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Research article

MOFs-derived N-doped carbon matrix superacid-catalyzed hydrocracking of a residue from thermal dissolution of Hefeng subbituminous coal

Zheng Yang[a], Xian-Yong Wei[a,b,*], Zhi-Xin Li[a], Min Zhang[a], Zhi-Min Zong[a], Zhe-Hao Wei[c], Yan Li[c]

[a] Key Laboratory of Coal Processing and Efficient Utilization, Ministry of Education, China University of Mining & Technology, Xuzhou 221116, Jiangsu, China
[b] State Key Laboratory of High-efficiency Coal Utilization and Green Chemical Engineering, Ningxia University, Yinchuan 750021, Ningxia, China
[c] Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA, 99163, United States

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ABSTRACT

An active, low-cost, and recyclable catalyst was prepared by impregnating trifluoromethanesulfonic acid (TFMSA) onto metal-organic frameworks (MOFs)-derived N-doped carbon matrix nanoparticles. The residue (R_{TD}) from thermal dissolution (TD) of Hefeng subbituminous coal in methanol was subjected to further TD and catalytic hydrocracking (CHC) over the catalyst, *i.e.*, TFMSA/MOFs at 300 °C in cyclohexane. Detailed molecular compositions of the soluble portions from TD (SP_{TD}) and CHC (SP_{CHC}) were characterized with a Fourier transform infrared spectrometer, gas chromatograph/mass spectrometer (GC/MS), and positive-ion atmospheric pressure chemical ionization orbitrap mass spectrometer (PIAPCIORMS). The results show that 15.60% of organic matter in R_{TD} was converted to a soluble portion by the CHC, whereas the yield of SP_{TD} is only 1.04%. According to the analysis with GC/MS, SP_{CHC} is rich in alkyl-substituted benzenes, while most of the GC/MS-detectable compounds in SP_{TD} are alkyl-substituted arenols, alkyl-substituted cyclenones, and phenylalkanones in addition to alkyl-substituted benzenes. The analysis with PIAPCIORMS shows that both the number and yields of basic nitrogen-containing species were dramatically reduced after the CHC. These facts indicate that TFMSA/MOFs effectively catalyzed the cleavage of C_{ar}–C_{alk} bridged bonds connecting some aromatic rings (ARs) and side chains on some ARs in R_{TD} to obtain soluble compounds. Di(1-naphthyl)methane and 2-(benzyloxy)naphthalene were used as coal-related model compounds (CRMCs) and their CHCs were investigated to further explore the catalysis of TFMSA/MOFs in the CHC of R_{TD}. As a result, TFMSA/MOFs effectively catalyzed the cleavage of C_{ar}-C_{alk} and C-O bonds in the CRMCs under moderate conditions. TFMSA/MOFs can be easily separated by using an external magnetic field and the recovered TFMSA/MOFs is still highly active for the CHC of DNM.

1. Introduction

The increasing energy and fuel demand, crude oil reserves crisis, and strict environmental regulation increased the attention towards transforming coals into value-added chemicals and cleaner fuels [1–3]. Direct coal liquefaction (DCL) is a valuable option to directly convert coals into liquid fuels and serviceable chemicals [4–7], which may alleviate the shortage of petroleum resources to some extent. Typically, the existing DCL processes performed at high temperatures and hydrogen pressures are not effective economically, which could generate more gaseous products and cokes compared to low-temperature DCL [8,9]. Therefore, many efforts have been tried to develop flexible protocols and technologies for DCL under mild conditions.

Catalysts offer an opportunity to enhance DCL efficiency and obtain clean liquid fuels through the catalytic hydrocracking (CHC) [1,10,11]. The CHC of coal-related model compounds (CRMCs) proved to be an effective approach for elucidating the mechanisms for DCL at molecular level [12,13]. Previous investigations revealed that activated carbon and metallic catalysts, such as Fe and Ni, mainly catalyzed CRMC hydrocracking *via* biatomic hydrogen transfer [14–16]. A survey of the literature manifested that acidic catalysts, such as trifluoromethanesulfonic acid (TFMSA), $AlCl_3$, and $ZnCl_2$, were also developed for the coal depolymerization and the reactions of CRMCs at lower temperatures [17–19]. Moreover, the strong corrosiveness to equipment and the serious environment pollution caused by homogeneous reactions limit the pervasive application of such catalysts. Supported acids (SAs) have gained great attention due to their relatively high-performance, low corrosiveness, and eco-friendly behaviors. Many researchers probed the CHC of di(1-naphthyl)methane (DNM) over SAs and proposed the cationic reaction mechanism [20,21].

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* Corresponding author.
E-mail address: wei_xianyong@163.com (X.-Y. Wei).

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Notably, SAs and metals are currently paid attention for their catalysis in H^+ transfer, leading to the cleavage of some bridged bonds (BBs), particularly C-O BBs [22–25]. In addition, since the residue (R_{TD}) from thermal dissolution (TD) of coals mainly remains macromolecular structures, the investigation on the CHC of R_{TD} facilitates speculating coal structures. The above reports indicate that SAs possess an improved catalytic activity for DCL. Thus, an appropriate and novel SA for cleaving strong BBs in coals under mild conditions is required.

