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Research article

Enhanced hydrocracking C_{ar}-C_{alk} bridged bonds in the extraction residue from Piliqing subbituminous coal over a recyclable and active magnetic solid superacid

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ABSTRACT

A novel and highly active magnetic solid superacid (MSSA) with extraordinary separable and recyclable properties was facilely developed by impregnating trifluoromethanesulfonic acid onto mesoporous zirconia coated ferroferric oxide nanoparticles. The extraction residue (ER) from Piliqing subbituminous coal was subjected to non-catalytic hydrocracking (NCHC) and catalytic hydrocracking (CHC) in cyclohexane over MSSA at 300 °C. Detailed molecular compositions of the soluble portions from NCHC (SP_{NCHC}) and CHC (SP_{CHC}) were characterized with a Fourier transform infrared spectrometer and gas chromatograph/mass spectrometer (GC/MS). As a result, the yield of SP_{CHC} is remarkably higher than that of SP_{NCHC} and most of the GC/MS-detectable compounds in SP_{CHC} are arenes, while SP_{NCHC} contains alkanes, arenes, arenols, and ketones, indicating that MSSA effectively catalyzed the cleavage of C_{ar}-C_{alk} bridged bonds connecting some aromatic rings (ARs) and side chains on some ARs in the ER. Di(1-naphthyl)methane (DNM) and 9-benzylphenanthrene (9-BP) were used as coal-related model compounds (CRMCs) and their CHCs were investigated to further probe the catalysis of MSSA in the CHC of the ER. The result suggests that MSSA is highly active for cleaving the C_{ar}-C_{alk} bond in the CRMCs and generating naphthalene and phenanthrene under mild conditions. Based on the exploration of controlling reactions, the catalytic mechanism was discussed. MSSA could be easily separated and still active for the CHC of DNM after 3-times recycle.

1. Introduction

Cleaving C_{ar}-C_{alk} bridged bonds during direct coal liquefaction (DCL) is a relatively viable protocol to obtain small molecular aromatics [1–4]. In conventional DCL processes, rigorous conditions, especially high temperatures and hydrogen pressures, lead to a severe increase in the yields of gases and heavy products and thereby limit the industrial application of DCL [5,6]. With this in mind, developing DCL technologies capable of proceeding under mild conditions is highly desirable.

Catalysts are an overwhelming interest in moderating the rigorous reaction conditions and improving DCL efficiency [7–11]. The hydrocracking of coal-related model compounds (CRMCs) proved to be an effective approach for revealing the mechanisms for DCL at molecular level [12,13]. Previous explorations revealed that sulfate-promoted metal oxides, metal-sulfur systems, and activated carbon effectively catalyzed CRMC hydrocracking via monatomic hydrogen transfer, while Lewis acids, such as $AlCl_3$ and $ZnCl_2$, also proved to be effective for C_{ar}-C_{alk} bond cleavage [13–20]. Notably, Shimizu et al. [21] examined the reactions of diphenylmethane and biphenyl in trifluoromethanesulfonic acid (TFMSA) to demonstrate the catalytic effect of TFMSA on coal depolymerization. The results show that although the C_{ar}-C_{alk} bonds in some CRMCs could be efficiently cleaved under moderate conditions, the formation of by-products was significant. Solid acids received great interest due to their relatively high catalytic activity, low corrosiveness, and eco-friendly features. Many researchers explored the reaction of di(1-naphthyl)methane (DNM) catalyzed by solid acids and proposed that the hydrocracking was attributed to the cationic reaction mechanism [22,23]. A survey of the literature revealed that trimethylsilyltrifluoromethanesulfonate/activated carbon particularly exhibited high activity for hydrocracking the extraction residue (ER) from Lingwu bituminous coal [24]. An appropriate and novel solid acid with superior catalytic performance is required.

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Practical applications of solid acids in hydrocracking coals and CRMCs are tedious and hamper because of the complicated separation from the reaction mixture and subsequent recycling problems. To overcome these shortcomings, magnetic solid acids received increasing attention since such solid acids can be easily separated by an external magnetic field (EMF) [25–27]. Among magnetic materials, a mesoporous magnetic core (MPMC) could provide more platforms for the conversion of simple compounds and biomass, but there are few reports issued on coal conversion [28–33]. Notably, noble metals such as Rh, Pt, Ag, and Sb supported on MPMC were proverbially applied for hydrogenation and organic synthesis [34–36]. Inspired by these useful applications, the development of a novel and stable magnetic solid acid with high performance is a promising research for the directional conversion of organic matter in coals.

Herein, we developed an active and separable magnetic solid superacid (MSSA) using MPMC as the support. We explored its activity for catalytic hydrocracking (CHC) of the ER from Piliqing subbituminous coal (PSBC). We focused on the difference in composition between soluble portions from non-catalytic hydrocracking (SP_{NCHC}) and catalytic hydrocracking (SP_{CHC}). Di(1-naphthyl)methane (DNM) and 9-benzylphenanthrene (9-BP) were used as CRMCs to confirm the catalyst activity and reveal the mechanisms for DCL at molecular level.

2. Experimental section

2.1. Materials

PSBC was collected from Piliqing Coal Mine, Xinjiang Uygur Autonomous Region, China and pulverized to pass through a 200-mesh sieve ($< 74\,\mu m$) followed by desiccation in a vacuum at 80 °C for 12 h before use. The ER was obtained from PSBC (5 g) via ultrasonic extraction with isometric carbon disulfide/acetone mixed solvent and subsequent desiccation in a vacuum at 80 °C for 24 h. Each extraction with the same solvent (200 mL) was conducted for 40 min and repeated at least 20 times under ultrasonication (53 kHz) at room temperature to extract the soluble species as exhaustively as possible. DNM was provided by Heowns Chemical Co., Ltd., Tianjin, China. 9-BP was prepared by heating phenanthrene with benzyl chloride in the presence of zinc powder. Zirconium (IV) butoxide, cetyl trimethyl ammonium bromide (CTMAB), aqueous ammonia (AA), NH_4NO_3, and TFMSA were purchased from Aladdin Industrial Inc. Solvents cyclohexane and ethanol were obtained from commercial sources and purified by distillation prior to use.

