

Electronic supplementary information (ESI) for Chemical Communications

Heterogeneous Selective Hydrogenation of Ethylene Carbonate to Methanol and Ethylene Glycol over a Copper Chromite Nanocatalyst

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1. Experimental details

1.1. Materials

Hydrogen (99.999%) was supplied by Beijing Haikeyuanchang Utility Gas CO., LTD (China). Pt/C (5.0 wt%), Ru/C (5.0 wt%), Rh/C (5.0 wt%) and Pd/C (5.0 wt%) were purchased from Alfa Aesar. Raney Ni was obtained from Shandong Jiahong Chemical CO. LTD (China). Raney Cu was purchased from Dalian Tongyong Chemical CO. LTD (China). Ethylene carbonate (Alfa, 99%), THF (Acros, 99.85%, Extra Dry) were used for catalysis tests. Other reagents were of analytical grade and used without further purification.

1.2. Preparation of the copper chromite catalyst

$K_2Cr_2O_7$ (4 mmol), $Cu(NO_3)_2 \cdot 2H_2O$ (8 mmol) and acrylamide (16 mmol) were dissolved in of water (150 ml). The solution was transferred into a 200ml teflon-lined autoclave, which was sealed and maintained at 160 °C for 12 h. The system was then

allowed to cool to room temperature, and a light-green precursor was collected at the bottom of the vessel. After being washed by water and dried, the precursor was calcined at 500 °C for 3 h. The resulting black copper chromite powder was washed by hydrochloric acid (1 M) to remove CuO on the copper chromite surface.

1.3. Characterization of the copper chromite catalyst

Scanning electron microscopy (SEM) was taken on a LEO-1530 field emission scanning electron microscope and the sample was prepared by pasting the copper chromite powder on a conductive adhesive tab directly. The powder X-ray diffraction (XRD) patterns were recorded with a Bruker D8-advance X-ray powder diffractometer with Cu K α ($\lambda = 1.5406 \text{ \AA}$) at an accelerating potential of 40 kV and a tube current of 40 mA. FT-IR spectrum was recorded from KBr pellet on a PerkinElmer Spectrum One FT-IR spectrometer.

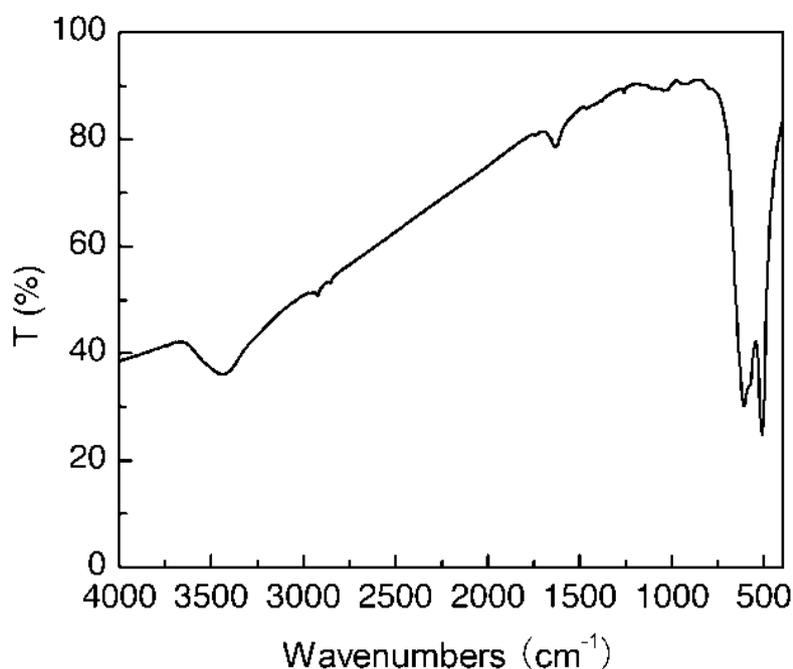


Fig. S1 FT-IR spectrum of the prepared copper chromite catalyst.

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was measured by a Thermo fisher X2. The copper chromite catalyst was analyzed by

energy-disperse X-ray spectroscopy (EDX, Oxford Instrument). X-ray Photoelectron Spectroscopy (XPS) was acquired using a Thermo fisher ESCALAB 250Xi spectrometer equipped with a monochromatic Al X-ray source. The binding energy scales for the samples were referenced by setting the C 1s binding energy of contamination carbon to 284.8 eV.

Table S1 Compositional analysis of the prepared copper chromite catalyst

Analysis method	Theoretical value	ICP-AES	EDX	XPS
Cu (wt.%)	27.45	28.42	29.36	-
Cr (wt.%)	44.91	42.31	42.93	-
Cu/Cr (atom ratio)	0.50	0.55	0.56	0.49

Hydrogen temperature-programmed reduction experiment (H₂-TPR) is an ideal tool to examine the reducibility of a solid oxide catalyst. H₂-TPR was carried out on a chemical adsorption analyzer (Micromeritics ChemiSorb 2720 apparatus). Before the TPR measurement, 0.1 g of the catalyst was first treated in a N₂ flow of 30 mL/min at 300 °C for 0.5 h in a quartz fixed-bed U-shaped microreactor (i.d. = 4 mm). After cooling to RT in the same atmosphere, the pretreated catalyst was exposed to a flow (50 mL/min) of 10% H₂-90% Ar (v/v) mixture and heated at a ramp of 10 °C/min to 1000 °C. The alteration in H₂ concentration of the effluent was monitored on-line by the chemical adsorption analyzer. As illustrated in Fig. S2, the reduction of the sample underwent in two steps: one in the range of 170-300 °C and the other in the range of 300-600 °C. The first reduction peak in the low-temperature range (212 °C) were due to the stepwise reduction of surface Cu²⁺ and Cu⁺ species in different local coordination environments to Cu⁰, whereas those in the high-temperature region (377

