

Metallic nickel supported on mesoporous silica as catalyst for hydrodeoxygenation: effect of pore size and structure

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Received: 2 September 2016/Accepted: 24 November 2016 © Springer Science+Business Media B.V., part of Springer Nature 2018

Abstract Catalytic hydrodeoxygenation (HDO) of anisole, a methoxy-rich ligninderived bio-oil model compound, was carried out over a series of Ni-containing (5, 10, 20, and 30 wt%) catalysts with commercial silica and ordered mesoporous silica SBA-15 as support. Both supports and catalysts were characterized by N₂ adsorption-desorption isotherms, X-ray diffraction, CO chemisorption, and transmission electron microscopy (TEM). Catalytic reaction was performed at 250 °C and 10 bar H₂ pressure. Depending on the catalyst support used and the content of active metal, the catalytic activity and product distribution changed drastically. Increase of the nickel loading resulted in increased anisole conversion and C₆ hydrocarbon (benzene and cyclohexane) yield. However, loading more Ni than 20 wt% resulted in a decrease of both conversion and C₆ yield due to agglomeration of Ni particles. In

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addition, Ni/SBA-15 samples exhibited much stronger catalytic activity and selectivity toward C_6 hydrocarbon products compared with Ni/silica catalysts. The differences in catalytic activity among these catalysts can be attributed to the effect of the pore size and pore structure of mesoporous SBA-15. SBA-15 can accommodate more Ni species inside channels than conventional silica due to its high pore volume with uniform pore structure, leading to high HDO catalytic activity.

Keywords Hydrodeoxygenation \cdot Supported Ni catalysts \cdot Mesoporous silica \cdot SBA-15 \cdot Anisole

Introduction

As a result of consumption of fossil fuels such as oil, coal, and natural gas, global warming and environmental pollution have become one of the most important issues in human history. The drive towards use of alternative and renewable energy source has gradually become a general tendency worldwide [1-3]. Among renewable energy sources, biomass has high utilization potential, not only for energy but also as transportation fuel or for chemical production. Many studies have reported investigations on processes for transformation of biomass into liquid-phase biofuel. Fast pyrolysis is a simple and effective method to convert high-molecular-weight biomass to low-molecular-weight bio-oil. However, bio-oil produced from fast pyrolysis contains high oxygen concentration, limiting its application on industrial scale [2, 4, 5]. The best strategy for removing these oxygen-containing compounds is catalytic hydrodeoxygenation (HDO) [2, 6–8].

The HDO process takes place during treatment of bio-oil by hydrogen in the temperature range from 250 to 450 °C and high pressure (20–300 bar), so that oxygen can be removed in the form of water [9, 10]. However, under these conditions, complete hydrogenation of the aromatic ring of substituted phenols is inevitable, leading to high hydrogen consumption [10]. Therefore, it is necessary to design a highly active catalyst for the HDO reaction to allow direct deoxygenation of lignin model compounds to aromatic hydrocarbons under mild reaction conditions. A remarkable number of catalysts have been investigated. Industrial sulfide CoMo and NiMo catalysts have been widely studied for hydrotreatment of model compounds [11–15]. Other catalysts based on transition metals [16, 17], supported noble metal [18–21], and metallic phosphides [22, 23] have been demonstrated, exhibiting comparable catalytic activity for HDO. Nickel-supported catalysts seem to be promising because of their low cost, stability, and high activity [5].

Recently, due to facile diffusion of reactants into pores, mesoporous materials have attracted considerable attention from many researchers [24–26]. Ru-promoted Co/mesoporous silica SBA-15 was reported to be a remarkable promising catalyst for many kinds of reaction, including Fischer–Tropsch synthesis, dry reforming, and ethane dehydrogenation [27–29]. Owing to their regular pore structure and inertness, mesoporous silica materials have been used as supports for catalysts for

HDO of biomass-derived compounds [5, 30]. However, studies on the role of the mesoporous structure of the support for hydrotreatment of lignin model compounds are limited.