2.2. Catalyst preparation

2.2.1. Synthesis of ferroferric oxide nanoparticles (FONPs)

The dispersible FONPs were synthesized according to the literature reported [37]. In a typical experiment, 20 mmol of $FeSO_4 \cdot 7H_2O$ was dissolved in deionized water (DIW, 200 mL) under ultrasonic irradiation for 0.5 h. Then 10 mL AA was added into the above mixture through a constant pressure funnel followed by vigorous agitation at 40 °C for 5 h. The resulting black precipitate was subsequently separated by the EMF and washed repeatedly with DIW and ethanol to remove excess AA, and finally oven dried at 60 °C for > 6 h.

2.2.2. MPMC synthesis

The core-shell MPMC was prepared by the sol-gel method. Briefly, 4.0 g FONPs were homogeneously dispersed into a mixture of DIW (150 mL) and ethanol (50 mL) under intense sonication for 0.5 h followed by adding zirconium (IV) butoxide (6 mL), CTMAB (2 g), ethanol (40 mL), and AA (6 mL). After agitation at 40 °C for 6 h, the solid mixture was collected by the EMF and washed with ethanol and DIW. Then CTMAB was removed by ion-exchange with a mixture of 300 mL NH_4NO_3 and ethanol ($10\,g\,L^{-1}$) at 60 °C for 12 h and subsequent desiccation at 60 °C for 12 h.

2.2.3. MSSA preparation

MSSA was prepared by impregnation without solvent. Specifically, 10 mL TFMSA was introduced dropwise into 2 g MPMC in a 25 mL Schlenk reaction vial under N_2 atmosphere at 50 °C for 12 h. After cooling down the vial, the mixture was filtered and dried under vacuum at 70 °C for 12 h. Besides MSSA, other 3 catalysts were also prepared under the same conditions using different supports, including attapulgite and zeolite 5A (Z5A).

2.3. Catalyst characterization

Transmission electron microscopic images of the samples were taken with a JEM-2100 microscope operating at 200 kV combined with an energy dispersive X-ray spectrometer (EDXRS). Powder X-ray diffraction (XRD) patterns were recorded on a Bruker Co. Ltd's D8 Advance X-ray diffractometer equipped with a Cu Kα source ($\lambda = 1.5406$ Å). Infrared spectral analysis was carried out a Nicolet Magna IR-560 Fourier transform infrared (FTIR) spectrometer in the range of $400–4000\,cm^{-1}$. Pyridine infrared spectral analysis was carried out on a Thermo Nicolet 380 infrared spectrometer. NH_3 temperature-programmed desorption (NH_3-TPD) measurements were carried out on a TP-5000 instrument. The sample was swept by an He flow at 650 °C for 1 h. After cooling to 100 °C and adsorbing NH_3, the sample was heated to 800 °C at $10\,°C\,min^{-1}$. The specific surface areas (SSAs) of the samples were evaluated by Brunauer-Emmett-Teller (BET) method at 77 K. Magnetic hysteresis loops were measured on a Lake Shore 7304 vibrating sample magnetometer at room temperature. X-ray photoelectron spectrum was collected on a Thermo Fisher Scientific K-Alpha 1063 spectrophotometer with the Al Kα radiation. Accurate binding energies were determined with reference to the C 1s peak at 284.5 eV and the beam spot size of 900 μm (energy step size 1.000 eV, pass energy 50.0 eV).

2.4. NCHC and CHC along with sample analyses

Both NCHC and CHC were carried out in a 100 mL stainless steel and magnetically stirred autoclave. A substrate (1 mmol a model compound or 1 g the ER), 0 or 0.4 g MSSA, and 20 mL cyclohexane were put into the autoclave. After replacing air in the autoclave 3 times and being pressurized with N_2 to 1 MPa at room temperature, the autoclave was heated to 300 °C for a stipulated period of time. After cooling the autoclave to room temperature, the reaction mixture in the autoclave was taken out and filtrated through a polytetrafluoroethylene membrane with 0.45 μm of pore size. The yields of SP_{NCHC} and SP_{CHC} were calculated as the mass ratio of the SP (m_{SP}) to the ER on dry and ash-free basis ($m_{S,\ daf}$), i.e., $Y_{SP} = m_{SP}/m_{ER,\ daf}$. Each filtrate was analyzed with the Nicolet Magna IR-560 FTIR spectrometer and an Agilent 7890/5973 gas chromatograph/mass spectrometer (GC/MS) assembled with a capillary column coated with HP-5MS (60 m × 0.25 mm × 0.25 μm) and a quadrupole analyzer, and operated in electron impact (70 eV) mode. Data acquired were processed using MSD ChemStation software. Compounds were identified by comparing mass spectra with NIST11 library data. The relative content (RC) of each compound was determined by the normalization method of peak area, i.e., the peak area of the compound divided by the sum of the peak areas of all the identified compounds in the total ion chromatogram. The quantitative analysis for the reaction of each model compound was performed with the GC/MS using the corresponding substrate as the external standard. In addition, each experiment under the same conditions was repeated at least 3 times to control the errors of conversion and product yields $< \pm 2\%$.