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Article

Effects of indium on Ni/SiO₂ catalytic performance in hydrodeoxygenation of anisole as model bio-oil compound: Suppression of benzene ring hydrogenation and C–C bond hydrogenolysis

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ABSTRACT

SiO₂-supported monometallic Ni and bimetallic Ni–In catalysts were prepared and used for hydrodeoxygenation of anisole, which was used as a model bio-oil compound, for BTX (benzene, toluene, and xylene) production. The effects of the Ni/In ratio and Ni content on the structures and performances of the catalysts were investigated. The results show that In atoms were incorporated into the Ni metal lattice. Although the Ni–In bimetallic crystallites were similar in size to those of monometallic Ni at the same Ni content, H₂ uptake by the bimetallic Ni–In catalyst was much lower than that by monometallic Ni because of dilution of Ni atoms by In atoms. Charge transfer from In to Ni was observed for the bimetallic Ni–In catalysts. All the results indicate intimate contact between Ni and In atoms, and the In atoms geometrically and electronically modified the Ni atoms. In the hydrodeoxygenation of anisole, although the activities of the Ni–In bimetallic catalysts in the conversion of anisole were lower than that of the monometallic Ni catalyst, they gave higher selectivities for BTX and cyclohexane as a result of suppression of benzene ring hydrogenation and C–C bond hydrogenolysis. They also showed lower methanation activity. These results will be useful for enhancing carbon yields and reducing H₂ consumption. In addition, the lower the Ni/In ratio was, the greater was the effect of In on the catalytic performance. The selectivity for BTX was primarily determined by the Ni/In ratio and was little affected by the Ni content. We suggest that the performance of the Ni–In bimetallic catalyst can be ascribed to the geometric and electronic effects of In.

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1. Introduction

Recently, sustainable and CO₂-netual biomass has attracted much attention because it is the only renewable energy source that can be converted to liquid transportation fuels and chemicals [1]. Biomass can be readily converted to a liquid product, namely bio-oil, via a well-developed and commercially viable

process, i.e., fast pyrolysis [2]. However, bio-oil cannot be directly used as fuel because its high oxygen content (usually 20–40 wt%) [2] results in undesired properties such as low thermal and chemical stabilities, a low heating value, high acidity, and immiscibility with fossil fuels [3]. Bio-oil therefore needs to be upgraded by removing oxygen to yield hydrocarbons compatible with petroleum-derived fuels [4,5]. In partic-

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ular, lignin-derived bio-oil, which consists mainly of phenolic compounds (e.g., phenol, anisole, guaiacol, cresol, and syringol), can be converted to benzene, toluene, and xylene (BTX) via hydrodeoxygenation (HDO) [4,5]. BTX consists of basic chemicals that are currently mainly derived from petroleum and coal and also have high octane numbers as gasoline components [6,7].

Selective cleavage of $C_{Ar}-O$ bonds (C_{Ar} denotes a benzene ring carbon atom), i.e., direct deoxygenation (DDO), is necessary for HDO of phenolic compounds to yield aromatic hydrocarbons (especially BTX) [8], and the benzene ring should remain intact. A low H_2 pressure and high temperature are thermodynamically favorable for producing BTX [9,10], but the use of catalysts is crucial for obtaining high BTX yields.

Conventional sulfide catalysts have been used for HDO of phenolic compounds [11]. $CoMo/Al_2O_3$ is more favorable than $NiMo/Al_2O_3$ for DDO [12]. However, to prevent sulfide catalyst deactivation because of sulfur loss, sulfur-containing reagents (e.g., H_2S) must be added to the reaction system, and products can be contaminated with sulfur during upgrading [4,13]. The development of non-sulfide catalysts is therefore important. Several researchers have reported that molybdenum carbide [14], $FeMoP$ [15], and Fe/SiO_2 [16] show high selectivities for the DDO pathway in HDO of phenolic compounds. Many studies of HDO of phenolic compounds have focused on noble-metal and Ni catalysts. Noble-metal catalysts are highly active in HDO, but they facilitate saturation hydrogenation of the benzene ring [17,18]. Moreover, their applications are limited because of their high cost and scarce resources. Low-cost monometallic Ni also shows excellent activity in HDO of phenolic compounds [9], but serious saturation hydrogenation of benzene rings occurs. Moreover, metallic Ni is highly active in C–C bond hydrogenolysis [19], resulting in a decreased carbon yield and increased H_2 consumption. Much research has been performed on suppressing deep hydrogenation of benzene rings on noble metal and metallic Ni catalysts. Strategies based on the effect of metal-support interactions [20] and modification with a second metal promoter have been investigated.

Metal promoters can be divided into two types, according to their oxophilicity, i.e., oxophilic metals (e.g., Fe, Zn, Re, and Mo) and less oxophilic metals (e.g., Cu). Chia et al. [21] developed a new class of bifunctional heterogeneous catalysts, i.e., highly reducible Rh metal combined with the oxophilic metal Re, which facilitate selective C–O hydrogenolysis of biomass-derived feedstocks (such as cyclic ethers and polyols). Density functional theory (DFT) calculations have shown that in HDO of *m*-cresol on a bimetallic Pt–Mo catalyst [17], oxophilic Mo atoms favor geometries in which aromatic surface species have an upright orientation through favorable Mo–O interactions at the surface; this reduces the barrier to $C_{Ar}-O$ bond scission. The addition of Fe to Pd [22] and Ni [23,24] also helps to retain the benzene ring structure by selective cleavage of $C_{Ar}-O$ bonds because the interactions between Fe and oxygen facilitate $C_{Ar}-O$ bond activation. A DFT calculation [23] indicated that the presence of oxophilic Fe causes repulsion by the π -electron system of the benzene ring. Notably, a monometallic Ni catalyst modified with a less oxophilic metal, i.e., Cu, still had high activ-

ity in saturation hydrogenation of benzene rings [25,26]; however, the presence of Cu suppressed C–C bond hydrogenolysis because of the geometric effect of Cu [27,28].

Metallic In, which is much less active than metallic Ni in hydrogenation, has been reported to be an efficient catalyst for selective hydrogenation of C=O bonds to form C–OH [29–31]. Our previous work [32] showed that Ni–In alloys and intermetallic compounds are much less active than metallic Ni in the hydrogenation of ethylene and C–C bond hydrogenolysis. This is attributed to the geometric and electronic effects of In. On the basis of these results, we speculate that a metallic-In-modified Ni catalyst could preferentially yield BTX in HDO of phenolic compounds. To the best of our knowledge, there have been no reports of HDO of phenolic compounds on Ni–In bimetallic catalysts.

In the present work, we prepared supported bimetallic Ni–In catalysts with different Ni/In ratios and Ni contents. SiO_2 was used as the support because of its inertness. Anisole, which has a typical $C_{CH_3}-O-C_{Ar}$ phenolic structure [33,34], was selected as a model compound for testing the HDO performances of bimetallic Ni–In/ SiO_2 catalysts. In thermodynamic terms, decreasing the reaction pressure is beneficial for BTX production [9,35], therefore the catalytic performances were evaluated at atmospheric pressure in the present work. We found that the geometric and electronic effects of In in the bimetallic catalysts increased the selectivity for BTX and suppressed saturation hydrogenation of benzene rings, C–C bond hydrogenolysis, and methanation. This enhanced the carbon yield and reduced H_2 consumption.