In the work presented herein, ordered mesoporous silica SBA-15 with high specific surface area and sharp pore size distribution was synthesized. The obtained mesoporous material was utilized as support for nickel catalysts to investigate their catalytic activity for HDO of a lignin model compound (anisole). A series of Nicontaining (5, 10, 20, and 30 wt%) catalysts were prepared and used in the HDO reaction at 250 °C for 2 h to understand the role of the active metal content. In addition to mesoporous silica, the activity of Ni on commercial silica (Ni/silica) catalyst was also studied to examine the effect of the mesopore structure of the support on the catalytic activity in the HDO reaction.

Experimental

Preparation of catalysts

SBA-15 was synthesized according to a preparation method described in literature [31]. The typical method was as follows: P-123 (8 g, Aldrich) was first dissolved in mixed solution of 320 g 2 M HCl and 60 g deionized water under vigorous stirring until completely dissolved. Then, tetraethylorthosilicate (17 g, Aldrich) was added to this solution, followed by stirring for 5 min. The solution was kept at 35 °C for 20 h, followed by posttreatment at 100 °C for 24 h. The resulting white powder was filtered and dried at 100 °C overnight. Finally, the dried powder was calcined at 550 °C for 2.5 h to obtain mesoporous silica SBA-15.

Nickel was incorporated on the surface of each silica support (conventional silica and SBA-15) by impregnation method using aqueous solution of nickel nitrate hexahydrate [Ni(NO₃)₂·6H₂O, Aldrich]. An exact amount of Ni precursor was impregnated into SBA-15 to obtain various Ni loadings (5, 10, 20, and 30 wt%). The samples were calcined in air flow at 500 °C for 3 h, followed by reduction in hydrogen flow at 400 °C within 3 h. Finally, the sample was passivated in oxygen environment at room temperature for 30 min before HDO reaction.

Characterization of catalysts

High-angle X-ray diffraction (D/MAX Ultima III, Cu K_{α}, Rigaku) and low-angle XRD (X/Pert PRO Multi Purpose, Cu K_{α}) analyses were used to characterize the phase structure of the pure supports and the Ni-supported catalysts. N₂ adsorption–desorption isotherms were collected at 77 K using a Micromeritics ASAP2020. The specific surface area was calculated according to the Brunauer-Emmett-Teller (BET) method. The pore size distribution was identified from the desorption isotherm using the Barrett–Joyner–Halenda (BJH) method. The Ni dispersion and particle size were calculated from the adsorbed amount of CO, measured by CO chemisorption at 50 °C. All samples were reduced at 400 °C for 3 h in 10% H₂ gas flow before treating with 10% CO + 90% He gas mixture. The morphology of Ni

crystallites was observed by transmission electron microscopy (TEM, CM200). The Ni loading on the catalysts was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, OPTIMA8300, PerkinElmer, USA).

Catalytic test

Hydrodeoxygenation of anisole was conducted in a 100-mL autoclave-type batch reactor. Typically, 1.0 g catalyst and 40 mL 10 wt% anisole solution were added into the reactor. Dodecane (Aldrich) was used as solvent for the anisole solution. Nitrogen gas was purged into the reactor to form an inert environment, then hydrogen gas was filled into the reactor to initial hydrogen pressure of 10 bar. The reactor was heated to 250 °C and maintained at this temperature for 2 h. The reactor was cooled naturally to room temperature after completion of the HDO process. The solid product of the HDO reaction was filtered and washed with toluene and acetone several times. The liquid product was analyzed by gas chromatography (GC, Agilent Technology 6890) using an HP-INNOWAX column and flame ionization detector (FID).

