

Preparation of NiCu Alloy Catalyst for the Hydrodeoxygenation of Benzofuran

Tianhan Zhu¹ · Hua Song¹ · Feng Li¹ · Yanguang Chen¹

Received: 6 August 2020 / Accepted: 3 October 2020 © Springer Science+Business Media, LLC, part of Springer Nature 2020

Abstract

A series of bimetallic Ni_xCu_(10-x)/SiO₂ (where *x* is the mass fraction of Ni and the total metal loading was fixed at 10 wt%.) catalysts with different Ni/Cu mass ratio are prepared and characterized by X-Ray diffraction (XRD), N₂ adsorption-desorption, inductively coupled plasma mass spectrometry (ICP-MS), H₂ temperature-programmed reduction (H₂-TPR) and transmission electron microscope (TEM). The benzofuran (BF) hydrodeoxygenation (HDO) performance of as-prepared catalysts are evaluated in a fixed flow reactor. The results showed that the incorporation of Cu to Ni/SiO₂ catalyst can increase surface area of catalyst and improve the reducibility of nickel oxide species, which contributed to higher catalytic activity and total deoxygenated compounds yield. Moreover, the strong synergistic effect between Ni and Cu led to the formation of NiCu alloy at the Ni mass fraction of 5 wt% and thus induced smaller crystallite size and exposure of more active particles, which inevitably contributed to the improved HDO performance for Ni₅Cu₅/SiO₂ catalyst reached 86.0%, which is increased by 10.8% and 77.4% as compared to those of monometallic Ni/SiO₂ (75.2%) and Cu/SiO₂ catalysts (8.8%), respectively. Finally, a possible reaction network for HDO of BF on Ni₅Cu₅/SiO₂ catalyst was proposed.

Hua Song songhua2004@sina.com

¹ Provincial Key Laboratory of Oil & Gas Chemical Technology, College of Chemistry & Chemical Engineering, Northeast Petroleum University, Daqing 163318, China

Graphic Abstract



Keywords NiCu alloy · Benzofuran · Hydrodeoxygenation

1 Introduction

In recent years, increasing demand for energy and strict environmental regulations have forced the researchers to seek for promising renewable and clean energy to ease the energy crisis. As the renewable and abundant sources, biomass has attracted many attentions due to its potential to be converted to transportation fuels [1]. Typically, fast pyrolysis is one of the most useful technology for biomass upgrading and the upgraded biomass is namely bio-oil. Unexpectedly, the obtained bio-oil via fast pyrolysis contains a mass of oxygenated compounds, which leads to the undesirable properties of oil, such as high viscosity, low chemical stability and low heat value [2–4]. Therefore, it is extremely necessary to remove oxygen atom from the bio-oil for further application.

The catalytic Hydrodeoxygenation (HDO) is one of the most efficient and promising methods to upgrade bio-oil. The challenge of bio-oil HDO is to develop an appropriate catalyst with desirable activity. Therefore, various kinds of HDO catalysts have been investigated to improve the removal of oxygen atom form bio-oil. Noble metal (such as Pt, Pd, Ru and Rh) [5–7] show high activity in the HDO process, their application are unfortunately limited by the high cost. Commercial CoMoS and NiMoS catalysts supported on γ -Al₂O₃ exhibit acceptable HDO performance, but their easy deactivation and sintering of the catalysts need to be inhibited by the addition of sulfur agent, which inevitably leads to the violation of strict environment regulation. Therefore, the non-noble catalysts with high activity for HDO have received a great deal of attention. Alternatively, low cost transition metals, such as Ni, Co, Fe and Cu, have been investigated and the Ni-based catalysts are found to be suitable for HDO process [8–13]. As another transition metal, the Cu can accelerate the reduction of Ni and promote the stability of Ni in HDO process [14–17].

In this work, bimetallic Ni-Cu/SiO₂ catalysts are prepared via co-impregnation and their HDO performances are evaluated using benzofuran (BF) as the oxygenated compounds. The BF is thought to be a good model compound because the bio-oil derived by fast pyrolysis contains either a phenolic or a furanic structure [18–20]. The catalysts are characterized by XRD, N₂ adsorption-desorption, ICP-MS, H₂-TPR and

TEM analysis. The effect of mass ratio of metal loading (Ni and/or Cu) on the BF HDO is investigated.

