available at www.sciencedirect.com

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

Article

Effect of IB-metal on Ni/SiO₂ catalyst for selective hydrogenation of acetylene

Hua Liu ^{a,b}, Mengqian Chai ^{a,b}, Guangxian Pei ^{a,b}, Xiaoyan Liu ^{a,*}, Lin Li ^a, Leilei Kang ^a, Aiqin Wang ^a, Tao Zhang ^{a,b,#}

^a CAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:

Received 12 October 2019

Accepted 9 December 2019

Published 5 July 2020

Keywords:

Acetylene

Selective hydrogenation

Ethylene

Ni

IB metals

ABSTRACT

The IB metal (Au, Ag and Cu) alloyed Pd single atom catalysts had been proved to be efficient in promoting the selectivity for hydrogenation of acetylene to ethylene. As a base metal in the same group as Pd, the Ni-based catalysts are also active for hydrogenation reactions. Herein, the effects of the IB metals on the Ni/SiO₂ catalyst for the selective hydrogenation of acetylene were systematically studied. Different from the Pd/SiO₂ catalyst, the monometallic Ni/SiO₂ catalyst is not active at low temperatures. The addition of the IB metals to the Ni/SiO₂ catalysts can greatly enhance the activity. Besides, the catalytic activity of the AuNi_x/SiO₂ and CuNi_x/SiO₂ catalysts increase with the reduction temperature, while the AgNi_x/SiO₂ catalysts are not sensitive to the pretreatment temperature. The origin of the effect of the different IB metals on the Ni-based catalysts for selective hydrogenation of acetylene is discussed based on the characterizations by XRD, TPR and microcalorimetric measurements.

© 2020, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

As one of the most important products of the petrochemical industry, ethylene is the raw material for synthesis of polyethylene. However, the impurity of little amount of acetylene is poisonous for the catalysts to produce polyethylene [1–4]. Selective hydrogenation of acetylene is the most efficient and widely used method in industry to remove acetylene from the ethylene feed gas. So it is necessary to seek the catalysts with both high activity for acetylene conversion and high selectivity for ethylene. The traditional industrial catalysts are supported

Pd-based systems, which usually show an excellent activity but a poor selectivity. To improve the selectivity, a second metal is usually added to modify the nature of Pd [5–12]. The IB-metal (Au, Ag and Cu) -alloyed Pd single-atom catalysts are proved to be highly efficient in promoting the selectivity to ethylene compared with the monometallic Pd catalysts in our previous work [7–9]. As a base metal in the same group as Pd, Ni-based catalysts also show excellent activity for hydrogenation reactions [13–19]. Besides, as non-precious metal, Ni has an absolute advantage in cost. Therefore, it is desirable if the Pd can be replaced by Ni for the selective hydrogenation of acetylene to

* Corresponding author. Tel: +86-411-84379416; Fax: +86-411-84685940; E-mail: xylu2003@dicp.ac.cn

Corresponding author. E-mail: taozhang@dicp.ac.cn

We are grateful for the support from the National Key R&D Program of China (2016YFA0202801), the Strategic Priority Research Program of Chinese Academy of Sciences (XDB17020400), the National Natural Science Foundation of China (21776271), and the China Postdoctoral Science Foundation (2017M621171).

DOI: 10.1016/S1872-2067(20)63568-9 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 41, No. 7, July 2020

ethylene.

