Supporting Information

Fabrication and Kinetics of Cu/MgO Catalysts for Selective Hydrogenation of Methyl Benzoate to Benzyl Alcohol

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1. Characterization of Catalysts

1.1. Inductively Coupled Plasma Emission Spectroscopy

Using inductively coupled plasma optical emission spectrometry (ICP-OES) to analyze the elements in catalysts. Before testing, the sample (about 5 mg) is dissolved in a small amount of concentrated nitric acid, allowing the catalyst to completely dissolve in the strong acid solution. The above solution is then diluted with deionized water to bring the measured elements to a concentration between 1 and 10 ppm. During testing, qualitative analysis is performed using characteristic spectral lines, and quantitative analysis is conducted using the standard curve method.

1.2. X-Ray Diffraction

Using an X-ray diffractometer (XRD, D8 Advanc, Bruker AXS) to analyze the crystal structure and phase of the catalyst and its precursors. Prior to testing, the sample was ground finely. A small amount of the sample was placed on the sample stage and flattened with a coverslip. During testing, Cu Kα radiation was used (λ=0.15406 nm) with tube voltage and tube current set at 40 kV and 4 mA, respectively. The 2θ range of the sample measurement was 10−80º with a step size of $0.1^{\circ} \cdot s^{-1}$. The results were analyzed using Jade 6 and compared with the XRD standard card.

1.3. Low-Temperature Nitrogen Adsorption-Desorption

Using low-temperature nitrogen adsorption-desorption analyzer to determine the textural properties of the Cu/MgO catalysts prepared and that recovered after the 6th cycle of catalytic test. The measurements of specific surface area, average pore volume, and average pore size were carried out using a multi-purpose adsorption analyzer

(ASAP 2020 HD88, Micromeritics). The samples were first degassed at 200 ℃ under a nitrogen atmosphere for 4 hours, and then their adsorption performance was tested at -196 ℃ in liquid nitrogen. The calculation of specific surface area was based on the Brunauer Emmett Teller (BET) isotherm equation, and the pore size distribution and pore volume were calculated using the Barrett-Joyner-Halenda (BJH) equation.

1.4. Scanning Electron Microscope

Using a Z5 type field emission scanning electron microscope (SEM) to observe the morphology characteristics of the catalyst. The sample is placed flat on a conductive adhesive-coated holder, and the catalyst surface is sprayed with gold in vacuum. The gold spraying time is about 35 seconds, and the samples are observed under a voltage of 5 kV to examine the surface morphology.

1.5. Transmission Electron Microscope

A model transmission electron microscope (TEM, Tecnai 12, Philips) is used to test the morphology of catalysts, with a maximum magnification of 650,000 times, a point resolution of 0.24 nm, and a line resolution of 0.14 nm. Before testing, the catalyst is finely ground and sieved through a 270-mesh screen. A small amount of powder is dispersed in anhydrous ethanol, ultrasonicated for 3 minutes to fully disperse. A small amount of liquid is transferred using a pipette, dropped onto a copper grid, dried under a red light, and then observed after sampling. Adjust the accelerating voltage and magnification according to the testing requirements.

1.6. High-Resolution Transmission Electron Microscopy Analysis

The lattice and elemental distribution of catalysts were tested using the Tecnai G2

F30 S-TWIN field emission transmission electron microscope from FEI company (USA). The accelerating voltage range is 50−300 kV, with a maximum magnification of 1,000,000 times for HRTEM, 3,000,000 times for STEM, a point resolution of 0.20 nm, a line resolution of 0.10 nm, and an information resolution of 0.14 nm. The method of sample preparation is the same as that of transmission electron microscopy.

1.7. H_2-Programmed Reduction

Hydrogen temperature-programmed reduction (H_2-TPR) was performed in a self-built fixed-bed flowing reactor (inner diameter: 4 mm, stainless steel U-tube) with a mass spectrometer (Omnistar, Pfeifer). About 200 mg of catalyst (40−60 mesh) was first heated at 150 °C for 30 min under 70 ml•min^{-1} of N_2. H_2-TPR profile was recorded from 30 to 950 °C with a heating rate of 5 °C min^{-1} under a 30% H_2/N_2 (v/v) flow of 100 ml•min^{-1}. The effluent gas was streamed to the mass spectrometer after passing through a cold trap to condense water vapor, and H_2 consumption was determined by the mass spectroscopy detector (MD).