2. Experimental

2.1. Catalyst preparation

SiO_2 -supported monometallic Ni and Ni–In bimetallic catalysts were prepared using an incipient impregnation method. SiO_2 was purchased from the Qingdao Haiyang Chemicals Co., Ltd. (Qingdao, China). First, SiO_2 particles (diameter 150–250 μm) were incipiently impregnated with an aqueous solution of $Ni(NO_3)_2$ or a mixed aqueous solution of $Ni(NO_3)_2$ and $In(NO_3)_3$. The resulting samples were kept at room temperature for about 48 h, followed by drying at 120 °C for 12 h in a drying oven and calcination at 500 °C for 4 h in a muffle furnace to obtain the catalyst precursors in an oxidized state. Two impregnations were used to prepare catalyst precursors with Ni mass contents greater than 30%. Secondly, the precursors were reduced in a H_2 flow on a quartz fixed-bed reactor at 450 °C for 3 h to prepare monometallic Ni and bimetallic Ni–In catalysts. Before the reduced catalysts were exposed to air for characterization using X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and N_2 sorption, they were passivated using a 0.5% $O_2/99.5\% N_2$ flow (320 mL/min) at room temperature for 4 h.

Two series of catalysts were prepared using this procedure: (1) a SiO_2 -supported Ni catalyst with a Ni mass content of 40% (denoted by Ni/ SiO_2), and SiO_2 -supported bimetallic Ni–In catalysts with different Ni/In atomic ratios (γ) and a Ni mass con-

tent of 40% (denoted by $\text{Ni}_x\text{In}/\text{SiO}_2$); (2) SiO_2 -supported bimetallic Ni-In catalysts with different Ni mass contents (x) and a Ni/In atomic ratio of 30:1, denoted by $x\text{Ni}_{30}\text{In}/\text{SiO}_2$. In all the catalysts, the Ni mass content was set according to the equation $m_{\text{Ni}}/(m_{\text{Ni}} + m_{\text{SiO}_2})$.

2.2. Catalyst characterization

H_2 temperature-programmed reduction (H_2 -TPR) was performed using laboratory-made apparatus. The catalyst precursor (50 mg) was loaded into a U-tube quartz reactor (diameter 4.0 mm). The sample was kept at 50 °C in a 10% H_2 /90% N_2 flow (60 mL/min) until the thermal conductivity detector (TCD) stabilized. The precursor was then reduced at a heating rate of 10 °C/min. The H_2 consumption was determined using a TCD.

NH_3 temperature-programmed desorption (NH_3 -TPD) was performed using the same apparatus as for H_2 -TPR. The catalyst precursor (150 mg) was loaded into the reactor and reduced by a H_2 flow (60 mL/min) at 450 °C for 1 h. After the system had cooled to 100 °C, NH_3 adsorption was performed for 30 min. Physically adsorbed NH_3 on the catalyst surface was purged using a He flow (40 mL/min) at 100 °C; NH_3 -TPD was conducted at a heating rate of 15 °C/min in the He flow. The NH_3 desorption signal was recorded using a TCD.

H_2 chemisorption was also performed using the same apparatus as for H_2 -TPR. The catalyst precursor (100 mg) was loaded into the reactor and reduced in situ by a H_2 flow (60 mL/min) at 450 °C for 1 h, followed by purging with a N_2 flow (60 mL/min) at the same temperature (450 °C) for 1 h to remove H_2 adsorbed on the catalyst surface. The U-tube quartz reactor was then cooled to 30 °C in the N_2 flow. When the TCD was stable, H_2 (50 μL) was pulsed into the N_2 flow until the effluent areas of consecutive pulses were constant. The total dynamic H_2 uptake was calculated.

XRD patterns were recorded using a D8-Focus X-ray diffractometer (Bruker, Germany) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154$ nm), operated at 40 kV and 40 mA. Powder samples were scanned from 10° to 90° at a rate of 8°/min.

N_2 adsorption/desorption isotherms were recorded using a Quantachrome Quadrasorb SI instrument at −196 °C in liquid N_2 . Passivated catalysts were used. The specific surface area (A_{BET}) was calculated using the multi-point Brunauer-Emmett-Teller (BET) method, and the pore volume (V_p) and average pore diameter (d_p) were determined using the Barrett-Joyner-Halenda method.

XPS was performed using a PHI5000 VersaProbe instrument with $\text{Al K}\alpha$ radiation (1486.6 eV). The binding energy (BE) was corrected based on adventitious carbon (C 1s at 284.8 eV). The oxide layer on the passivated catalyst was removed by sputtering with an Ar^+ ion beam (4 kV, 3.0 MPa, 1.5 min).

TEM and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) mapping and line scanning were performed using a JEM-2100F instrument (operated at 2000 kV) equipped with an energy-dispersive X-ray spectroscopy (EDS) facility. The passivated catalyst was ground to a powder, ultrasonically dispersed in anhydrous ethanol, and

then deposited on a Cu grid for characterization.

2.3. Catalytic tests

The catalytic performances in HDO of anisole were evaluated using a fixed-bed quartz-tube reactor (diameter 12 mm). An isothermal catalyst bed was maintained by diluting the catalyst precursor (400 mg) with quartz sand (3 g) of a uniform diameter. Quartz sand (diameter 380–830 μm , 2 g) was placed on the catalyst layer for feedstock preheating and dispersion. The catalyst precursor was reduced in situ by a H_2 flow (100 mL/min) at 450 °C for 3 h. The catalyst was then cooled to 300 °C. The H_2 flow rate was adjusted to 13.81 mL/min and an octane solution containing 8 wt% anisole was fed into the reactor at a rate of 0.047 mL/min using a micro pump. The weight hourly space velocity (WHSV) of anisole and the H_2 /anisole molar ratio were 0.4 h^{-1} and 25, respectively. The liquid products were analyzed using an SP-3420 gas chromatography (GC) system equipped with a flame ionization detector (FID) and a commercial SE-30 capillary column (50 m $\times$ 0.32 mm $\times$ 3.0 μm); ethylbenzene was used as an internal standard. The C1 gaseous products (i.e., CO, CO_2 , and CH_4) were detected using an on-line 102 GC equipped with a TCD and a TDX-101 packed column; N_2 was used as an internal standard. The gaseous light hydrocarbon products (C1–C5) were detected using an on-line SP-3420 GC system equipped with a FID and an HP-AL/S capillary column (50 m $\times$ 0.535 mm $\times$ 15 μm).

The performances of the catalysts were described by the anisole conversion (X), selectivity for product i (S_i), and BTX yield (Y_{BTX}), which were calculated using the following equations:

$$X = (1 - n_{\text{Anisole}}/n_{\text{Anisole},0}) \times 100\%$$

$$S_i = n_i/(n_{\text{Anisole},0} - n_{\text{Anisole}}) \times 100\%$$

$$Y_{\text{BTX}} = S_{\text{BTX}} \times X$$

where $n_{\text{Anisole},0}$ and n_{Anisole} are the number of moles of anisole in the feedstock and products, respectively, n_i is the number of moles of product i , and S_{BTX} is the selectivity for BTX.

The turnover frequency (TOF, s^{-1}) of anisole was calculated as

$$\text{TOF} = -\ln(1-X)/((W/F) \times 2M)$$

where X is the anisole conversion, W is the mass of catalyst used (g), F is the anisole feed rate ($\mu\text{mol/s}$), and M is the H_2 uptake ($\mu\text{mol/g}$). This equation was used because the conversions in the present work were mostly higher than 50%, and even close to 100%; these are far from differential conditions, therefore an integral analysis was required [36]. This equation, in which $-\ln(1-X)$ substitutes for X , assumes a pseudo-first-order reaction, which is reasonable because of the large excess of H_2 and the isothermal catalyst bed.

2.4. DFT calculations

DFT calculations were performed using Gaussian 09. The Lee-Yang-Parr correlation functional (B3LYP) and the 6-31g(d,p) basis set were used; the molecular structure of anisole was optimized and the interactions between anisole and single Ni and In atoms via adsorption of the oxygen atom in

anisole were calculated.

