Journal of Catalysis 349 (2017) 84–97

Contents lists available at ScienceDirect

Journal of Catalysis

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

Geometric and electronic effects of bimetallic Ni–Re catalysts for selective deoxygenation of m-cresol to toluene

Feifei Yang [a], Dan Liu [a], Hua Wang [a], Xiao Liu [a], Jinyu Han [a], Qingfeng Ge [a,b,*], Xinli Zhu [a,*]

[a] Collaborative Innovation Center of Chemical Science and Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
[b] Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901, United States

ARTICLE INFO

Article history:
Received 17 October 2016
Revised 21 December 2016
Accepted 4 January 2017

Keywords:
Ni–Re/SiO_2
Bimetallic catalyst
m-Cresol
Hydrodeoxygenation
Deoxygenation
Hydrogenation
C—C hydrogenolysis

ABSTRACT

Ni–Re/SiO_2 bimetallic catalysts were prepared using a co-impregnation method and tested in vapor phase hydrodeoxygenation of m-cresol at 300 °C and 1 atm H_2. In contrast to the use of unselective monometallic Ni/SiO_2 for catalyzing deoxygenation, hydrogenation, and C—C hydrogenolysis reactions, bimetallic 5% Ni–2.5%Re/SiO_2 improved the intrinsic reaction rate of the hydrodeoxygenation reaction by a factor of 6, with the turnover frequency for selective deoxygenation to toluene increased by four times, while that for C—C hydrogenolysis to methane was reduced by one-half. Characterization results from X-ray diffraction, Raman, transmission electron microscopy, X-ray photoelectron spectroscopy, infrared spectroscopy of CO adsorption, H_2 temperature-programmed reduction, and CO chemisorption indicate that adding Re increased Ni dispersion and resulted in Ni–Re surface alloy formation after reduction. The presence of Re in the surface alloy breaks the continuous Ni surface into smaller ensembles (geometric effect) and reduces the *d*-band electron density of Ni (electronic effect). Results from density functional theory calculations indicate that the Ni–Re neighboring site is the active site for breaking the C—O bond by adsorbing the O atom on Re and the phenyl ring on the neighboring Ni atoms, which facilitates deoxygenation to toluene. The reduced Ni ensemble size inhibits the hydrogenolysis of the C—C bond by destabilizing the transition state, whereas the reduction of the electronic density in *d* states of Ni weakens the adsorption of the phenyl ring, and both contribute to the greatly reduced methane production from successive C—C hydrogenolysis.

1. Introduction

The lignin fraction of lignocellulosic biomass has relatively low oxygen content in comparison to cellulose and hemicellulose [1,2]. Depolymerization (for example, fast pyrolysis) of lignin results in phenolic compounds, such as phenol, cresol, anisole, guaiacol, and syringol [3]. These are important building blocks for fuels and chemicals after complete or partial removal of the oxygen content. Catalytic hydrodeoxygenation (HDO) is a key step in oxygen removal [2].

Many studies on HDO of phenolics have been performed using various catalysts, including hydrodesulfurization (HDS) catalysts (CoMoS and NiMoS) [4,5], hydrogenating catalysts (Ni and Pt) [6,7], zeolites [8], metal oxides [9], and metal phosphides [10], and operated under very different conditions to achieve a high degree of oxygen removal and to explore the reaction mechanism. During HDO of phenolics, a number of reactions, such as hydrogenation of the phenyl ring, deoxygenation, C—C hydrogenolysis, and transalkylation, may take place at the same time, depending on the catalysts and operating conditions. These reactions, occurring in an uncontrolled manner, lead to a mixture of products with high hydrogen consumption and low liquid products yield. Recently, more attention has been paid to selective deoxygenation of phenolics to aromatics with reduced hydrogen consumption under mild conditions (low pressure and intermediate temperature) [11]. These mild conditions are suitable for processing phenolics produced from fast pyrolysis before their condensation to unstable liquids at low temperatures. Reducible metal oxides, such as FeO_x and MoO_x, appear to be highly selective for deoxygenation of phenolics to aromatics at relatively high temperatures [9,12]. On the other hand, typical hydrogenating catalysts, such as Pt, Pd, Ni, and Ru, are more active and could be operated at lower temperatures. However, they tend to hydrogenate the phenyl ring rather than to deoxygenate it [6,7,13–15]. In addition, Ni and Ru have been reported to be highly active for catalyzing C—C hydrogenolysis to form low-value short-chain hydrocarbons [6,13,14]. Combining a hydrogenating metal and an oxophilic metal (reducible metal