Results and discussion

Catalyst properties

Supported nickel catalysts were prepared using various metal loading contents and different supports for HDO of anisole to understand the mechanism of this complex reaction. The N₂ adsorption–desorption isotherms and pore size distribution of all samples are displayed in Fig. 1. According to the International Union of Pure and Applied Chemistry (IUPAC) classification, both supports and catalysts possessed type IV sorption isotherms, as seen in Fig. 1a, b, which is associated with porous materials. However, while the hysteresis loop of the conventional silica-based catalysts was type H2 with narrow neck and wider body (ink-bottle pores), the Ni catalyst supported on SBA-15 showed type H1 hysteresis, indicating a narrow distribution of relatively uniform (cylindrical-like) pores [32]. For all samples, loading of active metal onto both supports resulted in an evident drop of both specific surface area and total pore volume, indicating deposition of metal nanoparticles within the channels of the supports. The porous structure of both silica supports was maintained after incorporation of nickel.

Figure 1c, d shows the corresponding pore size distributions of the silica supports and catalysts. The Ni/SBA-15 catalysts and SBA-15 support exhibited uniform pores with sharp pore size distribution. The appearance of a small peak at 4 nm in these cases when a large amount of Ni was loaded may be due to presence of Ni species in the pores, resulting in a lower proportion of pores of intermediate size (6–7 nm). On the other hand, as can be observed, the silica support and Ni/silica catalysts displayed a wide range of pore size with average of 6–8 nm, meaning that the conventional silica had only a small portion of mesopores.



Fig. 1 N₂ adsorption–desorption isotherms of a Ni/SiO₂ and b Ni/SBA-15 catalysts; corresponding pore size distribution of c Ni/SiO₂ and d Ni/SBA-15 catalysts

The textural properties of the supports and corresponding supported catalysts are summarized in Table 1, which also lists the Ni loadings identified by ICP-OES. The actual Ni content values are slightly lower than the designed values. In spite of the similar average pore size (6–8 nm), the surface area of the catalysts supported on SBA-15 was much higher than for those supported on silica. Although the active component was loaded up to 20 wt%, the physical properties of the silica and mesoporous silica support did not change much compared with the pristine silica and SBA-15.

Figure 2 displays the XRD patterns of the supported nickel catalysts. The broad peak, observed in all patterns and centered at 2θ of 23° , is attributed to amorphous silica. In the case of the calcined supported nickel catalysts (Fig. 2a, c), four peaks appearing at $2\theta = 37.1^{\circ}$, 43.3° , 62.9° , and 76.5° can be matched with (111), (200), (220), and (311) crystal planes of monoclinic nickel(II) oxide (NiO), respectively, in Joint Committee on Powder Diffraction Standards (JCPDS) card no. 47-1049. After reduction at 400 °C, the XRD patterns (Fig. 2b, d) of the reduced Ni/silica and Ni/SBA-15 samples showed peaks at 2θ of 45.5° , 51.9° , and 76.3° , respectively, corresponding to lattice plane (111), (200), and (220) of metallic nickel (JCPDS 04-0850). No peaks corresponding to NiO were found in the XRD patterns of the reduced samples, demonstrating that NiO species in the calcined catalysts was completely reduced to active metallic Ni particles. In addition, with increasing

Catalyst	Ni loading (wt%)	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore size (nm)	CO uptake (µg/mol)	Dispersion (%)	Ni particle size (nm)
SiO ₂	_	510	0.79	7.1	_	_	_
5Ni/ SiO ₂	3.2	421	0.63	6.2	60	10.9	9.2
10Ni/ SiO ₂	9.1	391	0.55	6.2	159	10.2	9.9
20Ni/ SiO ₂	18.7	352	0.52	6.2	65	2.0	49.4
SBA-15	_	767	1.05	6.2	-	-	_
5Ni/ SBA- 15	4.0	747	1.05	6.2	82	12.1	8.4
10Ni/ SBA- 15	7.9	654	0.91	6.2	220	16.3	6.2
20Ni/ SBA- 15	16.2	574	0.77	6.2	67	2.4	42

 Table 1 Physicochemical properties of supports and supported metal catalysts

nickel loading from 5 to 20 wt%, the sharpness and intensity of the peaks increased, indicating presence of larger metallic particles.

