

Supporting information

Environmentally-friendly and innovative design of ZIF-67 and lignin modified composite for efficient catalytic transfer hydrodeoxygenation of lignin-related phenols

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1. Catalyst characterization

X-ray diffraction (XRD) analyses were performed using the Rigaku Smartlab 9KW instrument (Japan), scanning from 10 to 80° at a rate of 10°/min. Raman spectra were acquired using the HORIBA HR Evolution spectrometer (Japan) equipped with 532 nm excitation lasers, covering a wavenumber range from 50 to 4000 cm⁻¹. The N₂ adsorption-desorption measurements were conducted at -196 m°C using the Micromeritics ASAP 2460 (U.A.S) device to determine the specific surface area and pore size distribution. The scanning electron microscope (SEM) instrument was the ZEISS GeminiSEM 300(Germany), and high-resolution transmission electron microscope (HRTEM) patterns were obtained using the FEI Talos F200x (USA). X-ray photoelectron spectroscopy (XPS) was conducted using the Thermo Scientific K-Alpha spectrometer equipped with an Al K α X-ray radiation source to investigate the chemical surface composition and elemental states of the catalysts. H₂ temperature programmed reduction (H₂-TPR) and NH₃ temperature programmed desorption (NH₃-TPD) profiles were generated using the Micromeritics AutoChem II 2920 with a thermal conductivity detector (TCD). For H₂-TPR, 50 mg of catalyst powder was pre-treated by drying from room temperature to 300 °C at 10 °C/min. The sample was subsequently exposed to 10% H₂/Ar gas (50 mL/min) until stabilization, followed by reduction from 50 to 800 °C at 10 °C/min ramp rate, with H₂ consumption monitored by TCD. For NH₃-TPD, 50 mg of catalyst powder underwent preconditioning by heating from room temperature to 300 °C at a rate of 10 °C/min in a U-shaped quartz tube. The sample was then purged with airflow (30-50 mL/min) until reaching 50 °C, followed by exposure to 10%

NH₃/He gas (30-50 mL/min) until saturation. Adsorbed NH₃ was removed by varying the gas flow rate for 1 hour, and desorption occurred in He flow from 50 to 800 °C at 10 °C/min ramp rate, with evolved gases measured by TCD. Infrared absorption spectroscopy was performed using the Tensor 27 instrument, analyzing samples within the 800-4000 cm⁻¹ range. Fourier-transform infrared spectroscopy (FT-IR) utilized the Thermo Scientific iN10 instrument from the United States. Sample preparation involved grinding a small amount of sample and dried potassium bromide powder in a mortar, pressing the mixture into transparent thin films on a hydraulic press in a dry environment. During testing, the background spectrum and the infrared spectrum of the sample were collected, with a resolution of 4 cm⁻¹, 32 scans, and a wavenumber range of 400/600-4000 cm⁻¹.

The reaction filtrate was collected for GC/MS analysis (Fuli, GC9790 Plus) using n-dodecane as the internal standard. The GC-MS analysis utilized a 30 m*0.25*0.25 µm capillary column coated. High-purity helium served as the carrier gas at a flow rate of 1.0 mL/min. The specific inlet mode and temperature settings were applied. Initially, the column temperature was set to 60 °C and maintained for 2 minutes to facilitate sample injection. Subsequently, the temperature was ramped at 10 °C/min until reaching 240 °C, where it was held for 1 minute.

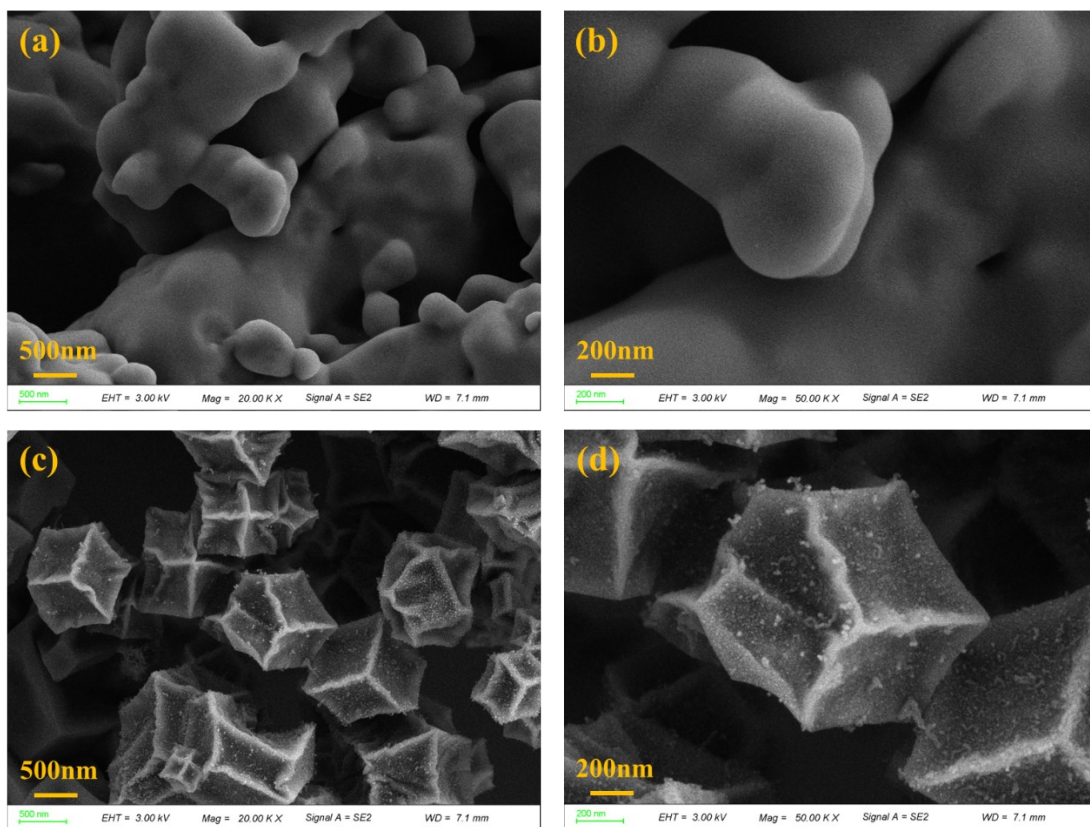


Fig. S1 SEM images of (a, b) Co@KL, (c, d) Co-ZIF catalysts.