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Short Communication

Characterization and catalytic properties of Ni and NiCu catalysts supported on ZrO_2–SiO_2 for guaiacol hydrodeoxygenation

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ABSTRACT

ZrO_2–SiO_2 complex oxides with Si/Zr mole ratio of 3 (SZ-3) were synthesized. ZrO_2–SiO_2 supported Ni and NiCu catalysts were prepared by impregnation method. Their catalytic performances were evaluated in the hydrodeoxygenation (HDO) upgrading of model reactant guaiacol to hydrocarbons. The physicochemical properties of the support materials and catalysts were characterized by FTIR, XRD, TPD, TPR, and BET techniques. The addition of Cu significantly affected the acidity, and thus influenced their catalytic performance for product distributions. Over the Ni5Cu/SZ-3 catalyst, the cyclohexane selectivity of 80.8% and the methylcyclohexane selectivity of 12.4% were obtained with complete conversion of guaiacol under the 300 °C, 5.0 MPa H_2 pressure.

1. Introduction

The expected growth of the production capacity of second-generation bio-fuels from biomass by fermentation process will lead to a vast source of lignin. It is important to obtain new sustainable carbon and energy sources from lignin which is a main constituent of lignocellulosic biomass (15–30% by weight, 40% by energy) [1,2]. Lignin is a three-dimensional amorphous polymer consisting of methoxylated phenylpropane structures [1]. It can be broken down to phenolic monomers by means of catalytic and thermochemical processes [2,3]. These phenolic compounds cannot be used as the transportation fuels directly due to their high oxygen content, poor chemical stability, corrosivity and immiscibility with hydrocarbon fuels [4,5]. However, the process of hydrodeoxygenation (HDO) is a crucial component of a number of strategies for better uses of lignin-derived phenolic monomers.

Recently, the catalytic HDO of lignin-derived phenolic monomers has been widely explored. Guaiacol is usually selected as the model compound because it contains three types of C–O bonds for $C_{AR}-OH$, $C_{AR}-OCH_3$ and $C_{AR}O-CH_3$, which are frequently found in various lignin-derived phenolic monomers [6,7]. Most of HDO catalysts combine active metals with various supports, such as sulfided Mo-based catalysts [6–11], Ni-based catalysts [12,13], noble metal catalysts [14–18] supported on Al_2O_3, zeolites, Al_2O_3–SiO_2, activated carbon, etc. For the HDO reaction of guaiacol, different catalysts lead to different reaction pathways and product distributions. The first stage of reaction is demethylation and demethoxylation over sulfided CoMo catalysts, and the main product is benzene [12], while the first stage of reaction is hydrogenation of aromatic ring over noble catalysts, and the main product is cyclohexane [12,19]. Generally, the noble metal catalysts exhibit the excellent catalytic performance in the HDO of guaiacol, and the main products are composed of saturated hydrocarbons. However, their high cost could lead to the limitation for industrial application with a large scale. With the sulfided Mo-based catalysts and conventional transition-metal-based catalysts, catechol, phenol and benzene are the major products, and the cyclohexane is the minor product [6,7]. For the case of sulfided Mo-based catalysts, the mercaptan was formed as the undesired product, which could increase the contamination risk of HDO products. In addition, these catalysts give the carbon deposition on the catalyst surface severely. As a result, exploring cheap and non-sulfided transition metal catalyst is important but still an open challenge.

Generally, ZrO_2 is considered as an appropriate support for the HDO catalysts. It usually shows very high catalytic activity in the HDO of guaiacol because the ZrO_2 seems to favor activation of O-compounds in the support surface [6,7,19]. Moreover, the carbon deposition on the surface of ZrO_2-supported catalyst is weaker than that of the sulfided CoMo/Al_2O_3 catalyst [7,19]. However, the surface area of ZrO_2 is very small, which is unfavorable for the improvement of catalytic performance. The addition of SiO_2 into ZrO_2 may overcome this disadvantage.