The low-angle X-ray diffraction patterns $(0.75-2.5^{\circ})$ of the pristine mesoporous silica SBA-15 support and corresponding SBA-15-based catalysts are shown in Fig. 2e. Three well-resolved peaks attributed to (100), (110), and (200) planes of pristine SBA-15 are clearly observed for all samples, indicating that the typical one-dimensional hexagonal mesopore structure of SBA-15 was retained after nickel incorporation. This is in good agreement with data collected from N₂ adsorption–desorption measurements.

TEM images of reduced Ni-supported catalysts are shown in Fig. 3, revealing Ni particles with sphere-like morphology. For the Ni/silica catalysts, Ni species were overlapped and incorporated with others in an irregular way. In contrast, the Ni/SBA-15 samples exhibited uniform long channels, and a large portion of the Ni particles located in cylinder-like pores. Generally, with increasing Ni loading, the Ni particles tended to agglomerate and form larger particles. When the Ni content was increased to 20 wt%, the overwhelming majority of Ni species were located outside the channels of the mesoporous SBA-15.

The dispersion and average Ni particle size estimated from CO chemisorption measurements are reported in Table 1. These results indicate that increasing the Ni content from 5 to 10 wt% led to an increase of CO uptake, because the amount of metal active sites was increased. However, further increase of the Ni loading to 20 wt% resulted in a drastic decrease in the amount of CO adsorbed, which is attributed to aggregation of Ni particles. Particle aggregation results in not only a



Fig. 2 XRD patterns of **a** nickel oxide supported on silica, **b** metallic nickel supported on silica, **c** nickel oxide supported on mesoporous SBA-15, and **d** metallic nickel supported on mesoporous silica SBA-15; **e** Low-angle XRD patterns of Ni/SBA-15 with different nickel loadings from 5 to 20 wt%

lower number of active sites but also larger particle diameter, in accordance with the XRD patterns and TEM images. Among the studied catalysts, 10 wt% Ni/SBA-15 exhibited the best metal dispersion and smallest Ni particle size. In summary, the data from TEM images and CO chemisorption measurements indicate that the distribution of active sites is strongly influenced by the pore size and pore structure of the support.



(a)



(b)

(e)



Fig. 3 TEM images of a Ni/silica, b 5Ni/silica, c 10Ni/silica, d 5Ni/SBA-15, e 10Ni/SBA-15, and f 20Ni/SBA-15

Catalytic activity

We evaluated and compared the catalytic activity of the Ni catalysts supported on two types of silica (silica and SBA-15) in HDO of anisole (methoxy-rich model compound). Since the investigated catalysts had almost the same nickel loading, it is expected that any activity disparity can mainly be attributed to differences in the pore size and pore structure of the support. Figure 4 presents the conversion of anisole over these two catalysts with different nickel contents. The supported Ni catalysts showed quite good conversion of anisole (> 50% for 10 wt% nickel loading). Metallic nickel is considered to be promising in terms of active sites for hydrodeoxygenation of lignin-derived compounds [5, 9]. At low Ni content (5 wt%), the silica- and SBA-15-based catalysts exhibited the same level of anisole conversion. However, there was a clear difference when a larger amount of nickel was incorporated into the channels of the support. The conversion over the Ni/SBA-15 catalyst drastically increased with increasing Ni content up to 20 wt%, being much higher than that over Ni/silica. This could be due to the uniformity of the pore structure and high pore volume of the mesoporous SBA-15 support. Higher total pore volume allows incorporation of more nickel particles deep inside pores, resulting in a uniform distribution of active sites over the support. In the case of the conventional silica support, some portion of the Ni particles had to be located on the external surface of the support because the pores were almost occupied due to the high Ni content. When the Ni loading was increased to 30 wt%, a decrease of anisole conversion appeared, which can be attributed to agglomeration of Ni particles for such high Ni content. Agglomeration of Ni particles, decreasing the active sites, was also observed for the 20 wt% Ni catalysts, and became much stronger for the 30 wt% Ni catalysts.