Practical applications of SAs in the CHC of coals are impeded by the difficulty in separating the SAs from the reaction mixture. Magnetic nanoparticles have attracted considerable interests as catalyst supports owing to their facile recovery by an external magnetic field [26,27]. Particularly, a novel metal nanomaterial consisting of metal-organic frameworks (MOFs)-derived N-doped carbon matrix nanomaterial has been extensively investigated [28,29]. MOFs represent privileged porous materials assembled with metal ions and organic linkers, which exhibit several superior chemical and physical properties [30–33]. Notably, by calcining the MOFs containing the metal centers, metal ions in the MOFs could be transformed into metal nanoparticles, which are embedded in a ligand-derived porous carbon matrix [34]. Herein, *via* thermal decomposition, MOFs proved to be important and ideal sacrificial templates for fabricating porous and magnetic N-doped carbon matrix nanomaterials [28,32]. Inspired by these advances, the development of a highly activity solid acid based on the MOFs-derived magnetic nanomaterials is strongly desired for the directional conversion of organic matter in coals.

Herein, we report a highly performance, low-cost, and recoverable solid superacid, *i.e.*, TFMSA/MOFs employing TFMSA impregnated onto MOFs-derived N-doped carbon matrix nanomaterials. We tried to probe its activity for the CHC of R_{TD} from Hefeng subbituminous coal (HSBC) and examined the difference in the composition between soluble portions from the TD (SP_{TD}) and CHC (SP_{CHC}) of R_{TD} using several analytical methods. Di(1-naphthyl)methane (DNM) and 2-(benzyloxy)-naphthalene (2-BON) were used as CRMCs to reveal the possible mechanisms for DCL at molecular level.

2. Experimental section

2.1. Catalyst preparation

ZIF-67 polyhedrons, *i.e.*, Co(2-methylimidazole)$_2$, was prepared according to literature [35] with some modifications. In a typical run, 1.5 mmol cobalt nitrate hexahydrate was dissolved into 2 mL deionized water (DIW) to form solution A and 50 mmol 2-methylimidazole was added into 100 mL DIW to form solution B. Then solution A was successively poured into solution B under magnetic agitation at room temperature for 12 h. The resulting purple precipitates were washed thoroughly with DIW and finally dried under vacuum at 80 °C for 12 h.

Co/NC was prepared by pyrolytic carbonization. ZIF-67 (3 g) was pyrolyzed by heating at 2 °C min^{-1} from room temperature to 700 °C under continuous Ar flow and holding the temperature for 8 h followed by cooling to room temperature. Subsequently, the desired Co/NC was afforded in the yield of 64%.

TFMSA/MOFs was prepared by dropwise adding 10 mL TFMSA into 2 g Co/NC in a 25 mL Schlenk reaction vial under N_2 atmosphere at 40 °C for 10 h. After cooling down the vial, the mixture was filtered and dried under vacuum at 80 °C for 12 h.

2.2. TD and CHC procedures

Cyclohexane (20 mL), TFMSA/MOFs (0 or 0.1 g), and a substrate (1 mmol a model compound or 1 g R_{TD}) were put into a 100 mL stainless steel and magnetically stirred 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 a set temperature and held at the temperature for a stipulated period of time. After cooling the autoclave to room temperature, the reaction mixture in the autoclave was taken out and filtrated from the autoclave as completely as possible. The yields of SP_{TD} and SP_{CHC} were calculated as the mass ratio of the SP (m_{SP}) to R_{TD} on dry and ash-free basis ($m_{S,\ daf}$), *i.e.*, $Y_{SP} = m_{SP}/m_{RTD,\ daf}$.

2.3. Sample analyses

Each filtrate was analyzed with a Nicolet Magna IR-560 Fourier transform infrared (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 compounds as the external standards. In addition, each experiment under the same conditions was repeated at least 3 times to control the errors of conversion and product yields less than ± 2%.

SP_{TD} and SP_{CHC} were also analyzed with a positive-ion atmospheric pressure chemical ionization orbitrap mass spectrometer (PIAPCIORMS). For the analysis with PIAPCIORMS, SP_{TD} and SP_{CHC} were dissolved in acetone to strengthen the ionization efficiency. In atmospheric pressure chemical ionization source, discharge current, capillary temperature, and vaporizer temperature were set at 4.0 μA, 275 °C, and 400 °C, respectively. The PIAPCIORMS was recalibrated with a known mass series in the sample followed by calibrated using sodium formate. Detailed data processing was performed with Custom software [36].

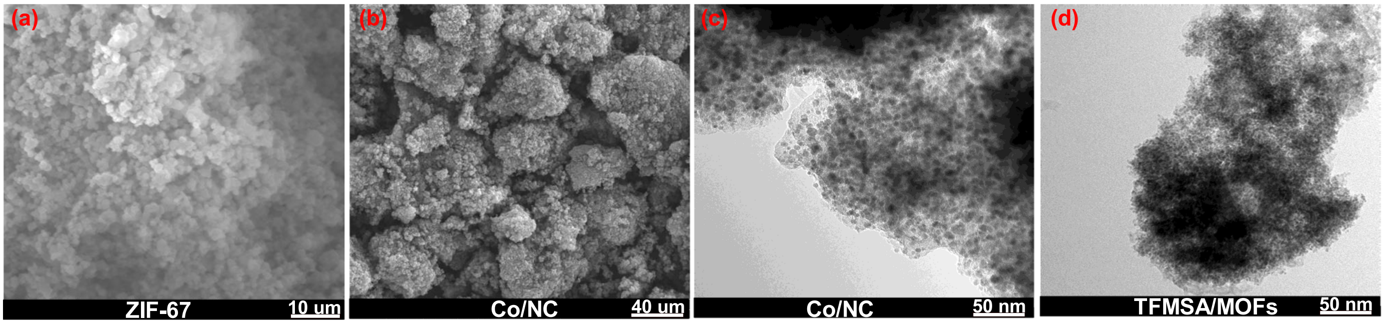

Fig. 1. Typical scanning electron microscopic images of (a) ZIF-67 and (b) Co/NC, and transmission electron microscopic images of (c) Co/NC and (d) TFMSA/MOFs.