2 Experimental

2.1 Chemicals

All chemicals were received without any further purification. Commercial SiO₂ (Cabot M-5) was used as support materials. Ni(NO₃)₂·6H₂O and Cu(NO₃)₂·4H₂O were used as precursors during the synthesis of catalysts. A mixture of decahydronaphthalene (Aladdin, \geq 98.5%) solution including 2 wt% benzofuran (Aladdin, \geq 99%) and 1 wt% tetradecane (Aladdin, \geq 99%) was used for activity test, in which benzofuran and tetradecane were used as a reactant and an internal standard, respectively.

2.2 Preparation of Catalysts

Bimetallic NiCu/SiO₂ catalyst was synthesized by coimpregnation using metal nitrate and commercial SiO₂. In a typical experimental, the calculated amount of Ni(NO₃)₂·6H₂O and Cu(NO₃)₂·4H₂O were dissolved in 50 mL deionic water under stirred for 30 min followed by the addition of SiO₂, then the mixture solution was impregnated over night at room temperature. After the solution was dried at 80 °C for 12 h, the obtained solid was calcined in air and reduced under a H₂ flow (30 mL/min) at 400 °C for 3 h with a heating rate of 3 °C/min. The as-prepared catalysts were named as Ni_xCu_(10-x)/SiO₂ (x = 0, 3, 5, 7, 10), where x is the mass fraction of Ni and the mass ratio of total metal (both Ni and Cu) loading to blank support was fixed at 10 wt%.

2.3 Characterization

The X-Ray diffraction (XRD) analysis were carried out on a D/max-2200PC-X-Ray diffractomerter using Cuk α radiation under the setting conditions of 40 kV, 30 mA, scan range from 10 to 80° at a rate of 10°/min.

The typical physico-chemical properties of supports and catalysts were analyzed by BET method using Micromeritics adsorption equipment of Tristar II 3020. All samples were outgassed at 200 °C until the vacuum pressure was 6 mm Hg. The adsorption isotherms for nitrogen were measured at -196 °C.

The content of Ni and Cu were measured by inductively coupled plasma mass spectrometry (ICP-MS) using a Perkin Elmer Nexion 300 instrument. Prior to analysis, the sample was digested with nitric acid using a microwave heating system.

The reducibility of precursors was characterized by the H_2 temperature-programmed reduction (H_2 -TPR) using a quartz U tube reactor (inner diameter of 6 mm), in which 50 mg of samples were loaded in the thermostatic zone. Reduction was conducted from 50 to 800 °C at a heating rate of 10 °C min⁻¹ in a 10 vol% H_2/N_2 flow (30 ml min⁻¹). The TPR spectrum was determined using a thermal conductivity detector (TCD) to monitor hydrogen consumption.

Transmission electron microscope (TEM) examinations were performed using the JEM-1010 instrument supplied by JEOL. The samples were dispersed in ethanol and placed on a carbon grid before TEM examinations.

2.4 Activity Tests

HDO performance is conducted in a continues fixed-bed reactor (8 mm in diameter, and 400 mm in length), using a feed of decalin solution of BF (2 wt%). The conditions of the HDO reaction are 300 °C, 3.0 MPa, WHSV=4 h⁻¹ and hydrogen/oil ratio of 500 (V/V). The activities of each catalyst are measured at different time on stream. The feed and reaction product are analyzed by FID gas chromatography (Shimadzu GC-14C, Japan) with a commercial SE-54 capillary column (length: 50 m, inside diameter: 0.25 mm, film thickness: 0.25 μ m). The conditions of temperature program of GC analysis are as follows: detector temperature 280 °C, injector temperature 280 °C, the initial oven temperature is 50 °C and held for 2 min, final oven temperature is 250 °C with a ramp of 10 °C/min and held for 3 min.

