

## Hydrocracking of benzyloxybenzene as a lignite-related model compound over a novel solid acid



Mei-Xia Zhao<sup>a</sup>, Xian-Yong Wei<sup>a,\*</sup>, Meng Qu<sup>a</sup>, Zhan-Ku Li<sup>a</sup>, Jing Liu<sup>a</sup>, Yan Li<sup>b</sup>, Jiao Kong<sup>a</sup>, Wei Zhao<sup>a</sup>, Zhi-Min Zong<sup>a</sup>

<sup>a</sup> Key Laboratory of Coal Processing and Efficient Utilization, Ministry of Education, China University of Mining & Technology, Xuzhou 221116, Jiangsu, China

<sup>b</sup> The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99164, USA

### ARTICLE INFO

#### Article history:

Received 17 December 2015

Received in revised form 10 February 2016

Accepted 13 February 2016

Available online 25 February 2016

#### Keywords:

Solid acid

Benzyloxybenzene

Hydrocracking

Lignite-related model compound

### ABSTRACT

A novel solid acid was prepared by impregnating trifluoromethanesulfonic acid (TFMSA) onto attapulgite powder (AP). Benzyloxybenzene (BOB) was used as a lignite-related model compound to evaluate the catalytic activity of TFMSA/AP for cleaving C<sub>alk</sub>-O bridged bonds in lignites. The results show that BOB was mainly hydrocracked to toluene, phenol, and (ethoxymethyl)benzene over TFMSA/AP in ethanol without adding gaseous hydrogen. In addition, ethanol participated in and significantly facilitated BOB hydrocracking. Based on the kinetic investigation, BOB hydrocracking over TFMSA/AP is absent of mass transfer limitations with the apparent activation energy of only 19.4 kJ mol<sup>-1</sup>, which is far smaller than the dissociation energy (209.2 kJ mol<sup>-1</sup>) of C<sub>alk</sub>-O bridged bond in BOB. The proton transfer directly from TFMSA/AP and/or via ethanol dehydrogenation to the oxygen atom of BOB could be the crucial step for BOB hydrocracking over TFMSA/AP.

© 2016 Elsevier B.V. All rights reserved.

### 1. Introduction

With diminishing reserves of crude oil and increasing energy demands, tremendous efforts have been dedicated to developing effective conversion processes of coals into fuels and chemicals. Low-rank coals, especially lignites, are abundant fossil resources, accounting for more than 40% of the total coal reserves in China, but their high moisture content, low calorific value, and easy spontaneous combustion may hamper their industrial application. Thus, it is necessary to develop efficient technologies to overcome the above disadvantages. Since lignites are rich in oxygen-containing bridged bonds, effectively cleaving the bridged bonds under mild conditions is crucially important for their directional degradation and subsequent value-added utilization of the resulting soluble portion [1–3].

Investigation on non-catalytic and catalytic hydrocracking of coal-related model compounds (CRMCs) proved to be a powerful approach for revealing the mechanisms for directional degradation of coals at molecular level [4–6]. Benzyloxybenzene (BOB) has been commonly selected as a CRMC to represent the typical C<sub>alk</sub>-O bonds in lignites. The dissociation of BOB has been extensively investigated since 1980s [7–13]. Schlosberg et al. [7] found that BOB reacts readily at 375 °C either in the presence or absence of added donor hydrogen sources. BOB pyrolysis in the temperature range from 500 to 700 °C was also investigated [13], but side reactions significantly proceeded at such high temperatures in addition to huge energy consumption.

Catalysts play key roles in directional degradation of coals and CRMCs [14–19]. Liquid acids, such as trifluoromethanesulfonic acid (TFMSA) [20], HF/BF<sub>3</sub> [21], and molten salts [22], were found to remarkably improve coal dissolution and CRMC degradation. However, their poor recyclability, strong corrosiveness to the equipment, and severe pollution to the environment lead to the difficulty in practical application. Solid acids were paid much attention because of their good recyclability, low corrosiveness, and eco-friendliness. Matsushita et al. [14] examined the catalytic activities of metal oxides promoted by sulfate for hydrocracking BOB and oxydibenzene. They pointed out that the catalyst acidity played an important role in the CRMC hydrocracking. Afterwards, Wang et al. [15] studied SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>-catalyzed hydrocracking of oxydibenzene, diphenylmethane, and bibenzyl. They suggested that the reactions mainly occurred on the Brønsted acid sites. Unfortunately, most of the solid acids, although effective, still suffer from severe reaction conditions, such as high temperatures and high hydrogen pressures, discouraging their industrial application. Therefore, developing novel catalysts is crucially important for selectively cleaving bridged bonds in low-rank coals, especially lignites, under milder conditions.

