Fuel 220 (2018) 101–108

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

A highly active bifunctional solid acid for di(1-naphthyl)methane hydroconversion

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ARTICLE INFO

Keywords:
Ni-TFMSA/TAP
Di(1-naphthyl)methane
Catalytic hydroconversion

ABSTRACT

Catalysts trifloromethanesulfonic acid (TFMSA)/treated attapulgite powder (TAP), Ni/TAP, and Ni-TFMSA/TAP with different Ni and TFMSA loadings were prepared. The typical catalysts were characterized with multiple instruments and used for catalyzing hydroconversion of di(1-naphthyl)methane (DNM), which was used as a coal-related model compound. The suitable loadings of Ni and TFMSA in Ni-TFMSA/TAP were determined to be 28.6% of Ni and 33% of TFMSA. Under optimal reaction conditions of 5 MPa of initial hydrogen pressure, 240 °C, and 4 h over Ni-TFMSA/TAP, DNM was completely converted, producing decalin and 1-methyldecalin as the main products. The result suggests that Ni-TFMSA/TAP is highly active for both cleaving the C_{ar}-C_{alk} bond in DNM and hydrogenating the resulting naphthalene and 1-methylnaphthalene under mild conditions. Based on the identification of reaction products, the catalytic mechanism for DNM hydroconversion was discussed.

1. Introduction

Direct coal liquefaction (DCL) is a feasible option to directly convert coals into liquid fuels and serviceable chemicals [1–4]. The cleavage of bridged bonds, especially C—C bridged bonds, in coals is one of the most important reactions for DCL [5–10]. However, conventional DCL processes have some disadvantages, including huge energy consumption and high investment cost [8,15] caused by harsh conditions, such as high temperatures and pressures, leading to a severe increase in the yields of gases and heavy products [11]. Thus, seeking a DCL process under mild conditions deserves great attention.

Catalysts play crucial roles in moderating the rigorous reaction conditions and improving DCL efficiency [12–18]. The hydroconversion of coal-related model compounds (CRMCs) proved to be an effective approach for revealing the mechanisms for DCL at molecular level [6,7–9,11,19–24]. Previous investigations revealed that some metallic catalysts such as Fe, Ni, and Pd/C mainly catalyzed di(1-naphthyl) methane (DNM) hydrogenation via biatomic hydrogen transfer, whereas their sulfides predominantly promoted DNM hydrocracking via monatomic hydrogen transfer, i.e., radical hydrogen transfer [8,11]. Ni/ZSM-5 exhibits dramatically high activity for hydrogenating arenes via biatomic hydrogen transfer [25], while some Lewis acids, such as $ZnCl_2$ and $AlCl_3$, proved to be effective for C—C bond cleavage [26] and hence could be used as catalysts for DCL [27,28].

Herein we report the preparation of a new bifunctional nickel-based solid acid for specifically hydrocracking C_{ar}-C_{alk} bridged bonds and hydrogenating aromatic rings in coals.

2. Experimental

2.1. Materials

Attapulgite powder (AP), DNM, and trifloromethanesulfonic acid (TFMSA) were purchased from Jiangsu Huahong Mining Chemical Co., Ltd. (in Xuyi City, Jiangsu Province, China), Heowns Chemical Co., Ltd. (in Tianjin City, China), and Aladdin Industrial Inc. (in Shanghai City, China), respectively. Solvents *n*-hexane, ethoxyethane, and acetone used in the experiments are commercially purchased analytical reagents and were purified by distillation using a Büchi R-210 rotary evaporator prior to use.

2.2. Catalyst preparation

AP was added into 0.5 $mol \cdot L^{-1}$ HCl solution under reflux with vigorous agitation for 4 h followed by filtrating and washing the mixture with deionized water several times until pH of the filtrate is close

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https://doi.org/10.1016/j.fuel.2018.01.093
Received 16 May 2017; Received in revised form 24 January 2018; Accepted 25 January 2018
0016-2361/

Nomenclature

BDM	bis(decal-1-yl)methane
BTM	bis(tetral-5-yl)methane
CHC	catalytic hydroconversion
CRMCs	coal-related model compounds
DCL	direct coal liquefaction
DNM	di(1-naphthyl)methane
DP	desorption peak
F & T	formation and transfer
FTIR	Fourier transform infrared
GC/MS	gas chromatograph/mass spectrometer
HTs	high temperatures
IP	*ipso*-position
IHP	initial hydrogen pressure
LTs	low temperatures
MASs	medium acid sites
1-MD	1-methyldecalin
1-MN	1-methylnaphthalene
5-MT	5-methyltetralin
MTFMS	methyl trifluoromethanesulfonate
NR	naphthalene ring
NM	naphth-1-ylmethylium
NMTFMS	naphth-1-ylmethyl trifluoromethanesulfonate
NNPs	nickel nanoparticles
NTC	nickel tetracarbonyl
SASs	strong acid sites
TAP	treated attapulgite powder
TFMSA	trifluoromethanesulfonic acid
TFMSOM	(trifluoromethylsulfonyloxy)methylium
TPs	target products
XRD	X-ray diffractometer
XRPES	X-ray photoelectron spectroscopy
TPD	temperature-programmed desorption
TPR	temperature-programmed reduction
WASs	weak acid sites

to 7. The filtrate was concentrated and then dried at 80 °C in vacuum for 4 h to obtain treated AP (TAP). Then the TAP was calcined in a tube furnace at 350 °C for 4 h followed by cooling to room temperature and then pulverizing to pass through 100–200 mesh sieves (particle size 0.15–0.074 mm).