---

* Corresponding authors.
E-mail addresses: qge@chem.siu.edu (Q. Ge), xinlizhu@tju.edu.cn (X. Zhu).

http://dx.doi.org/10.1016/j.jcat.2017.01.001
0021-9517/

oxide) forms a bimetallic catalyst, such as Ni–Co [16], Pt–Mo [17], Pt–Co [18], Pt–Zn [19], Pd–Fe [20], or Ni–Fe [21]. These bimetallic catalysts are expected to balance the activity and selectivity of deoxygenation and hydrogenation, and have been explored for HDO of phenolics. For example, Nie and Resasco reported that the Ni–Fe catalyst is selective for deoxygenation of m-cresol to toluene, and proposed that Fe helped the hydrogenation of the tautomerization intermediate from m-cresol to 3-methyl-3,5-cyclohexadienol, which is then quickly dehydrated to toluene [21]. It is noted that the Ni–Fe catalyst is less active than the Ni catalyst. Sun et al. reported deoxygenation of guaiacol and m-cresol to aromatics over a Pd–Fe catalyst and suggested that Fe is the active site for direct deoxygenation, whereas Pd is the active site for activating hydrogen [20,22]. The addition of 5% Pd improves the activity of Fe_2O_3 by a factor of 2 [22]. Clearly, more active and selective catalysts for conversion of phenolics to aromatics are desirable. Although catalysts based on bimetallics show promise in improving the selectivity, the nature of the active site and the mechanism for selective deoxygenation are not yet clear.

In this work, we report a highly active bimetallic Ni–Re/SiO_2 catalyst for selective deoxygenation of m-cresol to toluene that greatly inhibits C—C hydrogenolysis under mild conditions. m-Cresol was used as a model compound because it is an important intermediate product from HDO of complex phenolic compounds, such as guaiacol [23,24]. The inert silica was used to avoid complications due to the support, and therefore, to allow us to focus on better understanding the role of the bimetallic catalysts. Using a combination of detailed characterizations and density functional theoretical calculation, the active site for deoxygenation is determined to be the Ni–Re neighboring sites.

2. Experimental

2.1. Catalyst preparation

The bimetallic Ni–Re catalysts were prepared using incipient wetness co-impregnation of SiO_2 (Sigma, $S_{BET} = 200\ m^2/g$) with aqueous solutions of calculated amounts of $Ni(NO_3)_2{\cdot}6H_2O$ (Strem Chemicals) and NH_4ReO_4 (Alfa). After impregnation for 12 h, the samples were dried overnight at 120 °C, followed by calcination at 400 °C for 4 h with a heating rate of 2 °C/min. The amount of Ni loading was 5 wt.%, while Re loading was varied from 0 to 10 wt.%. The catalyst was denoted as 5Ni*X*Re, where 5 and *X* represent the weight percentages of Ni and Re, respectively, in the sample. The catalyst powder was pressed, crushed, and sieved to 40–60 mesh for reaction.

2.2. Catalyst characterization

Nitrogen adsorption was recorded at liquid nitrogen temperature in an automatic Micrometrics Digisorb 2600 analyzer. The catalysts were outgassed at 350 °C prior to measurements. The specific surface area of the catalysts was calculated using the Brunauer–Emmett–Teller (BET) method in the relative pressure range $0.005 < p/p_0 < 0.27$.

X-ray diffraction (XRD) patterns of the catalyst samples were recorded on a Rigaku D/max 2500 diffractometer with a Cu Kα radiation source ($\lambda = 1.54056$ A) in the 2θ range 20°–80°.

The Raman spectra were obtained on a Renishaw Raman spectrometer, with an Ar^+ ion laser (532 nm) being the exciting light source. The focusing spot size was about 1 μm. All spectra were collected at room temperature, with an acquisition time of 10 s/scan and a resolution of 2 cm^{-1}.