The adsorption energies of anisole on metallic Ni and In (M) atoms were calculated using the equation

$$E_{\text{ads}} = E_{\text{Anisole/M}} - E_{\text{M}} - E_{\text{Anisole}}$$

where E_{M} and E_{Anisole} are the total energies of the M atom and free anisole, respectively, and $E_{\text{Anisole/M}}$ is the total energy of anisole bound to the M atom through an oxygen atom.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. H_2 -TPR

Fig. 1 shows the H_2 -TPR profiles for the Ni/SiO₂ and Ni-In bimetallic catalyst precursors. As Fig. 1(a) shows, the Ni/SiO₂ and Ni₅₀In/SiO₂ catalyst precursors gave similar curves, i.e., a main peak (at ~355 °C) with a shoulder at higher temperature, attributed to reduction of NiO and nickel silicate, respectively [37,38]. The main peak shifted from 355 to 460 °C, and the shoulder also shifted to higher temperature, with decreasing Ni/In atomic ratio from 50:1 to 10:1, i.e., the introduction of In suppressed the reduction of Ni species. This could be because

reduction of indium oxide is more difficult than NiO reduction [32]; it also indicates interactions between Ni and In species. The presence of In species could retard the diffusion of hydrogen species during H_2 -TPR because metallic In interacts less with hydrogen than metallic Ni does [29], making reduction difficult. The results also indicate that there were interactions between Ni and In species. It is worth noting that the initially reduced Ni species can promote the reduction of indium oxides via spilt-over hydrogen [32]. The co-reduction of Ni and In species could occur during TPR, which would lead to strong interactions between Ni and In in the reduced catalysts.

Fig. 1(b) shows that for the $x\text{Ni}_{30}\text{In}/\text{SiO}_2$ catalyst precursors the main peak area increased but the shoulder peak area did not change obviously with increasing Ni content, i.e., an increase in the Ni content did not promote the formation of nickel silicate in the $x\text{Ni}_{30}\text{In}/\text{SiO}_2$ precursors. This can be explained by nickel silicate formation on the SiO₂ surface via a reaction between Ni^{2+} species and Si–OH groups [37], with the number of surface Si–OH groups on SiO₂ remaining constant.

3.1.2. XRD and N_2 sorption

Fig. 2 shows the XRD patterns for the Ni/SiO₂ and bimetallic

Fig. 1. H_2 -TPR profiles of catalyst precursors. (a) Ni/SiO₂ (1), Ni₅₀In/SiO₂ (2), Ni₄₀In/SiO₂ (3), Ni₃₀In/SiO₂ (4), Ni₂₀In/SiO₂ (5), and Ni₁₀In/SiO₂ (6); (b) 16%Ni₃₀In/SiO₂ (1), 24%Ni₃₀In/SiO₂ (2), 30%Ni₃₀In/SiO₂ (3), 40%Ni₃₀In/SiO₂ (4), and 50%Ni₃₀In/SiO₂ (5).

Fig. 2. XRD patterns of catalysts. (a) Ni/SiO₂ (1), Ni₅₀In/SiO₂ (2), Ni₄₀In/SiO₂ (3), Ni₃₀In/SiO₂ (4), Ni₂₀In/SiO₂ (5), and Ni₁₀In/SiO₂ (6); (b) 16%Ni₃₀In/SiO₂ (1), 24%Ni₃₀In/SiO₂ (2), 30%Ni₃₀In/SiO₂ (3), 40%Ni₃₀In/SiO₂ (4), and 50%Ni₃₀In/SiO₂ (5).

Ni-In catalysts. In all the patterns, three diffraction peaks are visible, at $\sim 44.5^\circ$, 51.8° , and 76.8° , assigned to the (111), (200), and (220) lattice planes, respectively, of metallic Ni (PDF 04-0850). For $\text{Ni}_y\text{In}/\text{SiO}_2$, the peaks from metallic Ni shift to slightly lower angles with decreasing Ni/In ratio (Fig. 2(a)). This shift to lower angles is not obvious because the Ni/In atomic ratios (50–10) are very high (i.e., the In content is very low). Our previous work indicated that this shift was more obvious when the Ni/In atomic ratio decreased to 6:1 and 4:1 [32]. This shift indicates incorporation of In atoms into the metallic Ni lattice, which is reasonable because the In atom (radius 0.166 nm) is larger than the Ni one (radius 0.124 nm) and In incorporation expands the metallic Ni lattice. The Ni-In bimetallic crystallite sizes for $\text{Ni}_y\text{In}/\text{SiO}_2$ were about 8.7 nm, regardless of the Ni/In ratio (Table 1), similar to the metallic Ni crystallite size (8.8 nm) for Ni/SiO_2 . This shows that introducing a small amount of In into Ni/SiO_2 has a negligible effect on the crystallite size. For $x\text{Ni}_{30}\text{In}/\text{SiO}_2$ (Fig. 2(b)), the diffraction peaks became stronger and sharper with increasing Ni content, and the crystallite size increased from 7.5 to 10.0 nm with increasing Ni content from 16 wt% to 50 wt% (Table 2).

Tables 1 and 2 show the textural properties of the catalysts. The $\text{Ni}_y\text{In}/\text{SiO}_2$ catalysts with different Ni/In atomic ratios had similar pore diameters, and the presence of In in $\text{Ni}_y\text{In}/\text{SiO}_2$ (apart from $\text{Ni}_{40}\text{In}/\text{SiO}_2$) led to a slight increase in the A_{BET} and pore volume compared with those for Ni/SiO_2 (Table 1). For $x\text{Ni}_{30}\text{In}/\text{SiO}_2$, the A_{BET} and pore volume decreased with increasing Ni content, but all the catalysts had similar average pore diameters (Table 2).

3.1.3. TEM

TEM was used to determine the distributions of Ni and In in $\text{Ni}_{10}\text{In}/\text{SiO}_2$. The TEM image in Fig. 3(a) shows that the Ni-In bimetallic particle size was mainly in the range 6–10 nm, with an average size of 8.5 nm; this is consistent with the calculated

value (8.5 nm) obtained using the Scherrer equation. The ED spectrum of a random region (Fig. 3(a)) shows that the Ni/In atom ratio was 11.1, close to the nominal value of 10:1, indicating uniform distributions of Ni and In. This was confirmed by a HAADF-STEM mapping image of a random region (Fig. 3(b)). HAADF-STEM-EDS line scanning further confirmed that Ni and In were uniformly distributed in the bimetallic particles (Fig. 3(c)), indicating intimate contact between Ni and In. Because of this intimate contact, In atoms would isolate Ni ones, leading to a decrease in the size of Ni atom ensembles. This is also shown by the H_2 uptakes.

3.1.4. H_2 chemisorption

H_2 chemisorption was used to determine the surface density of Ni. As shown in Table 1, the density for $\text{Ni}_{50}\text{In}/\text{SiO}_2$, which had the lowest In content (i.e., the highest Ni/In ratio, 50:1), was much lower (38 $\mu\text{mol/g}$) than that for Ni/SiO_2 (200 $\mu\text{mol/g}$). The H_2 uptake decreased almost linearly from 38 to 6.7 $\mu\text{mol/g}$ (Fig. 4) with decreasing Ni/In ratio from 50:1 to 10:1. For $x\text{Ni}_{30}\text{In}/\text{SiO}_2$, the H_2 uptake increased slightly from 21 to 25 $\mu\text{mol/g}$ with increasing Ni content from 16 wt% to 50 wt%. Clearly, the introduction of In significantly decreased the surface Ni site density. The surface energy of metallic In ($\sim 560 \text{ mJ/m}^2$ [39]) is lower than that of metallic Ni ($\sim 2700 \text{ mJ/m}^2$ [40]), therefore In enrichment of the surfaces of Ni-In bimetallic crystallites can occur. The resulting dilution of Ni atoms by In ones limits the capacity of Ni to adsorb and activate H_2 . This indicates that In metal atoms are inactive in H_2 adsorption, consistent with the inertness of metallic In in hydrogenation [29,32]. The Ni content had almost no effect on the H_2 uptakes by the $x\text{Ni}_{30}\text{In}/\text{SiO}_2$ catalysts because they had the same Ni/In atomic ratios. We suggest that consecutive Ni atoms were separated by In atoms in the Ni-In bimetallic catalysts and the ensembles of surface Ni atoms became smaller with decreasing Ni/In ratio.