°C) with a shoulder at 519 °C were due to the reduction of bulk CuCr_2O_4 as well as Cr_2O_3 ¹⁻³:

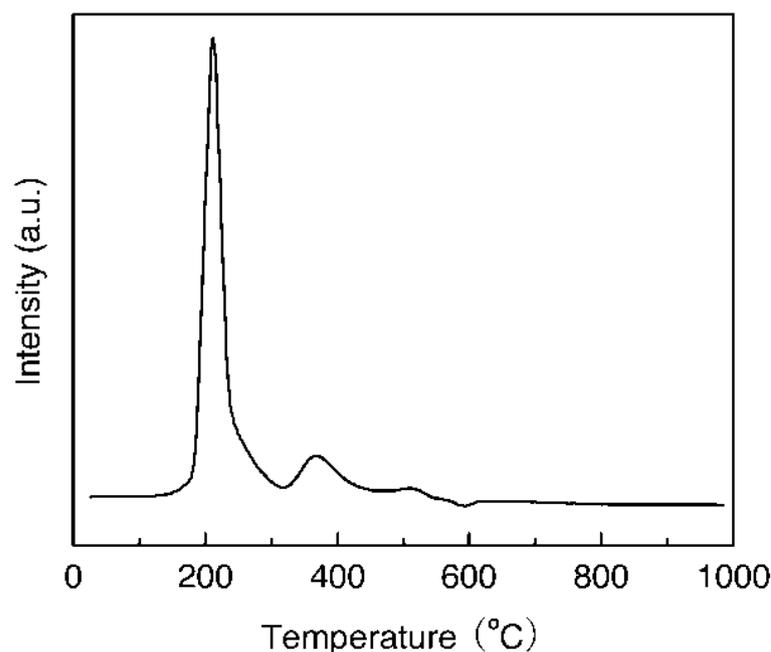
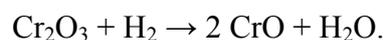


Fig. S2 H_2 -TPR profile for the prepared CuCr_2O_4 catalyst.

1.4. Catalytic hydrogenation of ethylene carbonate

Before catalysis tests, the copper chromite catalyst has been pretreated with H_2 (5 vol% in N_2) at 300 °C for 2 h. In a typical experiment, catalyst (0.5 g), ethylene carbonate (10 mmol) and THF (20 ml) were sealed in a 50-ml stainless steel autoclave. After being flushed with H_2 , the autoclave was charged with 5.0 MPa H_2 and then heated up to 180 °C. Hydrogenation reaction was carried out at 400 rpm mechanical agitation, followed by cooling in an ice-water bath. The reaction mixture with p-xylene (100 μl) as the internal standard was analyzed using a gas chromatograph equipped with a DB-WAX capillary column (Φ 0.25 mm \times 30 m) and a

flame ionization detector (FID). Reactants and products are identified by comparison with authentic samples or GC-MS coupling (Agilent 7980A).

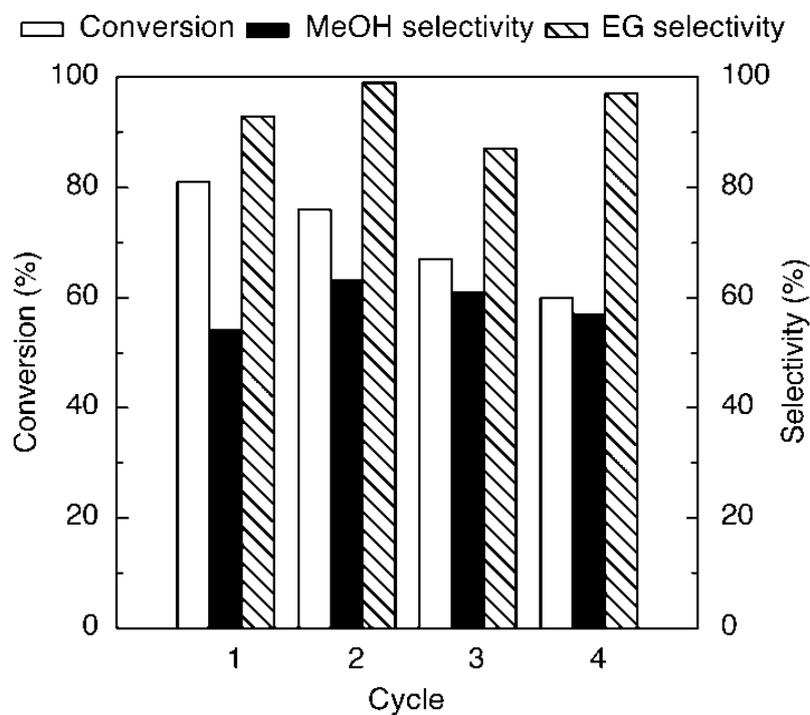


Fig.S3 Reusability of the CuCr_2O_4 catalyst for the hydrogenation of EC.

References

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