TFMSA/TAP was prepared by impregnation. In detail, TFMSA (1–4 mL) was added dropwise into TAP (2 g) under N_2 atmosphere followed by reflux at 80 °C for 12 h. After being cooled down to room temperature, the mixture was filtered and washed with acetone, then dried in vacuum at 80 °C for 12 h.

Nickel tetracarbonyl (NTC) was synthesized by the reaction of nickel nanoparticles (NNPs) with 5 MPa of CO at 100 °C for 2 h in a 100 mL stainless steel and magnetically stirred autoclave. Then the autoclave was cooled to room temperature and the gas was released from the autoclave. To make the NNPs conversion completely, the autoclave was pressurized with 5 MPa of CO again. Then the autoclave was heated to 100 °C and kept at the temperature for another 2 h. Ni/TAP and Ni-TFMSA/TAP was produced by decomposing NTC on TAP and TFMSA/TAP in the autoclave. About 30 mL ethoxyethane, 2 g TAP or solid acid (TFMSA/TAP), and 1–2 mL NTC were put into the autoclave in order. After replacing air inside the autoclave with N_2 3 times, the mixture was stirred in the autoclave at 100 rpm for 1 h for fully impregnating NTC onto TAP or TFMSA/TAP. Then the rotation speed was expedited to 200 rpm, at which the autoclave was slowly heated to 100 °C and kept at the temperature for 1 h followed by cooling the autoclave to room temperature and releasing CO. In order to make the load sufficient, such steps were repeated. Finally, the reaction mixture was taken out from the autoclave, filtrated, concentrated, and dried in a vacuum at 60 °C for 4 h to get Ni/TAP or Ni-TFMSA/TAP. All the catalysts prepared are listed in Table 1. By comparing the mass difference between the added TAP and TFMSA/TAP and between Ni/TAP and Ni-TFMSA/TAP, the masses of TFMSA and Ni loaded on TAP were calculated, respectively.

2.3. Catalyst characterizations

Transmission electron microscopic image was taken with a JEM-200 CX electron microscope operated at 200 kV with an energy dispersive spectrometer. X-ray diffraction (XRD) measurement was carried out on a Bruker Advance D8 X-ray diffractometer equipped with a Cu Kα source ($\lambda = 1.5406$ Å). X-ray photoelectron spectroscopic spectrum (XRPES) was obtained on a Thermo Fisher Scientific K-Alpha 1063 spectrophotometer with the Al Kα radiation and the beam spot size of 900 μm (energy step size 1 eV, pass energy 50 eV). Accurate binding energies were determined by referring to the C 1*s* peak at 284.8 eV with the beam spot size of 900 μm (energy step size 1.0 eV, pass energy 50.0 eV). Infrared spectral analysis was carried out on a Nicolet Magna IR-560 Fourier transform infrared (FTIR) spectrometer. The H_2 temperature-programmed reduction (TPR) was taken on a TP-5000 multifunction adsorption instrument at a temperature range from room temperature to 700 °C at a heating rate of 10 °C · min^{-1} in a gas flow of H_2: Ar = 1: 19 (volume ratio) with a GC-4000A chromatograph thermal conductivity detector. The NH_3 temperature-programmed desorption (NH_3-TPD) was obtained on the same adsorption instrument as the TPR.

2.4. Catalytic hydroconversion (CHC) of DNM

DNM (1 mmol), catalyst (0.02–0.1 g), and *n*-hexane (20 mL) were fed into a 100 mL stainless steel and magnetically stirred autoclave. After replacing air in the autoclave with H_2 3 times and pressurized with H_2 to 5 MPa, the autoclave was heated to an indicated temperature followed by reaction at the temperature for a prescribed period of time. Then the autoclave was cooled down in an ice-water bath and the reaction mixture was taken out and filtrated to filtrate and filter cake. The filtrate was analyzed with an Agilent 7890/5975 gas chromatograph/mass spectrometer (GC/MS), which is equipped with a quadrupole analyzer operated in electron impact (70 eV), and quantified with an Agilent 7890 gas chromatograph fitted with a flame ionization detector. The HP-5MS (60 m × 0.25 mm × 0.25 μm) capillary column was heated from 60 to 300 °C at a rate of 10 °C · min^{-1}.

3. Results and discussion

3.1. Catalyst characterizations

Catalysts I, II, and V shown in Table 1 were selected to be

Table 1
Ni-TFMSA/PAP prepared with different loadings of Ni and TFMSA.

Catalyst	NC (mL)	TFMSA (mL)	Loading (wt%)	
			Ni	TFMSA
I		4		33.3
II	1		28.6	0
III	1	1	28.6	7.2
IV	1	2	28.6	16.6
V	1	4	28.6	33.3
VI	1	6	28.6	42.6
VII	2	4	40.0	33.3

TAP 2 g.