The BF conversion us calculated from the ratio of converted BF to initial BF using Eq. (1):

$$XBF = \frac{n_{BF,0} - n_{BF,1}}{n_{BF,0}} \times 100\%$$
(1)

The selectivity to product i is identified as Eq. (2):

$$\mathrm{Si} = \frac{\mathrm{n_i}}{\sum \mathrm{n_i}} \times 100\% \tag{2}$$

The total deoxygenated product yield is defined as the content of all the hydrocarbons via Eq. (3):

$$YHDO = X_{BF} \times \frac{\sum n_{hydrocarbon}}{\sum n_i} \times 100\%$$
(3)

Where $n_{BF,0}$ and $n_{BF,1}$ mean the moles of BF in the feed and product, respectively, n_i is the mole of product i, and $n_{hydrocarbon}$ express the moles of all the hydrocarbons in the product.

3 Results

3.1 XRD

The XRD patterns of all the as-prepared samples are shown in Fig. 1. As shown, all of samples show a peak at around 23°, which is assign to the characteristic of the amorphous silica. It can be seen from Fig. 1a, for the calcined monometallic catalysts, the Ni/SiO₂ shows the peaks of NiO species (PDF=47-1049) at 37.2°, 43.3° and 62.9°, while the Cu/SiO₂ shows the peaks of CuO species (PDF=45-0953) at 35.5°, 38.7° and 48.7°. For the calcined bimetallic catalysts, with increasing the Cu content, the peaks of NiO broaden with its strength becomes weaker, showing that incoperation of Cu species could promote the disperson of NiO. Exceptionally, for Ni₇Cu₃/SiO₂ catalyst, only NiO species is detected, this is possibly due to the amount of Cu is small and highly dispersed CuO particles during the impregnation [21].

For the reduced catalysts (Fig. 1b), the peaks at 44.5°, 51.8° and 76.4° over monometallic Ni/SiO₂ catalyst are ascribed to Ni species (PDF=65-2865), the peaks at 43.3°, 50.4° and 74.1° for Cu/SiO₂ are assign to Cu species (PDF=04-0836). In the case of bimetallic catalysts, a significant shift of metallic phase peaks is observed and all peaks are located between the lattice plane (111) of Cu (43.3°) and lattice plane (111) of Ni (44.5°) phase, which is identified to be originated from the formation of Ni-Cu alloy [22–24]. Specially, the Ni- and Cu-rich binary phases were detected over Ni₃Cu₇/SiO₂ catalyst. Similar result has been reported by Lin et al. [23]. They prepared NiCu/CeLaO_x catalysts with different Ni/Cu ratios by supporting bimetallic Ni-Cu on La-doped mesoporous ceria, and

found that for Ni₁₀Cu₁₀/CeLaO_r the strong metal-support interaction inhibited the interdiffusion of Ni and Cu atoms, resulting in the formation of two populations of Ni- and Cu-rich nanoparticles. On the contrary, a single NiCu alloy can be obtained via the reduction of bulk NiO and CuO phases. Furthermore, the Ni/Cu ratio is also vital to obtain the single NiCu alloy for NiCu/CeLaO_x system. In our case, a Ni/Cu ratio of 1 favored the formation of a single NiCu alloy. Despite of the failing in formation of NiCu alloy, the Ni₃Cu₇/SiO₂ catalyst also showed considerable HDO performance. The crystallite size of monometallic Ni and Cu, and bimetallic Ni-Cu catalysts are summarized in column 7 of Table 1. Compared to monometallic Ni or Cu nanoparticles, bimetallic catalyst showed a relatively low particle size, indicating the synergistic cooperation between Ni and Cu species.

3.2 BET

The N₂ adsorption-desorption isotherms and pore size distributions from N₂ desorption branch of the as-prepared samples are shown in Fig. 2. All the samples display a typical IV hysteresis loop according to the IUPAC classification, which is the characteristic of mesoporous materials. Unlike blank SiO₂ support, the hysteresis loop of as-prepared catalysts is of similar size, indicating the similar total pore volume ranged from 0.97 to 1.02 cm³/g. As shown in Fig. 2b, the pore size of supported catalysts is much larger than that of pure SiO₂, which can be explained by that the small pore of support is blocked with the metal loading. As a result, the generation of large pore leads to the increase in pore size, showing the similar results with pore volume. It is notable that the lower value in pore volume and pore size of Ni₅Cu₅/SiO₂ results in the larger specific surface area.