The supported Ni catalysts were applied to the selective hydrogenation of acetylene in the literature. Recently, Chai *et al.* [20] reported that the cationic nickel confined in zeolite showed high ethylene selectivity and stability. Felix *et al.* [21,22] synthesized a series of Ni-Zn alloy catalysts on the MgAl_2O_4 spinel support. They found that the Ni-Zn catalyst with the highest Zn content showed high selectivity to ethylene. Bridier *et al.* [23] reported that the selectivity to ethylene over the Cu-Ni-Fe catalysts attained 80%, but the conversion of acetylene was relatively low. Boudjahem *et al.* [15] prepared Cu-Ni/SiO₂ catalysts by aqueous hydrazine reduction and studied their catalytic performance in acetylene hydrogenation, mainly at 60 °C. They found that the addition of Cu had various effects on the product selectivity, such as decreasing the formation of byproducts (*e.g.*, benzene, *etc.*) and increasing the production of ethylene, but the selectivity to ethylene (34.9%) was still not high. Liu *et al.* [18] synthesized quaternary Ni-CuMgAl-LDH through a co-precipitation method, and got pre-NiCuMgAl-mixed metal oxides (MMO) after calcination, which exhibited the superior catalytic performance with the conversion of 100% and selectivity of 70.2% (160 °C, 0.4 MPa) for the selective hydrogenation of acetylene. Nikolaev *et al.* [19] studied the catalytic performance of the acetylene hydrogenation over the Au-Ni/ γ -Al₂O₃ bimetallic catalysts and found pronounced synergism between Au and Ni in promoting the conversion of acetylene. Yang *et al.* [24,25] predicted the possible mechanism and catalytic activity of the IB metal alloyed Ni catalysts for selective hydrogenation of acetylene by density functional theoretical (DFT) calculations. They proposed that the activity of ethylene formation followed the following sequence: Au-Ni > Ag-Ni > Cu-Ni > Ni > Au [25]. Previously, we synthesized a series of Ag-Ni/SiO₂ and Au-Ni/SiO₂ catalysts and found that the interaction between Au/Ag and Ni was beneficial to the catalytic performance in the acetylene hydrogenation [16,17]. But at present, to the best of our knowledge, there was no report on systematically comparing the effect of IB metals on the Ni catalyst in the selective hydrogenation of acetylene by experimental results.

Herein, the IB metals modified Ni/SiO₂ catalysts were synthesized and applied to the selective hydrogenation of acetylene under the same reaction conditions. The results showed that the addition of the IB metals greatly enhanced the catalytic activity of the Ni/SiO₂ catalyst. The catalytic behaviors of the IB metals modified Ni/SiO₂ catalysts were different from that of the Ni/SiO₂ system. The origin of the effect of the different IB metals on the Ni/SiO₂ catalysts in the selective hydrogenation of acetylene was also investigated based on the characterizations by XRD, TPR, and TGA. The results in this work will provide good references for the further study of the nickel-based catalysts for selective hydrogenation reactions.

2. Experimental

2.1. Catalyst preparation

The CuNi_x/SiO₂ and AgNi_x/SiO₂ catalysts ($x = \text{Ni/Cu}$ or Ni/Ag

atomic ratios) with different atomic ratios were prepared by the incipient wetness co-impregnation method. Here we took the Cu-modified Ni/SiO₂ catalysts as an example. The silica (Qingdao Ocean Chemical Plant, BET surface area = 463 m²/g) was firstly impregnated with a mixture of Cu(NO₃)₂·3H₂O and Ni(NO₃)₂·6H₂O solution to obtain the catalysts with different Ni/Cu atomic ratios. The nominal loading of Cu was fixed at 4 wt%. After aging in air at room temperature for 12 h, the samples were dried in air at 120 °C for 12 h. Finally, the samples were calcined in air at 400 °C for 3 h. The as-prepared catalysts were named as CuNi_x/SiO₂ catalysts. In order to better compare the catalytic performance of the different catalysts, the corresponding monometallic Ni_x/SiO₂ and Cu/SiO₂ catalysts were prepared by the same method (the loading of Ni was the same as the corresponding CuNi_x/SiO₂ catalysts; the loading of Cu was 4 wt%). The AgNi_x/SiO₂ catalysts were obtained by the same method as that of the CuNi_x/SiO₂ catalysts.

The AuNi_x/SiO₂ catalysts were prepared by a two-step method previously developed by our group [26]. Briefly, the silica was functionalized with 3-aminopropyl triethoxysilane (APTES; Acros Organics, 99%), which was denoted as SiO₂-APTES. In the first step, the gold precursor was loaded on the surface of the SiO₂-APTES by successively dispersing in the HAuCl₄ solution (2.0 g_{Au}/L) and reducing by NaBH₄ solution. In the second step, the Ni(NO₃)₂ solution and tert-butylamine borane solution were used respectively instead of the HAuCl₄ solution and NaBH₄ solution in the first step. The resulting solid was dried at 60 °C for 1 d, and then calcined at 500 °C for 3 h to obtain the AuNi_x/SiO₂ catalysts (x refers to the mole ratio of Ni to Au).

2.2. Catalyst characterizations

By means of inductively coupled plasma spectrometry (ICP-AES; on a Thermo IRIS Intrepid II XSP instrument), the actual metal loadings of the Ag, Cu and Ni were measured. As shown in Table 1, the actual loading of metal Ag, Cu and Ni was agreement with their theoretical values.