1.8. CO_2-TPD

Population and strength of the surface basicity of the catalysts were analyzed by temperature programmed desorption of CO_2 (CO_2-TPD). The catalyst (ca. 200 mg) was pretreated in argon flow at 400 ºC for 4 h before every analysis. The sample was then adsorbed using CO_2 until saturation after cooling to 50 ºC. Then, the sample was subsequently flushed with argon at 50 ºC for 1 h to remove the physisorbed CO_2. TPD analysis was carried out from 50 ºC to 700 ºC at a ramp of 10 ºC/min and recorded with a thermal detector (TCD).

1.9. NH_3-TPD

The surface acidity of the catalysts was determined by temperature programmed desorption of NH_3 (NH_3-TPD). The catalyst (ca. 200 mg) was pretreated in argon flow at 400 ºC for 4 h before every analysis. The sample was then adsorbed using NH3 until saturation after cooling to100 ºC. Then, the sample was subsequently flushed with argon at 100 ºC for 1 h to remove the physisorbed NH3. TPD analysis was carried out from100 ºC to 700 ºC at a ramp of 10 ºC/min and recorded with a thermal detector (TCD).

1.10. X-Ray Photoelectron Spectroscopy Analysis

An X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo Scientific) to analyze the electronic state of the catalyst surface. Before testing, the sample was glued to the sample stage with double-sided adhesive tape. During the test, an Al target was used as the excitation source, with a target accelerating voltage of 1.5 kV, a working current of 15 mA, an analysis chamber vacuum of about 1.0×10^{-9} mbar, and a testing depth of approximately 3 nm. After the test, data was analyzed using the software Casa XPS.

2. Supplementary results

Table S1 CO_2 Desorption peak areas of Cu/MgO-0.8 and Cu/MgO-0.8-R_6 catalysts.

Catalyst	Peak area[a] (A·°C×10^{-12})		
	I (120–300 °C)	II (300–550 °C)	III (550–700 °C)
Cu/MgO-0.8	3.76	2.84	9.60
Cu/MgO-0.8-R_6	3.70	2.41	8.25

[a] Data obtained from the CO_2-TPD.

Table S2 NH_3 Desorption peak areas of Cu/MgO-0.8 and Cu/MgO-0.8-R_6 catalysts.

Catalyst	Peak area[a] (A·℃)	
	I (350–500 °C)	II (500–650 °C)
Cu/MgO-0.8	4287.8	5427.5
Cu/MgO-0.8-R_6	6894.6	2063.0

[a] Data obtained from the NH_3-TPD.

Table S3. A summary of the performance of catalysts reported in publications for selective hydrogenation of methyl benzoate to benzyl alcohol in comparison with this work.

Entry	Catalysts	Reaction condition	Conv.%	Sel.%(BAL)	References
1	MnO/γ-Al_2O_3	Fixed bed reaction, 420 ℃, 3 h	96.7	3.0	H.L. Xu et al, Chin. J. Chem. 19 (2001) 647–651
2	MnO_x/ZrO_2-Cr_2O_3	Fixed bed reaction, 390 ℃, 1 h	93.8	49.9	Y. Zhao et al, J. Fuel Chem. Technol. 49 (2021) 1709–1715
3	Mn/Ti-Zr	Fixed bed reaction, 390℃, HSV = 0.5h^{-1}	98.0	30.1	S. Liu et. al, Fine Chem. 38 (2021) 782–789
4	Cu/ZnO/Al_2O_3	160 ℃, 7 MPa,10 h	93.8	88.6	Y. Jiang et al, Catal. Lett. 149 (2019) 1359–1367
5	$Cu_2Mg_5Al_1$	100 ℃, 3 MPa, 7 h	96.7	95.4	Z. Zhao et al, ACS Appl. Nano Mater. 2024, 7, 25706−25720 (Our previous work)
6	Cu/MgO-0.8	80 ℃, 3 MPa, 5 h	98.0	97.8	This work