Table 1

Textural properties, crystallite sizes, and H_2 uptakes of Ni/SiO_2 and $\text{Ni}_y\text{In}/\text{SiO}_2$ catalysts.

Catalyst	A_{BET} (m^2/g)	V_p (cm^3/g)	d_p (nm)	Crystallite size ^a (nm)	H_2 uptake ($\mu\text{mol/g}$)	TOF ($10^{-2}/\text{s}$)
Ni/SiO_2	268	0.46	5.5	8.8	200	1.3
$\text{Ni}_{50}\text{In}/\text{SiO}_2$	294	0.51	5.6	8.8	38	5.9
$\text{Ni}_{40}\text{In}/\text{SiO}_2$	251	0.41	5.5	8.7	31	6.2
$\text{Ni}_{30}\text{In}/\text{SiO}_2$	267	0.61	5.6	8.6	25	5.3
$\text{Ni}_{20}\text{In}/\text{SiO}_2$	308	0.54	5.5	8.7	13	7.2
$\text{Ni}_{10}\text{In}/\text{SiO}_2$	278	0.61	5.6	8.5	6.7	6.2

^a Calculated using the Scherrer equation, based on the Ni (111) reflection.

Table 2

Textural properties and H_2 uptakes of $x\text{Ni}_{30}\text{In}/\text{SiO}_2$ with various Ni contents.

Catalyst	A_{BET} (m^2/g)	V_p (cm^3/g)	d_p (nm)	Crystallite size ^a (nm)	H_2 uptake ($\mu\text{mol/g}$)	TOF ($10^{-2}/\text{s}$)
16% $\text{Ni}_{30}\text{In}/\text{SiO}_2$	402	0.70	5.7	7.5	21	2.8
24% $\text{Ni}_{30}\text{In}/\text{SiO}_2$	401	0.61	5.7	8.0	22	4.8
30% $\text{Ni}_{30}\text{In}/\text{SiO}_2$	339	0.56	5.6	8.9	23	5.1
40% $\text{Ni}_{30}\text{In}/\text{SiO}_2$	267	0.43	5.6	8.6	25	5.3
50% $\text{Ni}_{30}\text{In}/\text{SiO}_2$	241	0.46	5.6	10.0	25	5.0

^a Calculated using the Scherrer equation, based on the Ni (111) reflection.

Fig. 3. (a) TEM image, particle size distribution, and ED spectrum, (b) EDS mapping, and (c) EDS line-scanning of $\text{Ni}_{10}\text{In}/\text{SiO}_2$.

3.1.5. XPS

Fig. 5 shows the XPS spectra of Ni/SiO_2 , $\text{Ni}_{30}\text{In}/\text{SiO}_2$, and $\text{Ni}_{10}\text{In}/\text{SiO}_2$ in the $\text{Ni } 2p_{3/2}$ and $\text{In } 3d$ regions. As shown in Fig. 5(a), the $\text{Ni } 2p_{3/2}$ BEs for Ni/SiO_2 , $\text{Ni}_{30}\text{In}/\text{SiO}_2$, and $\text{Ni}_{10}\text{In}/\text{SiO}_2$ are similar (~ 852.6 eV), and are ascribed to metallic Ni^0 [41,42]. This differs from a report that charge transfer from In to Ni occurred in Ni-In intermetallic compounds, shown by extended X-ray absorption fine structure results [29]. Charge transfer from In to Ni should be reflected in a decrease in the $\text{Ni } 2p_{3/2}$ BE. This discrepancy may arise because of the small amount of metallic In in the Ni-In bimetallic catalysts in our study. Our previous work shows that the BEs of $\text{Ni } 2p_{3/2}$ for metallic Ni and Ni_2In are 852.8 and 852.3 eV, respectively [32]. The $\text{In } 3d$ BEs provide information on the electronic interactions between metallic Ni and In. It has been reported that the

Fig. 4. H_2 uptakes by $\text{Ni}_y\text{In}/\text{SiO}_2$ with various Ni/In atomic ratios. Note: the catalyst with Ni/In ratio of 1:0 is Ni/SiO_2 .

In $3d_{5/2}$ and $\text{In } 3d_{3/2}$ BEs for metallic In^0 are 444.0 and 451.4 eV [43,44], respectively. Here, the $\text{In } 3d_{5/2}$ (444.5–444.6 eV) and $\text{In } 3d_{3/2}$ (452.0–452.2 eV) BEs for $\text{Ni}_{30}\text{In}/\text{SiO}_2$ and $\text{Ni}_{10}\text{In}/\text{SiO}_2$ are higher than those for metallic In^0 (Fig. 5(b)), indicating charge transfer from In to Ni. This is in agreement with the higher electronegativity of Ni (1.91) compared with that of In (1.78) [29]. There is therefore a higher electron density of Ni atoms in the Ni-In bimetallic catalysts than in the monometallic Ni one, and the In species in the Ni-In bimetallic catalysts are positively charged. Charge transfer from In to Ni also indicates strong interactions between Ni and In on the catalyst surface. Additionally, the surface Ni/In ratios for $\text{Ni}_{30}\text{In}/\text{SiO}_2$ and $\text{Ni}_{10}\text{In}/\text{SiO}_2$ were 8.2 and 3.3, respectively, i.e., lower than the nominal ones (30:1 and 10:1, respectively) in the bulk catalysts. This also indicates In enrichment on the catalyst surface, consistent with the H_2 chemisorption results.

3.1.6. NH_3 -TPD

It has been reported that only Lewis acidic sites are present on Ni/SiO_2 and $\text{Ni-In}/\text{SiO}_2$ [32]. For Ni/SiO_2 , unreduced Ni species (especially nickel silicate) contribute to the Lewis acidity [45,46]; In species with a small positive charge can also act as Lewis acidic sites.

Fig. 6 shows the NH_3 -TPD profiles for the catalysts. Ni/SiO_2 and $\text{Ni}_y\text{In}/\text{SiO}_2$ (Fig. 6(a)) gave two main NH_3 desorption peaks, at 180 and above 330 °C, and a shoulder at higher temperature. The second peak shifted to higher temperature with increasing In content (i.e., decreasing Ni/In ratio). There was also another weak peak at ~ 700 °C for $\text{Ni}_y\text{In}/\text{SiO}_2$ when the Ni/In atomic ratio was less than 20:1. $\text{xNi}_{30}\text{In}/\text{SiO}_2$ also gave two main NH_3 desorption peaks at around 180 and 330 °C, and the shoulder became more obvious with increasing Ni content (Fig. 6(b)). The total number of acidic sites on $\text{Ni}_y\text{In}/\text{SiO}_2$ (especially strong acidic sites) was lower than that on Ni/SiO_2 , and this became more obvious with decreasing Ni/In ratio. The amount of acidic sites on $\text{xNi}_{30}\text{In}/\text{SiO}_2$ increased with increasing Ni content. This is reasonable because Lewis acidic sites are mainly derived from Ni species, therefore a higher Ni content leads to an increased number of acidic sites.

Fig. 5. XPS spectra. (a) Ni $2p_{3/2}$ for Ni/SiO₂ (1), Ni₃₀In/SiO₂ (2), and Ni₁₀In/SiO₂ (3); (b) In $3d$ for Ni₃₀In/SiO₂ (1) and Ni₁₀In/SiO₂ (2).