Binary Ni–Cu catalyst has been tested in the hydrodechlorination of chlorinated hydrocarbons [20]. Recent screening studies on bimetallic Ni–Cu catalyst indicate its potential for HDO upgrading of vegetable oil [21], anisole and fast pyrolysis oils [22]. The pristine Ni is known for its high hydrogenation activity for a wide range of hydrogenation reactions [23]. Cu is applied as a promoter, which could

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reduce the reduction temperature of Ni, and prevent excessive carbon deposition on Ni [24].

In this work, the binary ZrO_2–SiO_2 oxide was synthesized as the support material, and then the non-noble and non-sulfided catalysts using Ni and NiCu as the active components were prepared by wetness precipitation method. Their catalytic performances were evaluated in the HDO of guaiacol to hydrocarbons. These catalysts exhibited the promising activity and selectivity toward hydrocarbons.

2. Experimental

2.1. Catalyst preparation

ZrO_2–SiO_2 support was prepared as the following method. Appropriate amounts of $Na_2SiO_3 \cdot 9H_2O$ and $ZrOCl_2 \cdot 8H_2O$ were dissolved in distilled water respectively. With continuous stirring, the solution of ammonium nitrate was dropped gradually into the solution of Na_2SiO_3 until the pH of the solution reached an approximate value of 8.0, by which the $Si(OH)_4$ precipitate was prepared. According to a similar procedure, the $Zr(OH)_4$ precipitate was prepared using ammonia as a precipitation agent. The two kinds of precipitates were mixed and whisked. The mixed precipitate was aged for 12 h at 75 °C. Subsequently, the precipitate was filtered and washed with distilled water to completely remove chloride ions. The obtained solid was dried overnight at 120 °C and then calcined at 500 °C for 5 h, by which the complex oxide was prepared. The sample was referred to as SZ-3 (3 is the molar ratio of Si/Zr). Pure ZrO_2 was prepared using the same method.

The calculated support, Ni $(NO_3)_2$ or the mixture of Ni $(NO_3)_2$ and Cu $(NO_3)_2$ was dissolved in superfluous distilled water, followed by agitating and evaporating to dryness. The solid that remained was dried in air at 120 °C overnight and then calcined at 500 °C for 5 h. The Ni loading was 10 wt.% for all catalysts tested in this work, and the Cu loading was 5 wt.% and 15 wt.% respectively. The catalysts were designated as Ni/SZ-3 or Ni*x*Cu/SZ-3(*x* is 5 and 15). All the catalysts were crushed and sieved to 120–200 BSS mesh, and reduced at 500 °C before use.

2.2. Catalyst characterization

The BET specific surface area, average pore diameter and pore volume of catalysts were determined by N_2 isothermal (77 K) adsorption using QUADRASORB SI analyzer equipped with QuadraWin software system. The supports and catalysts were characterized by X-ray diffraction (XRD) (XPert Pro MPD with Cu $K\alpha$ ($\lambda = 0.154$) radiation, Philip). FT-IR spectra of synthesized supports were taken on a TENSOR27 FT-IR spectrometer using KBr pellet technique. Scanning electron microscopy (SEM) images were recorded on a Hitachi S-4800 instrument operated at 20 kV. TEM investigations were carried out on a Jeol TEM-100CX instrument at 200 kV accelerating voltage.

H_2-TPR, NH_3-TPD and CO_2-TPD researches of the different catalysts were carried out in a quartz tube reactor with a thermal conductivity detector (TCD). A similar procedure was reported in literature [13]. TG studies of the used catalysts were carried out under an air flow rate of 30 ml/min with analyzers by using a 10–15 mg sample and a 10 °C/min temperature increment.

