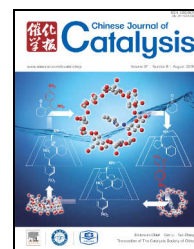


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Article

Preparation of a new solid acid and its catalytic performance in di(1-naphthyl)methane hydrocracking



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ABSTRACT

A new solid acid was prepared by trifluoromethanesulfonic acid (TFMSA) impregnation into an acid-treated attapulgite (ATA). Di(1-naphthyl)methane (DNM) hydrocracking was used as the probe reaction to evaluate the catalytic performance of TFMSA/ATA for cleaving C_{ar}–C_{alk} bridged bonds in coals. The results show that DNM was specifically hydrocracked to naphthalene and 1-methylnaphthalene over TFMSA/ATA in methanol in the absence of gaseous hydrogen. In particular, TFMSA/ATA was demonstrated to be stable after four cycles with slight loss in catalytic activity. Furthermore, a proposed H⁺ transfer mechanism successfully interprets the TFMSA/ATA-catalyzed hydrocracking reaction of DNM.

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1. Introduction

With decreasing fossil fuel reserves and soaring energy demands, efficient utilization of coals has attracted tremendous attention. Direct coal liquefaction (DCL) is a promising process for producing clean liquid fuels and value-added chemicals [1–3]. In the DCL process, catalysts play crucial roles in cleaving C–C bonds and facilitating hydrogen transfer [4–6]. Liquid acids such as trifluoromethanesulfonic acid (TFMSA) [7,8], HF+BF₃ [9], and molten salts [10] have been widely studied in DCL. However, poor recyclability, strong corrosiveness, and the serious environmental contamination issues restrict their industrial applications.

Solid acids are environmentally benign and easily recycled in comparison with liquid acids and have great promise as DCL catalysts. Because of the complexity of coal structures, investi-

gating coal-related model compound (CRMC) reactions proved to be a powerful approach for revealing molecular-level DCL mechanisms [11–13]. In recent years, significant efforts have been devoted to directional degradation of coals and CRMCs over solid acids. Wang et al. [14] investigated the decomposition of diphenylmethane and bibenzyl over sulfated zirconia. The work suggested that the acidic property of the catalyst contributed largely to CRMC bond rupture. Yue et al. [15] examined the hydrocracking of di(1-naphthyl)methane (DNM) over a solid acid prepared by pentachloroantimony and trimethylsilyl trifluoromethanesulfonate impregnation into an activated carbon. The results showed that heterolytic cleavage of H₂ into H⁺ and H⁻ was the key step for the cleavage of C_{ar}–C_{alk} bond in DNM. The aforementioned solid acids, although effective, still require the use of pressurized hydrogen at elevated temperatures. Therefore, it is imperative to develop nov-

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el catalysts that allow cleaving the bridged bonds in coals under mild conditions, especially in the absence of pressurized hydrogen.

Catalyst supports play vital roles in improving catalytic activity and stability. Attapulgite is a type of hydrated magnesium aluminum silicate having lath or fibrous morphology, being desirable as a solid acid catalyst support because of its large specific surface area, considerable porosity, and excellent thermal stability [16].

In this study, a new solid acid was prepared using an acid-treated attapulgite (ATA) as the support and TFMSA as the active component. The catalytic performance of as-prepared TFMSA/ATA was investigated by cleaving $C_{ar}-C_{alk}$ bond in DNM in the absence of H_2 . The potential cleavage route of DNM over TFMSA/ATA was also deduced.

2. Experimental

2.1. Materials

Attapulgite powder (AP) was purchased from Jiangsu Huahong Mining Chemical Co., Ltd., Xuyi, China. DNM is an analytical reagent purchased from Heowns Chemical Co., Ltd., Tianjin, China. Both methanol and TFMSA were purchased from Aladdin Industrial Inc., Shanghai, China. Methanol was purified by distillation prior to use.