Fig. 6. NH₃-TPD profiles. (a) Ni/SiO₂ (1), Ni₅₀In/SiO₂ (2), Ni₄₀In/SiO₂ (3), Ni₃₀In/SiO₂ (4), Ni₂₀In/SiO₂ (5), Ni₁₀In/SiO₂ and (6); (b) 16%Ni₃₀In/SiO₂ (1), 24%Ni₃₀In/SiO₂ (2), 30%Ni₃₀In/SiO₂ (3), 40%Ni₃₀In/SiO₂ (4), and 50%Ni₃₀In/SiO₂ (5).

3.2. Catalytic activity

In HDO of anisole on different catalysts, apart from anisole and *n*-octane (i.e., the solvent), the compounds detected in the liquid effluent included benzene, toluene, xylene, cyclohexane, phenol, cresol, and *n*-hexane. No cyclohexanol, cyclohexanone, and methoxycyclohexane were found. In the gaseous effluent, C1–C5 hydrocarbons were detected. According to the literature [4,25,47–49], two parallel routes can occur in HDO of anisole (Scheme 1). One is DDO, which involves direct cleavage of C_{Ar}–O bonds (the area marked by a dashed line in Scheme 1). Demethoxylation of anisole can occur to form benzene; demethylation and methyl transfer can also initially occur to yield phenol, cresol, and xylenol, which can be converted to benzene, toluene, and xylene, respectively, via C_{Ar}–O bond cleavage. Benzene can be further hydrogenated to cyclohexane. The other route is hydrogenation-deoxygenation (HYD), in which benzene ring hydrogenation yields methoxycyclohexane and cyclohexanol, followed by demethoxylation-hydrogenation and dehydration-hydrogenation to form cyclohexane. Ring opening of cyclohexane via C–C bond hydrogenolysis gives *n*-hexane,

and then further C–C bond hydrogenolysis yields C1–C5 hydrocarbons. As discussed below, in the present work, benzene was the main product. Given that methoxycyclohexane and

Scheme 1. Possible reaction pathways in HDO of anisole.

cyclohexanol were not detected, the DDO route may be more favorable than HYD at atmospheric pressure [35]. The $C_{Ar}O-CH_3$, $C_{Ar}-OH$, and $C_{Ar}-OCH_3$ bond dissociation energies are 339, 468, and 422 kJ/mol, respectively [4,35], therefore the $C_{Ar}O-CH_3$ bond is the most easily broken to produce phenol, followed by the $C_{Ar}-OCH_3$ and $C_{Ar}-OH$ bonds. In thermodynamic terms, demethoxylation of anisole to yield benzene is more favorable than conversion of phenol to benzene.

Additionally, as indicated below, *n*-heptane was predominantly generated by hydrogenolysis of *n*-octane (i.e., the solvent).

3.2.1. Activity of Ni_5In/SiO_2

As shown in Fig. 7(a), the introduction of In led to a decrease in anisole conversion. The anisole conversion on Ni/SiO_2 was 99.3%, and it gradually decreased to 55.7% as the Ni/In atomic ratio decreased to 10:1. This is primarily ascribed to the large decrease in the surface density of Ni, as indicated by the H_2 uptake results (Table 1). Metallic In is inert in hydrogenation [29,32]. The decrease in the surface density of Ni with decreasing Ni/In atomic ratio (Table 1) is not favorable for anisole conversion. The presence of In enhances the anisole TOF. The data in Table 1 show that the TOF for Ni/SiO_2 was $1.3 \times 10^{-2} s^{-1}$, whereas the values were $(5.3-7.2) \times 10^{-2} s^{-1}$ for Ni_5In/SiO_2 with Ni/In ratios between 50:1 and 10:1. This suggests that although metallic In is inert in hydrogenation, it may be active in anisole conversion.

Here, the target products are BTX, and the introduction of a suitable amount of In enhanced the selectivity for BTX. The selectivity for BTX was 52.0% on Ni/SiO_2 , and increased to 64.0% with decreasing Ni/In atomic ratio to 30:1, followed by a drop to 49.8% at a Ni/In ratio of 10:1. The BTX yield reached the maximum, i.e., 60.4%, at a Ni/In ratio of 40:1 (Fig. 7(a)). The total selectivity for phenol and cresol was low, and increased from 0.8% to 3.1% when the Ni/In atomic ratio decreased from 1:0 to 10:1.

Benzene was the main BTX component produced, and the trend in its selectivity changes was the same as that for BTX (45.9%, 58.6%, 60.0%, 62.2%, 60.0%, and 47.6% at Ni/In

atomic ratios of 1:0, 50:1, 40:1, 30:1, 20:1, and 10:1, respectively). Toluene and xylene were formed by methyl transfer during the reaction. The total selectivity for toluene and xylene decreased from 6.0% to 2.1% with decreasing Ni/In ratio from 1:0 to 10:1, showing that the presence of In restrained the methyl-transfer reaction. This is also clearly shown by the molar ratio of benzene to toluene and xylene combined (denoted by n_B/n_{TX}). The n_B/n_{TX} ratio was 27.7–21.2 at Ni/In ratios between 50:1 and 10:1, much larger than that (7.7) for Ni/SiO_2 . The reduced activity in methyl transfer can be explained by a decrease in the total amount of acidic sites because these sites are involved in methyl transfer [10,36,50].

Fig. 7(b) shows the selectivities for cyclohexane and *n*-hexane. The selectivity for cyclohexane slowly increased from 1.6% to 8.4% with decreasing Ni/In atom ratio from 1:0 to 10:1; conversely, the selectivity for *n*-hexane decreased from 22.5% to 0.11%. As mentioned above, *n*-hexane and *n*-heptane were both detected in the liquid effluent. The selectivity for *n*-heptane (calculated on the basis of consumed anisole) and total selectivity for C6–C8 compounds also decreased with decreasing Ni/In atomic ratio. The total selectivities for C6–C8 compounds exceeded 100% on Ni/SiO_2 and $Ni_{50}In/SiO_2$, which is impossible. Reasonably, *n*-hexane can be derived from the ring opening of cyclohexane. *n*-Heptane could be generated by hydrogenolysis of specific C–C bonds in methylcyclohexane; however, no methylcyclohexane was detected in the liquid effluent. Given the high activity of metallic Ni in hydrogenolysis of C–C bonds [9,19], *n*-heptane might be produced by hydrogenolysis of *n*-octane (i.e., the solvent). To verify this, *n*-octane alone was pumped into the reactor to evaluate the activities of Ni/SiO_2 , $Ni_{30}In/SiO_2$, and $Ni_{10}In/SiO_2$; the *n*-octane conversions were 42.4%, 24.5%, and 6.89%, respectively, and C1–C7 hydrocarbons were detected. This shows that hydrogenolysis of *n*-octane occurred on Ni/SiO_2 and Ni_5In/SiO_2 , and the activity of metallic Ni in C–C bond hydrogenolysis was significantly suppressed by the introduction of In. Because *n*-hexane could also be produced by hydrogenolysis of the solvent (*n*-octane), the selectivity for *n*-hexane calculated on the basis of the anisole conversion is not an accurate value. The selectivity for

Fig. 7. Performances of Ni/SiO_2 and Ni_5In/SiO_2 with different Ni/In atomic ratios. (a) Anisole conversions (1), BTX yields (2) and BTX selectivities (3); (b) Selectivities for cyclohexane (1) and *n*-hexane (2); (c) $n_{CH_4}/n_{Anisole}$ (1) and $n_{CO}/n_{Anisole}$ (2). Note: the catalyst with Ni/In ratio of 1:0 is Ni/SiO_2 . Reaction conditions: 300 °C, 0.1 MPa, H_2 /anisole molar ratio 25, and anisole WHSV 0.4 h⁻¹.

n-heptane is also not the real value because it was calculated on the basis of anisole consumption. Nevertheless, the selectivity for *n*-hexane can be used to reflect the catalytic activity in C–C bond hydrogenolysis, i.e., a higher selectivity for *n*-hexane indicates a higher activity in C–C bond hydrogenolysis. In short, the activity of Ni/SiO₂ in the hydrogenolysis of C–C bonds was suppressed by the introduction of metallic In, and the higher the In content was, the greater the suppression. This low activity in C–C bond hydrogenolysis increases the selectivity for cyclohexane.