Fig. 1 XRD pattern of calcined (a) and reduced (b) $Ni_xCu_{(10-x)}/SiO_2$ (x = 0, 3, 5, 7, 10) catalysts.

Table 1 Textural properties of the support and Ni_xCu_(10-x)/SiO₂ (x=0, 3, 5, 7, 10) catalysts

Samples	Conte	ent ^a (%)	$S_{BET} (m^2/g)$	V_p^{b} (cm ³ /g)	D _{pore} ^b (nm)	Crystallite size (nm)
	Ni	Cu				
SiO ₂	_	_	203	0.51	11.8	_
Ni/SiO ₂	8.8	-	154	1.0	25.1	19.6 ^c
Ni ₇ Cu ₃ /SiO ₂	6.1	2.5	166	1.0	20.2	19.4 ^c
Ni ₅ Cu ₅ /SiO ₂	4.4	4.3	180	0.97	19.8	18.5 ^d
Ni ₃ Cu ₇ /SiO ₂	2.6	6.2	179	1.02	19.8	17.2 ^c /22.2 ^e
Cu/SiO ₂	-	8.7	174	0.97	20.3	31.3 ^e

^aDetermined by ICP-MS analysis

^bCalculated from the desorption branch of the N₂ isotherm by the BJH method

^cCalculated by the Scherrer equation using Ni (111) lattice plane

^dCalculated by the Scherrer equation using NiCu (111) lattice plane

^eCalculated by the Scherrer equation using Cu (111) lattice plane



Fig. 2 N₂ adsorption-desorption isotherms (**a**) and pore size distribution from N₂ desorption branch (**b**) of Ni_xCu_(10-x)/SiO₂ (x = 0, 3, 5, 7, 10) catalysts

Textural parameters of all samples are presented in Table 1. Compared to pure SiO_2 support (203 m²/g), the specific surface area of supported catalysts slightly decreased

after the loading of metal species, which is caused by the pore channel blockage during the impregnation of metal sites. The surface area of monometallic Ni/SiO_2 is 154

m²/g. With incorporation and increasing the Cu content, the surface area of $Ni_xCu_{(10-x)}/SiO_2$ increased, and the Ni_5Cu_5/SiO_2 shows the largest value of 180 m²/g, much higher than that of Ni/SiO₂, indicating the positive effect of Cu on the improvement in specific surface area of the sample.

3.3 H₂-TPR

The reducibility of calcined samples is measured by H₂-TPR and the results are shown in Fig. 3. For monometallic Ni/ SiO₂, the peak at around 380 °C is observed, which is assigned to the reduction of NiO species [16, 17, 25] In the case of Cu/SiO₂, a relative lower reduction peak of 250 °C is found, which is attributed to the reduction of CuO [15, 21]. However, for the bimetallic Ni-Cu/SiO₂ samples, only one hydrogen consumption peak is detected. Moreover, upon incorporation of Cu species, the temperature of consumtion peak shifts from 380 °C to lower region, indicating the incorporation of Cu is beneficial for the reduction of NiO [15, 22] and thus promotes the formation of more Ni active sites. It is interesting to find that the peak position of Ni₅Cu₅/ SiO₂ is very close to that of Cu/SiO₂. This can be explained by the formation of NiCu alloy, which has been certified by the results of XRD, similar results have been reported by Liu [24].

