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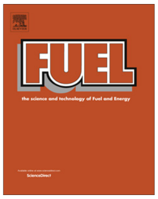

Full Length Article

Difunctional nickel/microfiber attapulgite modified with an acidic ionic liquid for catalytic hydroconversion of lignite-related model compounds

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HIGHLIGHTS

- Ni/MFA@AIL was prepared by thermally decomposing NC onto MFA modified with an AIL.
- Ni/MFA@AIL effectively induced the formation of H^+, H^-, and biatomic active hydrogen.
- Ni/MFA@AIL effectively catalyzed the CHCs of LRMCs to cyclanes.

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ABSTRACT

Modified microfiber attapulgite (MFA)-supported nickel was prepared by thermally decomposing nickel tetracarbonyl on MFA modified with an acidic ionic liquid (AIL, 1-sulfobutyl-3-methylimidazolium trifluoromethanesulfonate). It was characterized with multiple instruments and used for catalyzing hydroconversion of lignite-related model compounds (LRMCs) oxydibenzene, benzyloxybenzene, and oxybis (methylene)dibenzene. The results indicate that $Ni_{15\%}$/MFA@AIL effectively catalyzes hydroconversion of the LRMCs to afford cyclanes by inducing the formation of H^+, H^-, and biatomic active hydrogen.

1. Introduction

Along with the dramatically shrinking amount of petroleum and growing energy consumptions, coal conversion into materials, chemicals, and liquid fuels becomes a crucially important subject [1–3]. Direct coal liquefaction (DCL) is a feasible choice to directly convert coal into liquid fuels and value-added chemicals, which may provide an ideal alternative of petroleum to some extent [4]. However, conventional routes of DCL have some disadvantages, particularly severe reaction conditions [5]. Thus, it is imperative to develop DCL technologies under mild conditions.

Lignites are very abundant in natural resource over the world [6], accounting for more than 40% of the total coal reserves in China [7]. However, in spite of its abundance, easy access, and low mining cost, lignites have not been used as widely as high-rank coals because of their high moisture content, lower calorific value, high spontaneous combustion susceptibility, and high weathering degree [8,9]. Hence, developing efficient technologies for lignite conversion is needed to overcome the above disadvantages.

In the last few years, the thermal dissolution (TD) of coals, especially lignites, has attracted the attention of researchers owing to the high yield of soluble portion (SP) [10,11]. During coal TD in CH_3OH-NaOH, hydrolysis and cleavage of ether bonds are considered to be the main reactions [12,13]. Due to abundant oxygen-containing moieties, including ether linkages, in lignites, such a TD could be especially effective for lignite conversion. Therefore, the resulting SP from lignite TD should contain a large number of oxygen-containing compounds (OCCs, most of which contain aromatic rings) in addition to non-oxygen aromatics [14,15]. For using the SP as clean fuel, both deoxygenation and hydrogenation of the SP are very important [16,17].

Because of the inherent complexity of lignite composition, the investigation on lignite-related model compounds (LRMCs) proved

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Nomenclature

AIL	acidic ionic liquid	MFA	microfiber attapulgite
BOB	benzyloxybenzene	MPs	metal particles
BRs	benzene rings	NH_3-TPD	NH_3 temperature-programmed desorption
CAs	carbon atoms	NNPs	nickel nanoparticles
CH	cyclohexane	NTC	nickel tetracarbonyl
CHC	catalytic hydroconversion	OCCs	oxygen-containing compounds
CHM	cyclohexylmethanol	OBMDB	oxybis(methylene)dibenzene
CHOB	(cyclohexyloxy)benzene	ODB	oxydibenzene
DCL	direct coal liquefaction	ODCH	oxydicyclohexane
EDS	energy dispersive spectrometer	PC	phenyl cation
FTIR	Fourier transform infrared	PM	phenylmethanol
GC/MS	gas chromatograph/mass spectrometer	PMCs	precious metal catalysts
H···H	biatomic active hydrogen	SP	soluble portion
IHP	initial hydrogen pressure	TD	thermal dissolution
ILs	ionic liquids	TGA	thermogravimetric analysis
LRMCs	lignite-related model compounds	XRD	X-ray diffraction
MCH	methylcyclohexane		

to be a powerful tool for revealing the mechanisms for directional degradation of lignites at molecular level [18,19]. The dissociation of benzyloxybenzene (BOB) used as a LRMC has been extensively investigated since 1980s [20,21]. Schlosberg et al. [20] found that BOB contains the ether functionality believed to be present in lignites and reacts readily at 375 °C either in the presence or absence of a hydrogen donor. BOB pyrolysis in the temperature range of 500–700 °C was also investigated [22], but side reactions significantly proceeded in the temperature range, consuming large amount of energy.