The above results indicate that the introduction of In into Ni/SiO₂ increased the selectivities for BTX and cyclohexane. Given the large difference between the anisole conversions on Ni/SiO₂ and Ni_yIn/SiO₂ under the same reaction conditions, this comparison of product selectivities may be unsatisfactory. We therefore also compared the selectivities for BTX and cyclohexane at similar anisole conversions. Similar anisole conversions of ~60.0% on Ni/SiO₂ and Ni_yIn/SiO₂ were obtained by changing the anisole WHSV. The selectivity for BTX was 71.3% on Ni/SiO₂, about 2%–5% lower than those on Ni_yIn/SiO₂ (apart from Ni₁₀In/SiO₂). We suggest that the presence of In suppressed benzene ring hydrogenation, resulting in higher selectivities for BTX on Ni_yIn/SiO₂. This is confirmed by the lower activity of Ni_yIn/SiO₂ compared with that of Ni/SiO₂ in the hydrogenation of benzene. Under the same conditions (300 °C, 0.1 MPa, H₂/benzene molar ratio 17.4, and benzene WHSV 0.55 h⁻¹), Ni/SiO₂, Ni₃₀In/SiO₂, Ni₂₀In/SiO₂, and Ni₁₀In/SiO₂ gave benzene conversions of 65.4%, 39.3%, 22.9%, and 17.0%, respectively. Clearly, the activity of Ni_yIn/SiO₂ decreased with increasing In content. Additionally, at similar anisole conversions, i.e., ~60%, the selectivity for cyclohexane on Ni/SiO₂ was 0.7, and it increased from 3.2 to 9.9 with decreasing Ni/In ratio from 50:1 to 10:1. This is consistent with a lower activity of Ni_yIn/SiO₂ in C–C bond hydrogenolysis, as indicated above.

The molar ratio of CH₄ to converted anisole (denoted by $n_{\text{CH}_4}/n_{\Delta\text{Anisole}}$) also reflects the catalytic activity in C–C bond hydrogenolysis. CH₄ was the main gaseous product on Ni_yIn/SiO₂ and can be derived from the methoxy group in anisole via the following pathways: (1) ArO–CH₃ bond hydrogenolysis; (2) demethoxylation (i.e., Ar–OCH₃ bond cleavage) to form

methanol followed by hydrogenation; and (3) methanation of CO derived from methanol decomposition. CH₄ can also be produced by C–C hydrogenolysis of *n*-hexane (from cyclohexane) and *n*-octane (i.e., the solvent). If C–C hydrogenolysis does not occur, the $n_{\text{CH}_4}/n_{\Delta\text{Anisole}}$ ratio should be ≤ 1.0. As shown in Fig. 7(c), Ni/SiO₂ gave an $n_{\text{CH}_4}/n_{\Delta\text{Anisole}}$ ratio of 13.3, and In introduction significantly decreased the $n_{\text{CH}_4}/n_{\Delta\text{Anisole}}$ ratio. The $n_{\text{CH}_4}/n_{\Delta\text{Anisole}}$ ratio decreased from 3.6 to 0.5 with decreasing Ni/In ratio from 50:1 to 10:1. CO was not detected on Ni/SiO₂, but was generated on Ni_yIn/SiO₂. The molar ratio of CO to consumed anisole ($n_{\text{CO}}/n_{\Delta\text{Anisole}}$) increased from 0.1 to 0.3 with decreasing Ni/In atomic ratio from 50:1 to 10:1 (Fig. 7(c)), i.e., the Ni–In bimetallic catalysts were less active than the mono-metallic Ni catalyst in methanation of CO.

3.2.2. Activity of $x\text{Ni}_{30}\text{In}/\text{SiO}_2$

The effects of the Ni content on the performances of Ni–In bimetallic catalysts in HDO of anisole were investigated using $x\text{Ni}_{30}\text{In}/\text{SiO}_2$ catalysts with various Ni contents.

Fig. 8(a) shows that the anisole conversion increased with increasing Ni content, and exceeded 90% on $x\text{Ni}_{30}\text{In}/\text{SiO}_2$ with a Ni content ≥ 30 wt%. This is because of the increased surface density of Ni (Table 2). The TOFs for anisole on $x\text{Ni}_{30}\text{In}/\text{SiO}_2$ were also calculated. The data in Table 2 show that the TOF was $2.8 \times 10^2 \text{ s}^{-1}$ on 16%Ni₃₀In/SiO₂, and $\sim 5.0 \times 10^{-2} \text{ s}^{-1}$ on $x\text{Ni}_{30}\text{In}/\text{SiO}_2$ with Ni contents between (24 and 50) wt%. The Ni–In bimetallic crystallite size did not affect anisole conversion when the Ni–In bimetallic crystallites were larger than 8.0 nm.

The most abundant products were still BTX; their selectivities and yields on $x\text{Ni}_{30}\text{In}/\text{SiO}_2$ are shown in Fig. 8(a). For $x\text{Ni}_{30}\text{In}/\text{SiO}_2$, the BTX selectivity remained at ~ 61%, and the BTX yield increased from 42.6% to 59.0% with increasing Ni content from 16 to 40 wt%. The Ni content therefore did not affect the selectivity for BTX, indicating that the BTX selectivity was determined by the Ni/In atomic ratio rather than the Ni content. The BTX yield increased with increasing Ni content because of the increase in the anisole conversion. Small amounts of phenol and cresol were detected in the liquid effluent, and the total selectivity for phenol and cresol was low (ranging from 0% to 2%).

Fig. 8. Activities of $x\text{Ni}_{30}\text{In}/\text{SiO}_2$ catalysts in HDO of anisole. (a) Anisole conversions (1), BTX yields (2), BTX selectivity (3), and cyclohexane selectivity (4); (b) Molar ratios of CH₄ (1) or CO (2) to converted anisole. Reaction conditions: 300 °C, 0.1 MPa, H₂/anisole molar ratio 25, and anisole WHSV 0.4 h⁻¹.

Benzene was the main BTX component produced on $x\text{Ni}_{30}\text{In}/\text{SiO}_2$. The selectivity for benzene on $x\text{Ni}_{30}\text{In}/\text{SiO}_2$ did not change significantly, and ranged from 59% to 62%. The total selectivity for toluene and xylene on $x\text{Ni}_{30}\text{In}/\text{SiO}_2$ was low (ranging from 1.5% to 1.9%), indicating that $x\text{Ni}_{30}\text{In}/\text{SiO}_2$ had low activity in the methyl-transfer reaction. This is also clearly shown by the $n_{\text{B}}/n_{\text{TX}}$ ratio on $x\text{Ni}_{30}\text{In}/\text{SiO}_2$; the ratio remained at ~ 35 with increasing Ni content from 16 wt% to 40 wt%, which is much higher than that (7.7) on Ni/SiO_2 . Consistent with the above results, for $\text{Ni}_2\text{In}/\text{SiO}_2$, the introduction of In has a negative effect on the methyl-transfer reaction, mainly because of the decreased amount of acidic sites.