Hydrogen temperature-programmed reduction (H_2 TPR) was performed on a Chemisorb 2750 (Micrometrics). Prior to measurement, a catalyst sample of 40 mg was loaded in a U-tube quartz reactor and pretreated with flowing N_2 at 300 °C for 1 h. After the sample was cooled to room temperature, the gas was shifted to 5% H_2/Ar (25 mL/min). After the signal was stabilized, the sample was heated linearly to 800 °C at a rate of 10 °C/min. The amount of hydrogen uptake was monitored on line by a thermal conductive detector.

The transmission electron microscopy (TEM) images were obtained on a JEM 2010F field emission system operated at 200 kV. The fine catalyst powder was dispersed ultrasonically in ethanol for 30 min and a drop of the suspension was deposited on a carbon-coated copper grid for TEM measurement.

X-ray photoelectron spectroscopy (XPS) was performed on a PHI 1600 ESCA spectrometer equipped with an Al*K*α X-ray radiation source ($h\nu = 1486.6$ eV). Catalyst samples were prereduced at 450 °C for 1 h ex situ before each measurement. The binding energy (BE) values were referenced to the C1*s* peak at 284.5 eV.

Fourier transform infrared spectra (FTIR) of CO adsorption were recorded on a Nicolet 6700 (Thermo Scientific), equipped with a liquid-N_2-cooled mercury–cadmium–tellurium detector and a transmittance cell. The catalyst wafer (20 mg) was reduced in situ at 450 °C for 1 h with flowing H_2 at 30 mL/min. After that, the sample was cooled to room temperature in flowing He at 30 mL/min and then the background was recorded. The sample was exposed to 5% CO/He (30 mL/min) for 30 min, followed by He purging for another 30 min. The spectra were recorded at a resolution of 4 cm^{-1} and 128 scans.

The dispersion of Ni was estimated based on dynamic CO chemisorption, measured in a microreactor system equipped with a Cirrus 200 mass spectrometer (MKS). The system consisted of an oven with a temperature controller, gas delivery system, micro quartz reactor (6 mm o.d.), and six-port valve. Catalyst samples (50 mg, 40–60 mesh) were reduced at 450 °C for 1 h in flowing H_2, followed by He purging (30 mL/min) for another 30 min. Then the temperature was decreased to room temperature. Pulses of 5% CO/He (100 μL) were sent to the catalyst through the six-port valve until a constant CO peak area was reached.

NH_3 and isopropylamine temperature–programmed desorption (NH_3 TPD and IPA TPD) were measured on the same system as CO chemisorption. A catalyst sample of 100 mg was reduced at 450 °C for 1 h and then purged with flowing He (30 mL/min) for another 30 min. The temperature was reduced to 100 °C. For NH_3 TPD, the sample was exposed to a stream of 2% NH_3/He (30 mL/min) for 30 min. For IPA TPD, liquid IPA (5 μL/pulse, 10 pulse, 3 min/pulse) was injected using a microsyringe manually and vaporized before entering the reactor. After the sample was flushed with flowing He (30 mL/min) for 30 min, the temperature was increased to 650 °C at a rate of 10 °C/min. The quantification was done by injecting pulses of 2% NH_3/He (10 mL/pulse).

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of pyridine adsorption were measured using a Frontier spectrometer (PerkinElmer), equipped with a diffuse reflectance accessory and a reaction chamber (Harrick). A fine powder catalyst was loaded into the sample cup of the chamber. After the sample was reduced at 450 °C for 1 h and purged with He for 30 min, it was cooled to 100 °C, at which a background spectrum was recorded. Pyridine vapor was then introduced for 30 min, followed by purging using He for another 30 min. The DRIFT spectra were recorded at a resolution of 4 cm^{-1} with 64 scans.

2.3. Density functional theory calculations of phenol adsorption

Density functional theory (DFT) periodic slab calculations were carried out using the Vienna Ab Initio Simulation Package (VASP) [25–27]. The periodic DFT code uses the projector-augmented wave (PAW) method to describe the effective core potentials and