3.4 TEM

The dispersion of metal active sites is measured via TEM analysis, the images and particle size distribution are shown in Fig. 4. For Ni/SiO₂ catalyst (Fig. 4a), some large dark particles can be seen, showing that the Ni particles are easily aggregated to form large particle size on the surface of SiO₂. And the mean diameter of Ni/SiO₂ is about 15.2 nm. Upon the incorporation of Cu species, the aggregation of metal



Fig. 3 H₂-TPR spectra of calcined Ni_xCu_(10-x)/SiO₂ (x=0, 3, 5, 7, 10)

particles is inhibited and particles size decreases obviously. With the theoretical loading of Cu increases to 5 wt%, the bimetallic Ni₅Cu₅/SiO₂ catalyst shows much smaller particles size and more uniformly dispersed active sites. As a result, the mean diameter of Ni₅Cu₅/SiO₂ catalyst reduced to 7.6 nm. However, the excessive incorporation of Cu species leads to the slightly increased particle size (Ni₃Cu₇/SiO₂ and Cu/SiO₂ catalysts), which is in line with the results of crystallite size calculated by XRD analysis (shown in column 7 of Table 1). The improved dispersion of active metal sites for Ni₅Cu₅/SiO₂ catalyst is contributed to the improved reducibility of the catalyst after the introduction of Cu (shown in H₂-TPR) and formation of NiCu alloy (shown in XRD), which is consistent with the results reported by Ambursa et al. [21]

3.5 HDO Activity

The HDO performance for the as-prepared catalysts is evaluated under the reaction condition of $T = 300 \text{ }^{\circ}\text{C}$, P = 3 MPa, MHSV=3.0 h⁻¹ and H₂/oil = 500(v/v). The conversion of BF over all the catalysts is shown in Fig. 5. The BF conversion for monometallic Ni/SiO₂ catalyst is stable, which reaches 91.8% within 8 h under the experimental condition. The BF conversion over Ni₇Cu₃/SiO₂ catalyst is 89.9%, which is decreased slightly as compared to that of Ni/SiO₂. However, a sharp increase of BF conversion is observed for Ni₅Cu₅/SiO₂ catalyst, the conversion of BF reached 97.0% at 8 h. Further increase the Cu amount, BF conversion is decreased. For Ni₃Cu₇/SiO₂, the BF conversion goes down to 92.5%, but it is still slightly higher than that of Ni/SiO_2 catalyst. Unexpectedly, the monometallic Cu/SiO₂ catalyst shows BF conversion of 94.0%. Generally, high conversion is expected, however the selectivity to desirable deoxygenated products is more important for HDO process. In our case, the monometallic Cu/SiO₂ catalyst exhibits acceptable BF conversion, but it shows a low selectivity to desirable deoxygenated products, indicating the Cu/SiO₂ is not suitable for the HDO of BF. This will be discussed further in next part.

3.6 HDO Product Distribution

The product distributions of the as-prepared catalysts are depicted in Fig. 6. The detected products are as follows: methylbenzene (MB), methylcyclohexane (MCH), ethyl-cyclohexane (ECH), ethylbenzene (EB), benzene (B), 2,3-dihydrobenzofuran (2,3-DHBF), 2-ethylphenol (2-EtPh), and phenol (Ph).

Among them, ECH is the desirable deoxygenated product since the reservation of carbon atom is beneficial to preserve heat value of the molecule and therefore high selectivity to ECH is favorable [26]. For monometallic Ni/SiO₂ catalyst,