Fig. 8(a) shows that the selectivity for cyclohexane on $x\text{Ni}_{30}\text{In}/\text{SiO}_2$ was maintained at around 5.0%. *n*-Hexane and *n*-heptane were always detected in the liquid products. The selectivity for *n*-hexane was $\sim 2\%$ on $x\text{Ni}_{30}\text{In}/\text{SiO}_2$. CH_4 was the main gaseous product on $x\text{Ni}_{30}\text{In}/\text{SiO}_2$. Fig. 8(b) shows that the $n_{\text{CH}_4}/n_{\Delta\text{Anisole}}$ ratios were between 1.2 and 1.5 on $x\text{Ni}_{30}\text{In}/\text{SiO}_2$, much lower than that (13.3) on Ni/SiO_2 , further indicating much lower activities in C–C bond hydrogenolysis on the Ni–In bimetallic catalysts.

As mentioned above, CO can be formed by methanol decomposition. CO was always detected on $x\text{Ni}_{30}\text{In}/\text{SiO}_2$; $n_{\text{CO}}/n_{\Delta\text{Anisole}}$ was 0.14–0.18 on $x\text{Ni}_{30}\text{In}/\text{SiO}_2$ (Fig. 8(b)). Clearly, the Ni content had little effect on the Ni–In bimetallic catalytic activity in CO methanation.

We also investigated the performances of Ni/SiO_2 with various Ni contents (denoted by $x\text{Ni}/\text{SiO}_2$). The conversion was 90.6% at a Ni mass content of 16% and $\sim 99.5\%$ for Ni mass contents between 24% and 50%. At the same Ni content, the anisole conversion on $x\text{Ni}_{30}\text{In}/\text{SiO}_2$ was lower than that on $x\text{Ni}/\text{SiO}_2$. This is because of the smaller H_2 uptake (21–25 $\mu\text{mol/g}$) by $x\text{Ni}_{30}\text{In}/\text{SiO}_2$. For $x\text{Ni}/\text{SiO}_2$, the H_2 uptakes were 44, 94, 138, 200, and 244 $\mu\text{mol/g}$ for Ni mass contents of 16%, 24%, 30%, 40%, and 50%, respectively. However, $x\text{Ni}_{30}\text{In}/\text{SiO}_2$ gave higher selectivities for BTX and cyclohexane in all cases. The selectivity for BTX on $x\text{Ni}/\text{SiO}_2$ ranged from 51.5% to 59.1%, and that for cyclohexane ranged from 1.1% to 1.6%.

In summary, the introduction of a small amount of metallic In suppressed the activity of Ni/SiO_2 in benzene ring hydrogenation, C–C bond hydrogenolysis, and methanation. This is important in terms of increasing the carbon yield and reducing H_2 consumption. Additionally, the effect of the Ni/In atomic ratio on the product selectivities was greater than that of the Ni content.

3.2.3. Effect of In on Ni/SiO_2 activity in HDO of anisole

As mentioned above, the introduction of In into Ni/SiO_2 has the following effects. (1) It decreases the catalytic activity in anisole conversion and increases the selectivity for BTX (mostly benzene), i.e., it decreases the activity in benzene ring hydrogenation. (2) It increases the selectivity for cyclohexane and decreases the selectivity for *n*-hexane, i.e., it decreases the catalytic activity in C–C bond hydrogenolysis. (3) It decreases the catalytic activity in methanation. All these effects are related to geometric and electronic modification of metallic Ni by metallic In. Specifically, ensembles of Ni atoms become smaller, and the

electron density on Ni is increased by charge transfer from In.

The H_2 uptakes indicate that the surface Ni site density decreased significantly when In was introduced into Ni/SiO_2 (Tables 1 and 2). This is unfavorable for anisole conversion because metallic Ni is active in hydrogenation, whereas metallic In is relatively inert [29]. However, the introduction of metallic In enhanced the selectivity for BTX. We speculate that there are two reasons for these results. One is that the selectivities for $\text{C}_{\text{Ar}}\text{--O}$ bond cleavage of the Ni–In bimetallic catalysts could be higher than that of the monometallic Ni catalyst. The other is that Ni–In bimetallic catalysts might have lower activities in benzene ring hydrogenation. In the first case, given that reduction of indium oxide is more difficult than NiO reduction [29], metallic In is more oxophilic than metallic Ni. It has been reported that when more oxophilic Fe and Zn were introduced into Ni [51], Pd [22], or Pt [52] catalysts, they facilitated selective cleavage of $\text{C}_{\text{Ar}}\text{--O}$ bonds to produce benzene series hydrocarbons in HDO of *m*-cresol, guaiacol, and anisole; this is because of the strong interactions between Fe or Zn and oxygen. Additionally, Ni–In intermetallic compounds have high selectivities for hydrogenation of C=O bonds in α,β -unsaturated aldehydes [29] and fatty acids [30,31], producing C–OH groups. In this study, DFT calculations using Gaussian 09 were used to determine the interactions between metallic Ni or In atoms and anisole via oxygen adsorption. The results show that the adsorption energies of anisole on metallic Ni and In atoms were -86.9 and 5.80 kJ/mol, respectively, i.e., there are strong interactions between metallic Ni and anisole via adsorption of oxygen, but spontaneous adsorption of anisole on In atoms via the anisole oxygen is not possible. The data in Table 3 show that the $\text{C}_{\text{Ar}}\text{--O}$ and $\text{C}_{\text{CH}_3}\text{--O}$ (C_{CH_3} denotes the carbon in methyl) bonds in anisole both lengthen when anisole is adsorbed on a Ni atom, whereas their lengths are almost unchanged when anisole is adsorbed on an In atom. These results indicate that the presence of In does not favor anisole adsorption via oxygen, and activation and cleavage of the $\text{C}_{\text{Ar}}\text{--O}$ bond, and that metallic Ni atoms are the predominant active sites for $\text{C}_{\text{Ar}}\text{--O}$ bond cleavage. The higher selectivities for BTX on Ni–In bimetallic catalysts compared with that on Ni/SiO_2 can therefore be mainly attributed to suppression of benzene ring hydrogenation, as discussed below.

Metallic Ni is highly active in benzene ring hydrogenation because of its high affinity for both H_2 and benzene rings [23]. Ni–In bimetallic catalysts have lower H_2 adsorption abilities as a result of In incorporation (Table 1). Charge transfer from In to Ni leads to increased electron density on the Ni atoms, which is unfavorable for the adsorption of electron-rich benzene rings [53–55]. The dilution of surface Ni atoms by In atoms may not favor adsorption and hydrogenation of benzene rings. As discussed in section 3.2.1, the activities of the Ni–In bimetallic cat-

Table 3
C–O bond lengths in free and adsorbed anisole.

System	$\text{C}_{\text{Ar}}\text{--O}$ bond length (nm)	$\text{C}_{\text{CH}_3}\text{--O}$ bond length (nm)
Anisole	0.1367	0.1418
Anisole/Ni	0.1408	0.1449
Anisole/In	0.1377	0.1425

alysts in benzene hydrogenation were lower than that of Ni/SiO₂, and the lower the Ni/In atomic ratio was, the lower the activity was. Additionally, it has been reported that, compared with monometallic Ni/SiO₂, Ni-In/SiO₂ bimetallic catalysts suppress the adsorption and hydrogenation of electron-rich ethylene [32,56].