2.2. Catalyst preparation

AP was treated in 0.5 mol/L HCl aqueous solution under reflux with vigorous agitation for 4 h. Thereafter, the suspension was filtered and washed with distilled water until Cl^- was undetectable by silver nitrate titration. The filter cake was dried under vacuum at 110 °C for 6 h to obtain ATA, which was then ground and sieved to 100–200 mesh size. TFMSA/ATA was prepared by impregnation, i.e., TFMSA (5 mL) was added dropwise into ATA (2 g) under a N_2 atmosphere followed by refluxing at 90 °C for 8 h. The mixture was cooled, filtered, washed with acetone, and calcined at 350 °C for 12 h. TFMSA loaded on ATA is ca. 14.7%, which was calculated according to the mass change. Besides TFMSA/ATA, TFMSA/ $\gamma-Al_2O_3$ and TFMSA/ZSM-5 were also prepared under the same conditions.

2.3. Catalyst characterization

Transmission electron microscopic (TEM) observation of ATA and TFMSA/ATA and corresponding elemental analysis were performed using a JEM-1011 JEOL microscope operating at 200 kV coupled to an energy-dispersive spectrometric detector. Fourier transform infrared (FTIR) analysis was performed using a Nicolet Magna IR-560 spectrometer with a resolution of 4 cm^{-1} over the spectral range of 4000–400 cm^{-1} using KBr pellets. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer with $Cu K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 30 mA in the 2θ range of 3°–80°. Specific surface area, pore volume, and average pore size of the samples were measured using an Autosorb-1-MP

apparatus at –196 °C. Samples were previously outgassed at 300 °C for 5 h. NH_3 temperature-programmed desorption (NH_3 -TPD) was conducted on a TP-5000 type multi-function adsorption instrument. The samples were pretreated at 650 °C for 1 h and then cooled to 100 °C. The introduction of NH_3 was performed for 0.5 h followed by purification with He for 1 h to remove physisorbed NH_3 . Desorption under He was performed in the range of 100–800 °C at 10 °C/min to remove chemisorbed NH_3 . X-ray photoelectron spectroscopic (XPS) measurements were determined using a Thermo Fisher ESCALAB 250Xi spectrophotometer with the $Al K\alpha$ radiation with a beam spot size of 900 μm (energy step size 1.000 eV, pass energy 50.0 eV). Accurate binding energies were determined by reference to the C 1s peak at 284.5 eV.

2.4. Catalytic reactions

DNM (1 mmol), catalyst (0–40 mg), and methanol (10 mL) were added into a 60-mL stainless steel and magnetically stirred autoclave. The autoclave was purged with N_2 and pressurized to 1 MPa at room temperature before heating to a desired temperature (260–320 °C). After reaction at a specific temperature for a prescribed period of time (0.5–5 h), the autoclave was immediately quenched to room temperature in an ice-water bath before filtering the reaction mixture. The filtrate was analyzed using an Agilent 7890/5975 gas chromatograph/mass spectrometer (GC/MS) equipped with a capillary column coated with HP-5MS (60 m \times 0.25 mm \times 0.25 μm) and a quadrupole analyzer operated in electron impact (70 eV) mode. The capillary column was heated from 60 to 300 °C at 10 °C/min and held at 300 °C for 6 min. The relative content of each compound was determined by normalizing 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. Quantitative analysis was performed using DNM as an external standard during analysis with GC/MS. Furthermore, each experiment, under the same conditions, was repeated at least three times to minimize DNM conversion and product yield errors to less than $\pm 1\%$.

3. Results and discussion

As Fig. 1 shows, ATA exhibits ordered fibrous morphology and a smooth surface with diameters between 20 and 30 nm. Conversely, the surface characteristics of TFMSA/ATA differ from ATA in which a rough surface is observed. Another different surface feature is the presence of irregular grains with diameters < 10 nm that are relatively uniformly distributed on the ATA surface without obvious aggregation. Among the detected elements, O, Mg, Al, and Si are mainly attributed to the ATA framework, while K and Fe most likely arise from impurities in the parent ATA. Additionally, F and S from TFMSA were also detected in TFMSA/ATA (Fig. 2). Energy-dispersive spectrometric (EDS) analysis demonstrates a F content of 5.2 wt% on TFMSA/ATA, which is close to the F loading (5.6%) calculated according to the mass difference between added ATA and the resulting TFMSA/ATA.

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