2.3. Catalyst testing

All the HDO reactions of guaiacol were carried out in a 500 ml stainless autoclave equipped with an electromagnetic driven stirrer. For each run, 1.5 g catalyst, 10.0 g of guaiacol and 100.0 g of solvent dodecane were loaded in the autoclave. After displacing air, the reactor was pressurized with H_2 to 5.0 MPa and sealed. The autoclave was heated to a desired reaction temperature, while the reagents were vigorously stirred at 800 rpm. Liquid samples were withdrawn from the reactor on line for subsequent off-line analysis. Each experiment of HDO catalytic reaction was repeated twice. Data are the average of results from two experiments.

The components of liquid products were confirmed by GC–MS equipped with a DB-5 pack column. Quantitative analysis of liquid products was performed by GC (SHIMADZU GC2010 with a FID detector and a DB-5 column) with benzyl alcohol as an internal standard. The vaporization temperature was 250 °C, and the oven temperature program ranged from 50 °C to 250 °C at the rate of 5 °C/min.

The conversions of guaiacol and the product mole distribution were calculated based on the following formulas:

$$X_{GUA}\% = \frac{moles(GUA)_{in} - moles(GUA)_{out}}{moles(GUA)_{in}} \times 100 \tag{1}$$

$$S_i\% = \frac{moles(product)_i}{\sum moles(product)} \times 100. \tag{2}$$

X_{GUA} represents the conversion of guaiacol, and S_i represents the product selectivity.

3. Results and discussion

3.1. Support and catalyst characterization

As shown in Fig. 1, the FTIR spectra show a sharp peak at 1100 cm^{-1} indicating Si–O–Si asymmetric stretching vibration, in comparison, which is found at 1150 cm^{-1} for pure silica. The shift in the stretching frequency is due to the deterioration of the silica framework after the insertion of Zr-atom [25]. The peak at 960 cm^{-1} indicates the presence of Si–O–Zr bond in the composite materials [25]. It implies that the solid phase reaction occurred between $Si(OH)_4$ and $Zr(OH)_4$ during the calcining process of mixed hydroxide $Si(OH)_4$ and $Zr(OH)_4$.

The XRD analysis of different supports and catalysts was carried out (Fig. S1 in the Supplementary material). ZrO_2 has two coexisting structurally stable phases, namely *m*-ZrO_2 and *t*-ZrO_2. The 2θ of 24.1°, 28.2°, 31.4°, and 34.1° are assigned to the *m*-ZrO_2, and the peaks centered at about 35.2°, 50.2°, and 60.3° are assigned to the *t*-ZrO_2 [26]. Binary oxide SZ-3, being an amorphous material, shows no distinct XRD peaks except a very broad weak feature between 18°and 37°. The diffraction peaks of NiO on the ZrO_2 and SZ-3 supports can be seen clearly in the XRD patterns ($2\theta = 37.3°$, 43.3° and 62.9°). However, the characteristic peaks of CuO ($2\theta = 35.7°$ and 38.8°) can only be seen in the XRD patterns of Ni15Cu/SZ-3. For the case of the low Cu loadings (5 wt.%), no diffraction peaks corresponding to CuO crystallite were

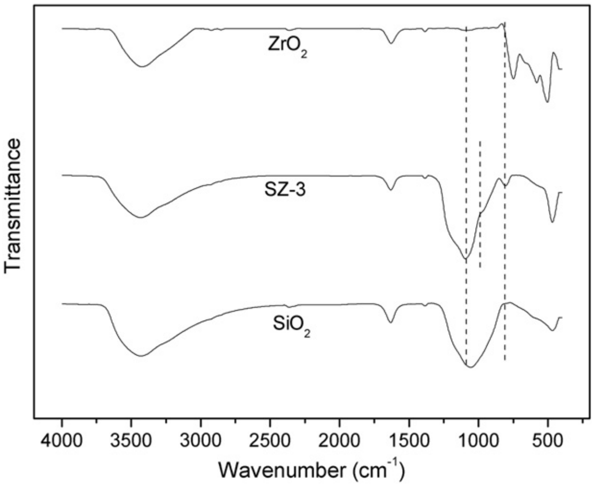

Fig. 1. FT-IR spectra of support material samples.