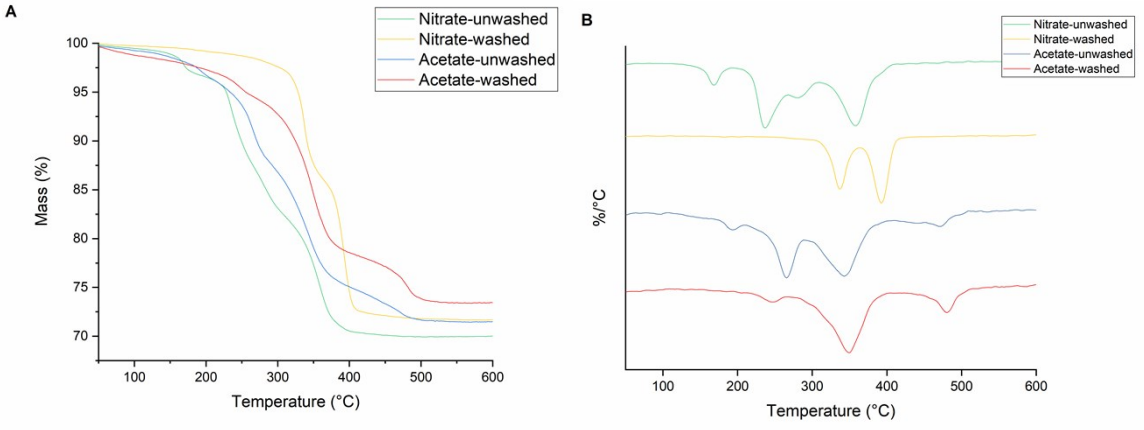

Figure S4. Thermogravimetric analysis (TGA) and differential thermal gravimetric (DTG) of washed and unwashed as-precipitated precursors derived from urea hydrolysis of nitrate and acetate metal salts with urea to metal molar ratio (U/M) of 10 at 80 °C. *T* = 30-600 ºC, ramp rate 10 ºC/min under air.