The introduction of In suppressed benzene hydrogenation, therefore the higher selectivity for cyclohexane on the In-modified catalysts compared with that on Ni/SiO₂ is puzzling. This can be explained by greater C–C bond hydrogenolysis on monometallic Ni than on the Ni-In bimetallic catalysts, i.e., ring opening of cyclohexane is easier on metallic Ni, therefore cyclohexane is consumed. The lower activities in C–C bond hydrogenolysis of the Ni-In bimetallic catalysts compared with that of monometallic Ni is mainly ascribed to a decrease in the size of Ni atom ensembles. It has been widely reported that C–C bond cleavage requires a large ensemble of contiguous Ni atoms [25,27,57]. The mechanism of ethane hydrogenolysis suggests that co-adsorption of two adjacent atoms is needed to activate and facilitate C–C bond cleavage [57]. Here, although the monometallic Ni and Ni-In bimetallic crystallites in Ni/SiO₂ and Ni₉In/SiO₂ were similar in size (Tables 1 and 2), the incorporation of In into the metallic Ni lattice decreased the size of the ensembles of Ni atoms. The H₂ uptakes (Tables 1 and 2, and Fig. 4), suggest that the Ni atom ensembles became smaller with decreasing Ni/In ratio. Consequently, the selectivity for cyclohexane increased with decreasing Ni/In ratio, and the selectivity for *n*-hexane and the $n_{\text{CH}_4}/n_{\Delta\text{Anisole}}$ ratio decreased (Fig. 7). Low activities of Ni-In alloys and intermetallic compounds in C–C bond hydrogenolysis have also been reported for HDO of acetic acid and selective hydrogenation of acetylene [31,32].

In anisole HDO, hydrogenolysis of C_{Ar}–OCH₃ bonds (i.e., demethoxylation) produces methanol, which can be either hydrogenated to CH₄ or decomposed to CO. Given that the Ni-In bimetallic catalysts were less active than monometallic Ni, methanol hydrogenation would be suppressed by the presence of In. It is reasonable that CO was not formed on Ni/SiO₂ because metallic Ni is highly active in methanation [58]. CO was detected on the Ni-In bimetallic catalysts, indicating that bimetallic Ni-In was less active than monometallic Ni in methanation. Charge transfer from In to Ni may favor methanation of CO because the increased electron density on Ni increases the strength of CO adsorption and therefore activation of CO [59,60]. However, the decrease in the size of Ni atom ensembles is unfavorable for methanation of CO [61]. Here, the geometric effect of In may be dominant in the methanation performance.

4. Conclusions

For Ni₉In/SiO₂ catalysts, the H₂ uptake decreased linearly from 38 to 6.7 μmol/g with decreasing Ni/In atomic ratio from 50:1 to 10:1; these values are much lower than that for Ni/SiO₂, namely 200 μmol/g. The H₂ uptake increased slightly from 22 to 25 μmol/g for xNi₃₀In/SiO₂ with increasing Ni content from 16 wt% to 50 wt%. The monometallic Ni crystallites in Ni/SiO₂

and the Ni-In bimetallic crystallites in Ni₉In/SiO₂ were similar in size (~8.7 nm), therefore dilution of Ni atoms by In atoms greatly suppressed H₂ chemisorption, and a higher In content led to a lower H₂ uptake. XPS showed that charge transfer from In to Ni occurred in the Ni-In bimetallic catalysts. There were strong interactions between metallic Ni and In, and metallic In geometrically and electronically modified metallic Ni in the Ni-In bimetallic catalysts. Additionally, the number of acidic sites on the Ni-In bimetallic catalysts was lower than that on Ni/SiO₂.

In anisole HDO, although the anisole conversions on the Ni-In bimetallic catalysts were lower than that on monometallic Ni, because of the lower density of surface Ni sites on the bimetallic catalysts, the selectivities for BTX (mainly benzene) and cyclohexane were higher as a result of suppression of benzene ring hydrogenation and C–C bond hydrogenolysis. Additionally, bimetallic Ni-In was less active than monometallic Ni in methyl transfer because of the smaller number of acidic sites. The selectivity for BTX increased with decreasing Ni/In ratio and was maximum at a Ni/In ratio of 30:1. However, the Ni content had little effect on the selectivity for BTX. At 300 °C, 0.1 MPa, an anisole WHSV of 0.4 h^{–1}, and a H₂/anisole ratio of 25, a BTX yield of 60.4% was obtained on Ni₄₀In/SiO₂ with a Ni content of 40%, i.e., higher than that (51.6%) obtained on Ni/SiO₂.

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Graphical Abstract

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Effects of indium on Ni/SiO₂ catalytic performance in hydrodeoxygenation of anisole as model bio-oil compound: Suppression of benzene ring hydrogenation and C–C bond hydrogenolysisXiaofei Wang, Jixiang Chen*
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In the hydrodeoxygenation of anisole, used as a bio-oil model compound, the activities of Ni-In/SiO₂ bimetallic catalysts in benzene ring hydrogenation and C–C bond hydrogenolysis were much lower than that of Ni/SiO₂, leading to higher selectivities for BTX and cyclohexane.

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In对Ni/SiO₂催化剂苯甲醚加氢脱氧性能的影响: 苯环加氢及C–C键氢解的抑制作用

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摘要: 由可再生木质素基生物质油加氢脱氧制三苯(苯、甲苯及二甲苯)及燃油可减少对化石能源依赖、缓解环境问题, 加氢脱氧催化剂的研究开发为众多学者密切关注. 我们以低成本金属Ni为加氢脱氧活性组分, 采用金属In对金属Ni催化剂进行改性, 旨在增加以苯甲醚为模型反应物加氢脱氧中的三苯收率、降低金属Ni的C–C键氢解及甲烷化活性, 提高反应过程中碳收率、降低耗氢量. 采用等体积浸渍-程序升温还原法制备了Ni/SiO₂及Ni-In/SiO₂催化剂, 研究了Ni/In比及Ni含量对In改性Ni/SiO₂催化剂结构和苯甲醚加氢脱氧性能的影响, 利用H₂-TPR, H₂化学吸附, XRD, NH₃-TPD, XPS, TEM及N₂物理吸附-脱附等手段对催化剂及其前驱体进行了表征, 采用石英管固定床反应器在300 °C、常压、H₂/苯甲醚摩尔比25及苯甲醚重时空速0.4 h⁻¹的反应条件下考察了催化剂苯甲醚加氢脱氧性能, 分析了催化剂结构与性能之间的关系.

H₂-TPR结果显示, 金属In的加入抑制了催化剂前驱体中Ni物种的还原. XRD, H₂化学吸附, HAADF-STEM-EDS及XPS等结果表明, 经450 °C还原制备的Ni-In/SiO₂双金属催化剂中Ni和In接触紧密. In的加入明显降低了催化剂表面金属Ni的活性位数量; 并且, Ni/In比越低Ni-In/SiO₂催化剂H₂化学吸附量越小. XPS结果还显示, Ni-In/SiO₂催化剂中存在金属In向Ni转移电子. 上述结果说明, 在Ni-In/SiO₂催化剂中金属Ni与In存在较强的相互作用. 在苯甲醚加氢脱氧反应中, 与Ni/SiO₂催化剂相比, Ni-In/SiO₂催化剂虽因表面Ni密度较低而具有较低苯甲醚转化率, 但其苯环加氢、C–C键氢解及CO甲烷化活性较低, 因而具有较高的三苯及环己烷选择性; 并且, 随Ni/In比的降低(即In含量的增加), Ni-In/SiO₂催化剂的加氢、氢解及甲烷化能力呈减弱趋势. 随Ni质量含量提高, Ni-In/SiO₂双金属催化剂上苯甲醚转化率提高, 但对三苯选择性及C–C键氢解能力影响不明显. 经分析认为, 与Ni/SiO₂相比, Ni-In/SiO₂催化剂较低的苯加氢及C–C键氢解活性与In对表面连续Ni位隔离作用及金属镍位电子云密度提高有关. 在优化的反应条件下, Ni质量含量为40%、Ni/In比为40的Ni-In/SiO₂催化剂上三苯收率为60.4%, 高于相同Ni质量含量Ni/SiO₂催化剂上三苯收率(51.6%).

关键词: 镍-铟双金属催化剂; 加氢脱氧; 碳-碳键氢解; 苯甲醚; 三苯

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