the selectivity to ECH is about 53.5% and much higher than those of other products. The selectivity to the deoxygenated product MCH, which is generated via the C-C cleavage, is 26.2% at 8 h. Additionally, the detected amount of oxy-compound 2,3-DHBF is 13.4%, the high content of 2,3-DHBF in the product indicates the incomplete removal of oxygen atom during the HDO of BF over Ni/SiO₂ catalyst. Similar to monometallic Ni/SiO₂ catalyst, ECH is still the main product for bimetallic NiCu/SiO2 catalysts. The selectivity to deoxygenated product ECH for Ni₇Cu₃/SiO₂ is 64.1%, which is increased significantly. While the selectivities to MCH and 2,3-DHBF are 17.2% and 10.7%, respectivily. When Cu content increases to 5 wt% (Ni₅Cu₅/SiO₂), the selectivities to ECH and MCH reached 71.2% and 15.8% at 8 h, respectively, showing that the selectivity to ECH increased remarkably and selectivity to MCH decreased slightly. It is worth noting that the selectivities to oxy-compound 2,3-DHBF and other products are 9.9% and 3%, respectively. However, further increase the incorporation amount of Cu, the selectivity to ECH decreased to 61.9%. On the contrary, the selectivities to MCH and 2,3-DHBF increase to 16.4% and 13.3%, respectively. As compare to monometallic Ni/ SiO₂ catalyst, all the bimetallic NiCu/SiO₂ catalysts show an obvious decline in MCH selectivity, which is lower than 20%. This phenomenon indicates that the inorporation of Cu to Ni-based catalysts contributes to reduce the cleavage of C-C bond. Similarly, Yang et al [27] found that unmodified monometallic Ni kept its intrinsic properties with a tendency towards C-C hydrogenolysis in m-cresol HDO despite of the decreasing Ni particle size. After the decoration of MoO_x species, the synergistic cooperation between Ni and MoO_x species resulted in no C-C hydrogenolysis activity at 350 °C, which was inevitably essential to achieve high HDO performance [28]. Recently, Liu et al [29] investigated the HDO of m-cresol on monometallic Ni and bimetallic NiFe using density functional theory calculations, they revealed that the length of C-OH bond in m-cresol was elongated over bimetallic NiFe (111) as compared to that of Ni (111), which contributed to lower activity barrier and more exothermic C-OH bond breaking, thus lead to the improved deoxygenation reaction. Obviously, bimetallic Ni-based catalysts showed superior HDO performance than that of monometallic Ni. In addition, the content of intermediate product 2,3-DHBF for all the Ni-based catalysts keep around 10% and



Fig. 4 TEM images and particle size distribution of $Ni_xCu_{(10-x)}/SiO_2$ (x=0, 3, 5, 7, 10) catalysts (**a**, **f**) Ni/SiO_2 ; (**b**, **g**) Ni_7Cu_3/SiO_2 ; (**c**, **h**) Ni_5Cu_5/SiO_2 ; (**d**, **i**) Ni_3Cu_7/SiO_2 ; (**e**, **j**) Cu/SiO_2





the proportion of 2-EtPh is lower than that 2,3-DHBF, which shows the ring open reaction of 2,3-DHBF is the controlled step for the HDO of BF. This suggests that the ring-opening reaction is the rate-controlling step in the BF HDO over all the Ni-based catalysts, which is consistent with the results reported by Cho et al. [30]. As for the monometallic Cu/SiO₂ catalyst (Fig. 6e), the product distribution of Cu/SiO₂ differs greatly from those of the Ni-based (both monometallic Ni/ SiO₂ and bimetallic NiCu/SiO₂) catalysts. In detail, the oxycompound 2,3-DHBF becomes predominant in the product

of Cu/SiO₂ differs As mentioned a monometallic Ni/ able in the HDO of In detail, the oxy- over $Ni_xCu_{(10-x)}/Si^2$

instead of ECH, and the selectivity to 2,3-DHBF reaches about 82.9% at 8 h, while the desired product ECH decreases remarkably to 4.6%. The high content of 2,3-DHBF means the low efficiency for removal of oxygen atom, which indicates that monometallic Cu/SiO₂ catalyst is not suitable for HDO of BF.

As mentioned above, high selectivity to ECH is desirable in the HDO of BF. Therefore, the selectivity to ECH over $Ni_xCu_{(10-x)}/SiO_2$ catalysts is depicted in Fig. 6f. As shown, the monometallic Ni/SiO₂ catalyst exhibits the ECH



Fig. 5 Conversion of BF over Ni_xCu_{(10-x}/SiO₂(x = 0, 3, 5, 7, 10) catalysts. Reaction condition: T = 300 °C, P = 3 MPa, MHSV=3.0 h⁻¹, H₂/oil = 500(v/v)