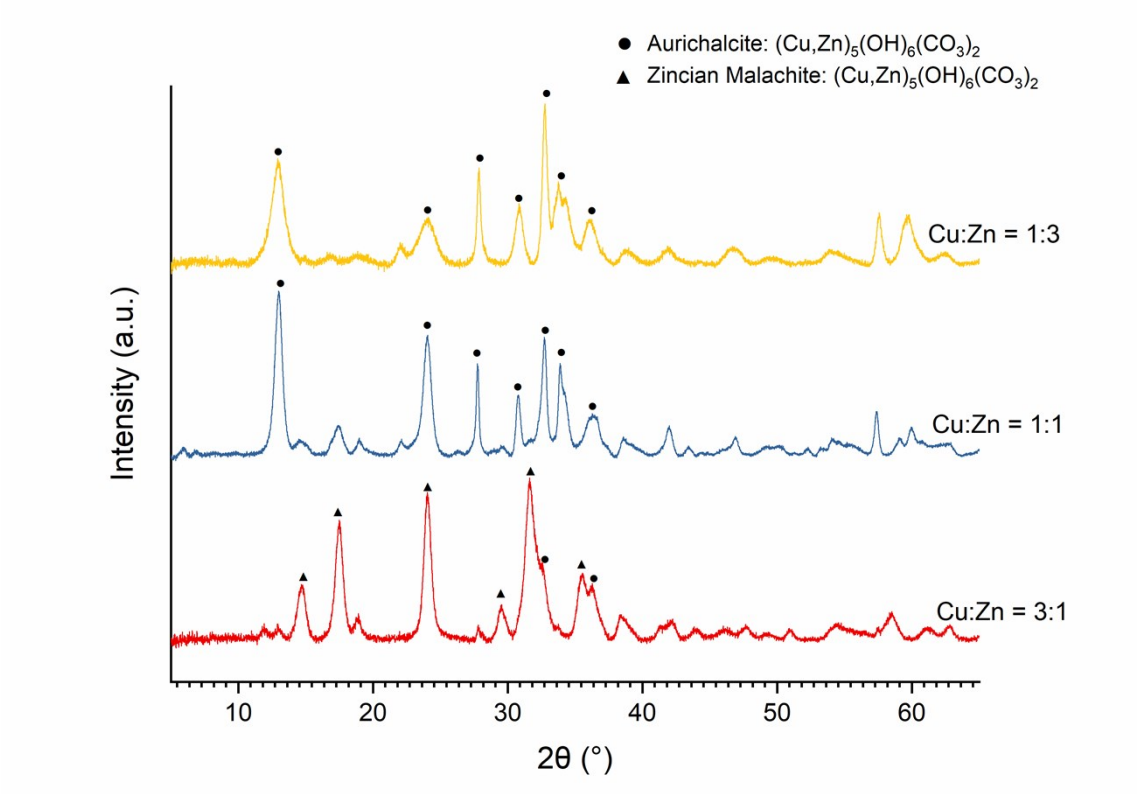

Figure S5. XRD patterns of as-precipitated precursors for Cu/ZnO with Cu:Zn of 1:3, 1:1 and 3:1 prepared by urea hydrolysis of acetate salts.

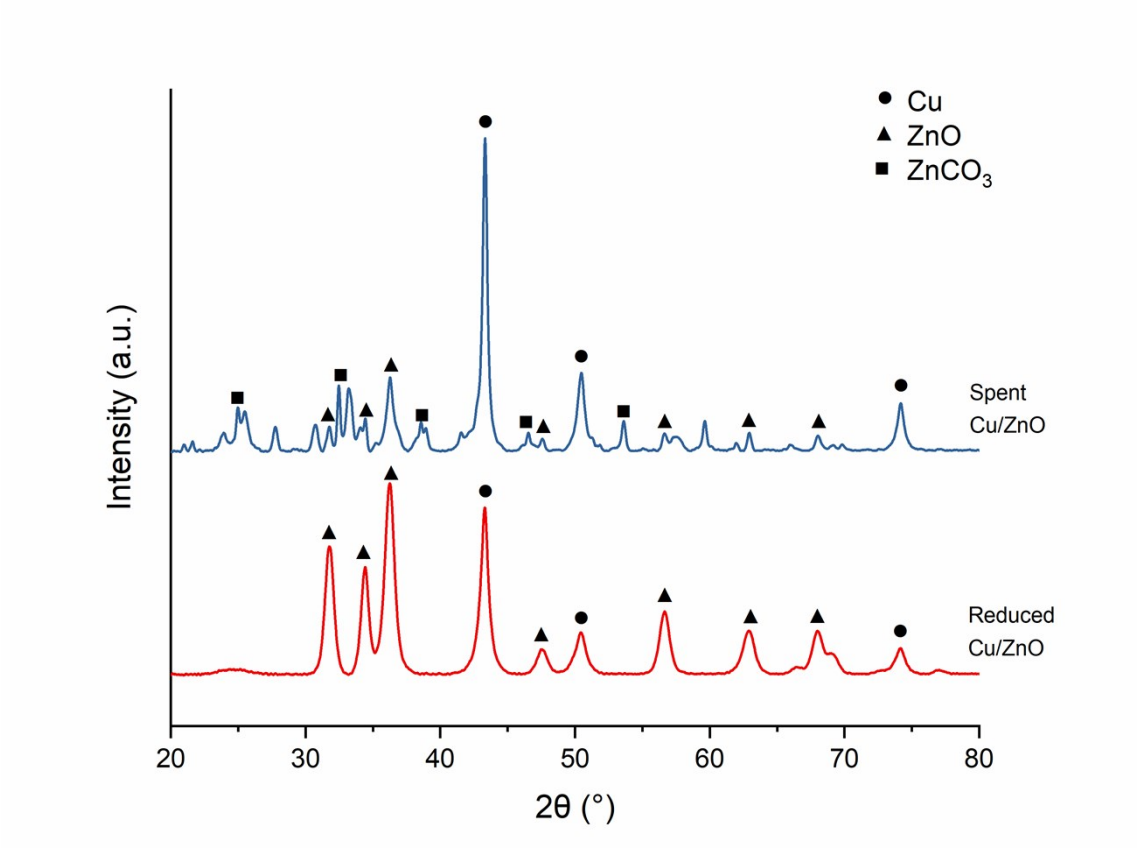

Figure S6. XRD patterns of Cu/ZnO (1:1) catalyst prepared by urea hydrolysis of acetate salts without washing step after reduction and stability test. H_2/CO_2 = 3, *T* = 280 °C, *P* = 331 bar, and GHSV 17,000 h^{-1}.