Besides active species, supports are also believed to play important roles in improving the catalyst activity and stability. Attapulgite is a kind of hydrated magnesium aluminum silicate with a lath or fibrous morphology and rich in reactive surface hydroxy groups. Due to its large specific surface area, considerable porosity, and excellent thermal stability, attapulgite exhibits distinctive potential as the support for solid acids [23].

In the present work, a novel solid acid was prepared using attapulgite powder (AP) as the support and TFMSA as the active

\* Corresponding author.

E-mail address: [wei\\_xianyong@163.com](mailto:wei_xianyong@163.com) (X.-Y. Wei).

component. Its catalytic activity for hydrocracking  $C_{alk}-O$  bond in BOB without charging gaseous hydrogen was investigated.

## 2. Experimental section

### 2.1. Materials

AP and BOB were purchased from Jiangsu Huahong Mining Chemical Co., Ltd., Xuyi City, Jiangsu Province, China and Heowns Chemical Co., Ltd., Tianjin, China, respectively. Both ethanol and TFMSA were purchased from Aladdin Industrial Inc., Shanghai, China. Ethanol was purified by distillation prior to use.

### 2.2. Catalyst preparation and characterization

AP was activated in a tube furnace at 350 °C for 3 h. Then it was cooled to room temperature and ground to pass through 100–200 mesh sieves. TFMSA/AP was prepared by impregnation, i.e., TFMSA (5 mL) was added dropwise into AP (2 g) under  $N_2$  atmosphere and then refluxed at 90 °C for 8 h. Then the mixture was cooled, filtered, washed with acetone, and dried under vacuum at 90 °C for 12 h. The amount of TFMSA loaded on AP is ca. 16.6%, which was calculated according to the mass change between added AP and the resulting TFMSA/AP. The catalyst was characterized using a Hitachi S-3700 N scanning electron microscope combined with an energy dispersive spectrometer, Nicolet Magna IR-560 Fourier transform infrared (FTIR) spectrometer, Bruker D8 Advance diffractometer, Thermo Fisher Scientific K-Alpha 1063 spectrophotometer, TP-5000 type multi-function adsorption instrument, and Autosorb-1-MP apparatus.

Likewise, TFMSA/ $\gamma-Al_2O_3$  and TFMSA/ZSM-5 were also prepared under the same conditions for comparison.

### 2.3. Catalytic hydrocracking of BOB

BOB (1 mmol), catalyst (0–40 mg), and ethanol (10 mL) were fed into a 60 mL stainless steel and magnetically stirred autoclave. After replacing air in the autoclave and being pressurized with  $N_2$  to 1 MPa at room temperature, the autoclave was heated to an indicated temperature (120–200 °C) and maintained at that temperature for a prescribed period of time (1–7 h) with rapid agitation. The reaction mixture was taken out from the autoclave and filtrated after cooling the autoclave in an ice-water bath. The filtrate was identified with an Agilent 7890/5975 gas chromatograph/mass spectrometer (GC/MS) equipped with a quadrupole analyzer operated in electron impact (70 eV) mode and quantified with an Agilent 7890 gas chromatograph fitted with a flame ionization detector. The HP-5MS (60 m  $\times$  0.25 mm  $\times$  0.25  $\mu m$ ) capillary column was heated from 60 to 300 °C at a rate of 10 °C  $min^{-1}$  for the analysis.

## 3. Results and discussion

### 3.1. Catalyst characterization

As Fig. 1 shows, AP exhibits fibrous structure of several micrometers in length and formed a densely packed network with pores. Different from AP, TFMSA/AP displays a rough surface and there are irregular grains with diameter less than 5  $\mu m$  adhered to the AP surface. As exhibited in Fig. S1 of the Supplementary Material, the existence of O, Mg, Al, Si, K, and Fe on the surface of AP can be observed. Characteristic element F (5.7 wt%) from TFMSA in TFMSA/AP was also confirmed, which is near 6.0% of F load calculated according to the difference in mass between added AP and the resulting TFMSA/AP.