Catalysts play very important roles in directional degradation of lignites and LRMCs. Transition metals, especially precious metals, are used for catalyzing aromatic hydrogenation and C–O bond hydrocracking at relatively low temperatures. For example, naphthalene was totally converted over Pd/TiO_2, Pd/Al_2O_3, or Pt/Al_2O_3 at lower temperatures. However, the primary product was decalin at 200 °C and tetralin at 300 °C [23]. Although precious metal catalysts (PMCs) exhibit high catalytic activities, the actual use of such PMCs faces a number of challenges in their high price and strong tendency to be poisoned by heteroatoms existing in industrial raw materials. Ni-loading catalysts have been extensively investigated because of their relative availability [24,25]. However, lowly dispersed Ni-loading catalysts were usually prepared using their salts as precursors and agglomeration behavior of nickel nanoparticles (NNPs) on surface of the supports was observed during subsequent reduction of the supported nickel salts. Metal carbonyls, which could be thermally broken down into highly active metal particles (MPs), are ideal precursors of highly active MPs [26,27]. Microfiber attapulgite (MFA) is one of the most important catalyst support due to its high specific surface, adjustable acidity, and excellent thermal/mechanical stability [28]. Ionic liquids (ILs), which proved to be effective for many catalytic processes, have provided new strategy for developing catalytic materials [29,30]. Ni/ZSM-5 prepared by thermally decomposition of nickel tetracarbonyl (NTC) onto ZSM-5 turned out to be highly active for hydrogenating polymethylbenzenes and coal tars [31].

In the present work, we prepared a highly active and selective difunctional supported nickel catalyst Ni/MFA@AIL. Oxydibenzene (ODB), BOB, and oxybis(methylene)dibenzene (OBMDB) were used as LRMCs to confirm the catalyst activity for catalytic hydroconversion (CHC) of LRMCs to cyclohexane (CH) and methylcyclohexane (MCH).

2. Experimental

2.1. Materials

ODB, BOB, and OBMDB are analytical reagents purchased from Aladdin Industrial Inc., Shanghai, China. Acidic IL (AIL, 1-sulfobutyl-3-methylimidazolium trifluoromethanesulfonate) was purchased from Chengjie Chemical Co., Ltd., Shanghai, China. NNPs and MFA were purchased from Jien Nickel Co., Ltd., Jilin, China and Jiangsu Huahong Mining Chemical Co., Ltd., Xuyi city, Jiangsu, China, respectively. MFA was pulverized to pass through a 200-mesh sieve (particle size <74 μm). The commercially available *n*-hexane was purified by distillation prior to use.

2.2. Catalyst preparation and characterization

NTC was produced by reacting 5.0 g NNPs with 6.0 MPa CO at 100 °C in a 100 mL stainless and magnetically stirred autoclave for 2 h (Caution: NTC is one of the most lethal chemicals and thereby should be paid attention during the experiment). MFA@AIL was prepared according to the procedures reported previously [32]. MFA was added to 0.5 M HCl solution and magnetically stirred at 60 °C for 4 h followed by filtration and washing the filter cake with deionized water to remove unreacted HCl. The washed filter cake was dried under vacuum at 110 °C overnight followed by calcination in a tube furnace at 350 °C for 3 h. Subsequently, acid-treated MFA (3 g) was dispersed into 100 mL of aqueous solution of AIL (3 g) and stirred at 90 °C for 24 h. Then the resulting mixture was separated via centrifugation, washed with deionized water and ethanol, and dried in vacuum at 70 °C overnight. Ni/MFA@AIL was prepared by in-situ decomposition of NTC onto MFA@AIL at 100 °C. In detail, ethoxyethane (20 mL), MFA@AIL (2 g), and NTC were put into the autoclave. After replacing air inside the autoclave 3 times with N_2, the mixture in the autoclave was stirred at 100 rpm for 1 h at room temperature to completely impregnate NTC onto MFA@AIL. Then the autoclave was heated to 100 °C and the mixture in the autoclave was stirred at 200 rpm for 1 h. After cooling the autoclave to room temperature, CO in the autoclave was released followed by repeating the above steps to decompose NTC as completely as possible. Finally, the reaction mixture was removed from the autoclave and filtrated to obtain Ni/MFA@AIL after desiccation in a vacuum at 60 °C for 4 h.