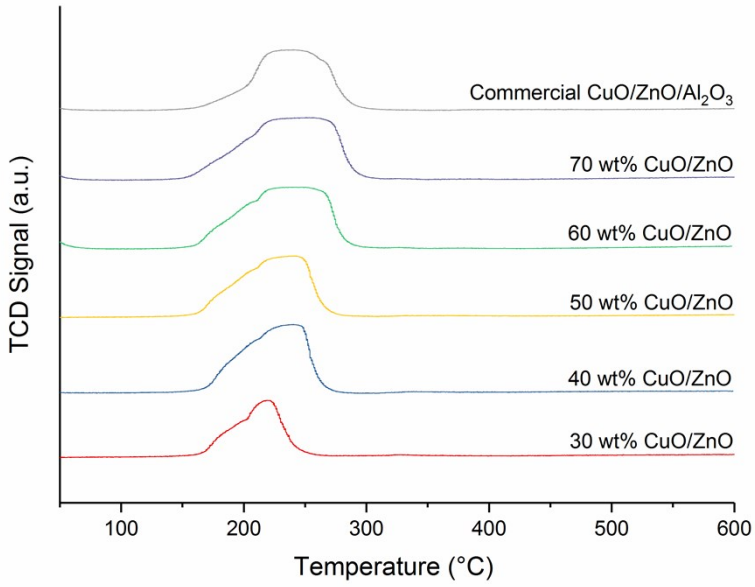

Figure S7. H_2-TPR profiles of the CuO/ZnO catalysts with various Cu contents.

Reduction conditions: 5% H_2/N_2, F = 20 mL/min, T = 50-600 °C and Ramp rate = 2 °C/min.

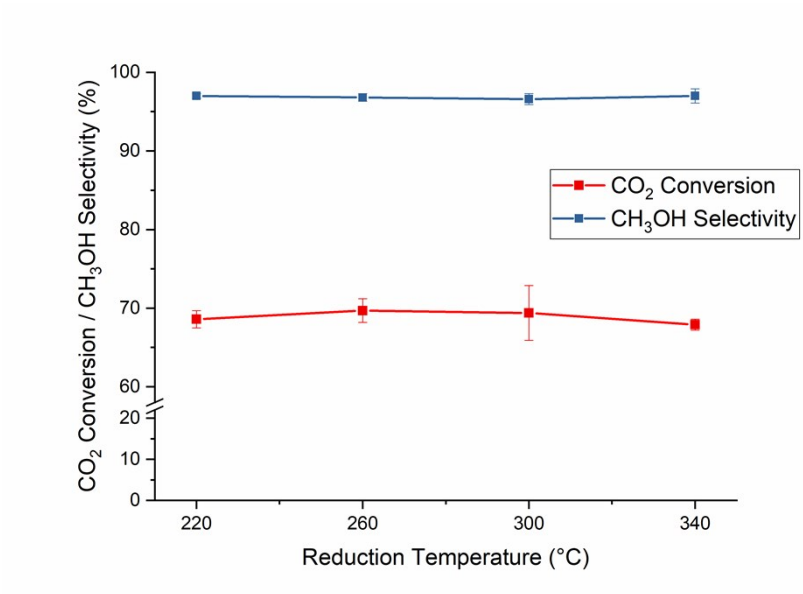

Figure S8. Effect of reduction temperature on catalytic activity of the Cu/ZnO (1:1) catalyst. Reduction conditions: 90% H_2/Ar, F = 20 mL/min, and T = 220-340 °C. Reaction conditions: H_2/CO_2 = 3, T = 260 °C, P = 331 bars, GHSV = 8500 h^{-1}, and TOS = 6 h.