selectivity of 53.5%. With the introduction of Cu, the selectivity to ECH over bimetallic NiCu/SiO2 catalysts gradually improves and the Ni₅Cu₅/SiO₂ catalyst shows the highest value of 71.2%. Particularly, the Ni₃Cu₇/SiO₂ catalyst shows a decreased ECH selectivity of 61.9% with the increasing amount of Cu species. While the ECH selectivity over monometallic Cu/SiO₂ catalyst is only 4.6%, which is remarkably lower than those of Ni-based catalysts. This phenomenon shows isolating Ni atoms on Cu nanoparticles would afford a highly active catalyst for HDO of BF. It is worth noting that regardless of whether the NiCu alloy was formed or not, the presence of two populations (Ni and Cu nanoparticles) would contribute to higher HDO performance than that of monometallic Cu/SiO₂. Similar result has been reported by Luo et al. [31]. They found that the co-impregnated individual Ru and Ni nanoparticles would shorten H• radicals transfer lengths in hydrogenolysis of C–O bonds in guaiacol, which results in improved catalytic activity. Yang et al. [28]. also points out that the synergistic cooperation between Ni and MoO_x species plays a vital role in HDO of m-cresol in spite of the existence of that two mixed species rather than NiMo alloy. In sum, the selectivity to ECH over $Ni_xCu_{(10-x)}/2$ SiO₂ catalysts is in the order: Ni₅Cu₅/SiO₂(71.2%)> Ni₇Cu₃/ SiO₂(64.1%)≈Ni₃Cu₇/SiO₂(61.9%)> Ni/SiO₂(53.5%)> Cu/ SiO₂(4.6%). As shown in the Fig. 6f, the Ni₅Cu₅/SiO₂ catalyst shows stable and outstanding selectivity to ECH, which can be explained by the high surface area (BET), improved reducibility (H₂-TPR), more and highly dispersed active sites (TEM), and the formation of NiCu alloy instead of the active phase Ni or Cu (shown in XRD results) [32, 33]. "In addition, the comparison of the typical catalytic activity of BF HDO from literatures with our present results were summarized in Table 2. It can be seen that the BF HDO activity of Ni₅Cu₅/SiO₂ is higher than most of the reported catalysts."

3.7 HDO Reaction Network and Deoxygenated Product Yield

Based on the product distribution, the possible reaction network is drawn in Scheme 1, which has been proposed in our previous studies [37, 39]. The first step in the reaction is the hydrogenation of the heterocyclic ring to form 2,3-DHBF, and the formed 2,3-DHBF converted into 2-EtPh via the cleavage of C-O bond of heterocyclic ring [34]. It is worth noting that the cleavage of C_{aliphatic}-O bond is easier than C_{aromatic}-O linkage in the HDO of BF, which has been reported by Liu et al. [20]. In turn, 2-EtPh was transformed into EB via deoxygenation and the EB was mainly converted into ECH by hydrogenation. The MCH was finally formed via demethylation of ECH. The low selectivity to MB, Ph and B showed the low reaction rate of corresponding reaction step.

The total yield of deoxygenated products (TYDP) is depicted in Fig. 7. The TYDP for Ni/SiO₂ catalyst remains approximately stable during the experimental condition and the yield reaches 75.2% at 8 h. The TYDP for Ni₇Cu₃/SiO₂ is about 75.3%, showing no sharp change with incorporation of a low amount of Cu to Ni/SiO2 catalyst. Interestingly, the TYDP for Ni₅Cu₅/SiO₂ catalyst reaches about 86.0%, remarkably higher than those of others. Subsequently, with the increasing Cu loading, the Ni₃Cu₇/SiO₂ shows a declining TYDP of 77.5% with the increasing Cu loading, which is still higher than that of monometallic Cu/SiO₂. This indicates that the isolating Ni atoms on Cu nanoparticles would result in a great improvement in HDO performance compared to monometallic Cu species. Similar results were reported by Yang et al. [28] and Luo et al. [31]. They found the synergistic cooperation between different metal species plays a crucial role in catalytic reaction, thought the alloy phase is not formed. Obviously, the Ni-based catalysts show much higher ability for oxygen removal than that of the monometallic Cu catalyst, which is due to the low activity of Cu for the cleavage of C-O bonding. This is line with the results reported by others [13-15]. From the above results it seems that the yield of deoxygenated product does not increases linearly with the continuously increasing Cu loading, and the incorporation of appropriate amount of Cu contributes to sharp improve in HDO performance. This can be attributed to the high surface area (BET), improved reducibility (H₂-TPR), more and highly dispersed active sites (TEM). What's more, the formation of NiCu alloy caused by the strong synergistic effect between Ni and Cu atom also accelerates the HDO performance [32, 33].