As Fig. 2 demonstrates, there are appreciable differences in FTIR spectra between AP and TFMSA/AP. The absorbance around 3616  $cm^{-1}$  is attributed to the  $-OH$  stretching vibration of bonds to Al and Mg in dioctahedral coordination, while the band around

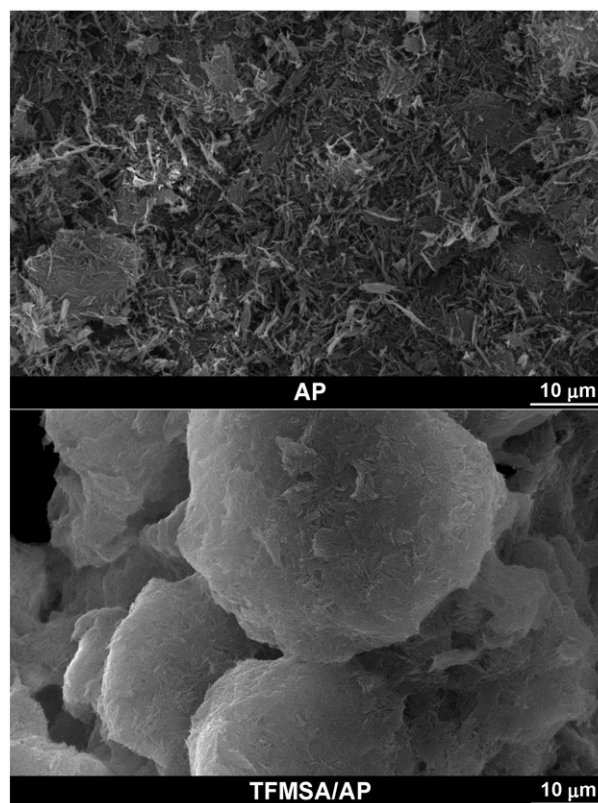


Fig. 1. Scanning electron microscopic images of AP and TFMSA/AP.

3550  $cm^{-1}$  is ascribed to the  $-OH$  stretching vibration of adsorbed water coordinated to Al and Mg at the edges of the channels [24]. The band around 1630  $cm^{-1}$  is assigned to the bending vibration of zeolite water [25]. The characteristic absorbances around 1015 and 801  $cm^{-1}$  result from the vibrations of Si–OR and Si–O–Si bonds, respectively [26]. FTIR spectrum of TFMSA/AP displays additional bands around 1255 and 1173, 1035, and 614  $cm^{-1}$ , which correspond to symmetric and asymmetric stretching vibrations of SO bond, C–F stretching vibration, and C–S bending vibration, respectively [27,28]. These results evidently indicate that TFMSA was successfully loaded on AP, which is consistent with the observation shown in Fig. 1.

As Fig. 3 displays, the peaks at 8.5, 16.9, and 35.1° are defined as the characteristic diffraction peaks of AP, while those at 13.7, 20.0, and 21.1° can be attributed to the Si–O–Si crystalline layers in AP. The peak at 24.6° could be ascribed to quartz as an impurity [29]. Compared with AP, the diffraction peaks of TFMSA/AP located at 8.5, 16.9, and 35.1° become weaker or broaden, implying that the crystalline structure was significantly destroyed by loading TFMSA.

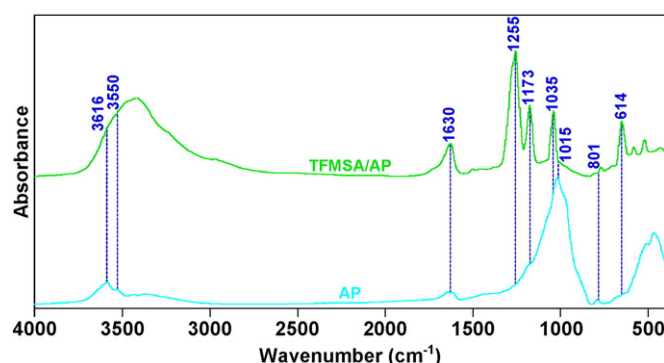


Fig. 2. FTIR spectra of AP and TFMSA/AP.

Download English Version:

<https://daneshyari.com/en/article/209232>

Download Persian Version:

<https://daneshyari.com/article/209232>

[Daneshyari.com](https://daneshyari.com)