The product distributions of HDO of anisole using various Ni contents are shown in Fig. 5. The main identified products were saturated compounds such as cyclohexane, methoxycyclohexane, and cyclohexanol, directly deoxygenated



Fig. 4 Anisole conversion over supported nickel catalysts. Reactions carried out using 1.0 g catalyst at 250 $^{\circ}\mathrm{C}$ for 2 h



Fig. 5 Product distributions of a Ni/SiO₂ and b Ni/SBA-15 catalysts. Reactions carried out using 1.0 g catalyst at 250 °C for 2 h

benzene, along with intermediates such as cyclohexene, cyclohexanone, *n*-hexane, and phenol. As seen in Fig. 5, the product distribution changed significantly depending on the nickel loading and kind of silica support used. Anisole was mainly converted to cyclohexanol when using the 5 wt% Ni/silica catalyst, while most of

the anisole was converted to methoxycyclohexane when using 5 wt% Ni/SBA-15, indicating that hydrogenation (HYD) was the dominant reaction pathway at low Ni loading. With increasing nickel loading, this trend shifted toward the direct deoxygenation (DDO) route with a drastic increase of the yield toward the unsaturated product (benzene) over both supports (conventional silica and SBA-15). In particular, the Ni/SiO₂ catalysts directly deoxygenated anisole to form benzene without hydrogenation. In contrast, the Ni/SBA-15 catalysts enhanced the DDO route and saturation of the aromatic ring via HYD to form cyclohexane simultaneously.

From the viewpoint of hydrodeoxygenation, the yield of hydrocarbons such as cyclohexane and benzene is an important indicator to investigate the degree of HDO reaction. Therefore, the yield of C_6 hydrocarbons is shown in Fig. 6, calculated as the sum of benzene and cyclohexane yields, to compare the influence of the silica and mesoporous silica supports. The yield of C_6 products increased suddenly as the level of nickel loading was increased. Furthermore, the type of support also affected the C_6 hydrocarbon yield. In case of using mesoporous SBA-15 as support, the yield of C_6 hydrocarbon was much higher (approximately twice) than for the silica support. This result can mainly be attributed to the differences in the mesoporous structure of the support controls the HDO reaction route. In spite of the fact that the particle diameter of the 20 wt% Ni/SBA-15 catalyst was larger than that of 10 wt% Ni/SBA-15 due to agglomeration of Ni particles, this catalyst exhibited the strongest catalytic activity for HDO of anisole and the highest yield of



Fig. 6 C₆ hydrocarbon yield versus kind of catalyst. Reactions carried out using 1.0 g catalyst at 250 °C for 2 h

 C_6 hydrocarbons. Ni loading of 30 wt% resulted in not only decreased anisole conversion but also decreased C_6 hydrocarbon yield. Thus, 20 wt% can be considered to be the maximum Ni loaded onto the support. Selection of a suitable active site support system and optimization of the content of active sites for specific reaction conditions are necessary steps for further application of such catalysts on industry scale.

Conclusions

Nickel nanoparticles supported on silica and ordered mesoporous silica SBA-15 were prepared as catalysts for HDO of lignin model compound anisole. High nickel loading decreased the surface area and pore volume of the silica supports, but did not affect their mesoporous structure. The catalytic activity of the catalysts for HDO reaction of anisole depended drastically on the level of nickel content and the kind of support used. High nickel incorporation resulted in strong catalytic activity and selectivity toward directly deoxygenated product, indicating that nickel has promising active sites for catalytic upgrading of biomass. Moreover, the mesoporous structure of the SBA-15 support facilitated diffusion of Ni species into the pores, promoting these active sites, which led to higher anisole conversion and C_6 product yield.

Acknowledgements This work was conducted under the framework of the Research and Development Program of the Korea Institute of Energy Research (KIER) (B8-2426-1). This work was also supported by the National Research Council of Science & Technology (NST) grant by the Korea government (MSIP) No. CAP-16-05-KIMM.

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