4 Conclusion

A series of bimetallic $Ni_xCu_{(10-x)}/SiO_2$ catalysts with different Ni/Cu mass ratio are prepared by co-impregnation method and the HDO performances of BF over the



Fig. 6 The selectivity to products and ECH over Ni_xCu_(10-x)/SiO₂(x = 0, 3, 5, 7, 10) catalysts. **a** Ni/SiO₂; **b** Ni₇Cu₃/SiO₂; **c** Ni₅Cu₅/SiO₂; **d** Ni₃Cu₇/SiO₂; **e** Cu/SiO₂;(f)Selectivity to ECH; reaction condition: T = 300 °C, P = 3 MPa, MHSV = 3.0 h⁻¹, H₂/oil = 500(v/v)

as-prepared catalysts are investigated in a fixed flow bed. The results show that the incorporation of Cu can improve the reducibility of nickel oxide species and reduction peaks shifts to lower temperature (H₂-TPR). In addition, the strong synergistic effect between Ni and Cu leads to the formation of NiCu alloy (XRD) and thus induces smaller crystallite size and exposure of more active particles, which inevitably contributes to the improved HDO

Table 2 Comparison of the typical results of BF HDO from literatures with our present results

Samples	Temperature	Pressure (MPa)	Conversion (%)	Ref. no.
	(K)			
Sulfided NiMo/Al ₂ O ₃ ^a	553	2.0	74.6	[34]
Sulfided NiMo/Al ₂ O ₃ ^a	553	5.0	82.5	[34]
NiMoP/Al ₂ O ₃ ^a	613	7.0	80.7	[35]
Pt/SiO ₂ -Al ₂ O ₃	553	3.0	80	[36]
Pd/SiO ₂ -Al ₂ O ₃	553	3.0	97	[36]
W ₂ C(Ar-2-1023 K-1 h)	613	4.0	41	[20]
Ni ₂ P-N/MCM-41	493	3.0	31	[37]
Ni ₂ P-O/MCM-41	493	3.0	57	[37]
Ni ₂ P/Al ₂ O ₃	573	3.0	78	[38]
Ni ₂ P/TiO ₂	573	3.0	85	[38]
Ni ₂ P/Al ₂ O ₃ @TiO ₂	573	3.0	95	[38]
Ni ₅ Cu ₅ /SiO ₂	573	3.0	97	This work

^aWith H₂S in the feed



Scheme 1 Reaction network for HDO of BF over Ni₅Cu₅/SiO₂ catalyst



Fig. 7 Total yield of deoxygenated products over $Ni_xCu_{(10-x)}$ $SiO_2(x=0, 3, 5, 7, 10)$ catalysts. (Reaction condition: T = 300 °C, P = $3 \text{ MPa}, \text{ MHSV} = 3.0 \text{ h}^{-1}, \text{ H}_2/\text{oil} = 500(\text{v/v}))$

performance for Ni₅Cu₅/SiO₂ catalyst. In detail, under the experimental condition of 300 °C, 3.0 MPa, MHSV = 3.0 h^{-1} and $H_2/oil=500(v/v)$, the total yield of deoxygenated products over Ni₅Cu₅/SiO₂ catalyst reaches 86.0% at 8 h on stream, which is increased by 10.8% and 77.4% as compared to those of monometallic Ni/SiO₂(75.2%) and Cu/ SiO_2 catalysts (8.8%), respectively. This indicates the formation of NiCu alloy at appropriate amount of Cu incorporation played a positive effect on the removal of oxygen atom. Finally, a possible reaction network for HDO of BF on Ni_5Cu_5/SiO_2 catalyst is proposed.

Acknowledgements The authors acknowledge the financial supports from the Graduate Innovation Project of Northeast Petroleum University (JYCX_CX03_2018).

Compliance with Ethical Standards

Conflict of interest The authors declare no conflict of interest.

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