X-ray diffraction (XRD) patterns of the catalysts were obtained on a PW 3040/60 X'Pert Pro Super (PANalytical) diffractometer equipped with a Cu K α radiation source ($\lambda =$

Table 1

The ICP results of the CuNi_x/SiO₂ and AgNi_x/SiO₂ catalysts.

Catalyst	Nominal loading		Actual loading		Actual Ni/IB atomic ratio
	M (wt%)	Ni (wt%)	M (wt%)	Ni (wt%)	
CuNi ₁ /SiO ₂	4	3.69	3.54	3.19	0.98
CuNi _{0.5} /SiO ₂	4	1.85	3.66	1.61	0.48
CuNi _{0.25} /SiO ₂	4	0.92	3.79	0.82	0.23
CuNi _{0.125} /SiO ₂	4	0.46	3.77	0.41	0.12
CuNi _{0.0625} /SiO ₂	4	0.23	3.71	0.22	0.063
Cu/SiO ₂	4	—	3.51	—	—
Ni _{0.125} /SiO ₂	—	0.46	—	0.39	—
AgNi ₁ /SiO ₂	4	2.18	3.47	1.64	0.86
AgNi _{0.5} /SiO ₂	4	1.09	3.60	0.85	0.43
AgNi _{0.25} /SiO ₂	4	0.54	3.49	0.44	0.23
AgNi _{0.125} /SiO ₂	4	0.27	3.64	0.27	0.14

0.15432 nm), operating at 40 kV and 40 mA. The scanning angle (2θ) was 10° – 80° with a scan rate of $10^\circ/\text{min}$.

Temperature-programmed reduction (TPR) experiments were carried out on a Micromeritics AutoChem II 2920 automated characterization system. First, about 110 mg of the calcined sample was loaded into a U-shaped quartz reactor, followed by pretreating with air at 150°C for 60 min to remove the adsorbed water. After cooling to 50°C , the flowing gas was switched to 10 vol% H_2/Ar , and then the catalyst was heated to 700°C at a ramp of $10^\circ\text{C}/\text{min}$.

Microcalorimetric measurements of acetylene adsorption were performed at 40°C using a BT 2.15 heat-flux calorimeter connected to a gas handling system and a volumetric system equipped with MKS 698A baratron capacitance manometers to achieve precise pressure measurement. Prior to measurement, the samples were reduced with flowing 80 vol% $\text{H}_2/20$ vol% He (20 mL/min) at the optimized temperature for 70 min, evacuated for 30 min at 410 or 460°C to remove adsorbed H_2 , cooled to room temperature in vacuum and followed by refilling with He and sealing samples in a thin quartz tube. After being sealed in thin quartz tubes, the samples were placed into the calorimetric cell fixed in the isothermal calorimetric block. The adsorption experiment was performed at 40°C .

Thermogravimetric analysis (TGA) was performed on an SDTQ 600 instrument. About 10 mg of the sample was loaded into the cell, stabilized at 30°C for 20 min in air, and then heated to 900°C at a ramp of $10^\circ\text{C}/\text{min}$.

2.3. Reaction tests

The selective hydrogenation of acetylene was carried out in a fixed-bed reactor. First, 30 mg of the catalyst was reduced

with flowing 80 vol% $\text{H}_2/20$ vol% He (20 mL/min) at the selected temperatures for 70 min, followed by cooling to room temperature in pure He (20 mL/min). Then, the feed gas (30 mL/min; volume ratio of $\text{C}_2\text{H}_2/\text{H}_2/\text{He} = 1:20:79$) was introduced into the fixed-bed reactor. The performance of the catalysts for the selective hydrogenation of acetylene was tested from 100 to 300°C at a heating rate of $8^\circ\text{C}/\text{min}$. The data were collected at every 40°C with holding each reaction temperature constant for 25 min. The outlet gas components were analyzed by an online gas chromatograph (Agilent Technologies 6890 N) equipped with a FID detector.

In this study, C_2H_4 and C_2H_6 were the only C_2 products. Therefore, the acetylene conversion and ethylene selectivity were calculated as $X(\text{C}_2\text{H}_2) = [\text{C}_2\text{H}_2(\text{in}) - \text{C}_2\text{H}_2(\text{out})]/\text{C}_2\text{H}_2(\text{in}) \times 100\%$ and $S(\text{C}_2\text{H}_4) = \text{C}_2\text{H}_4(\text{out})/[\text{C}_2\text{H}_2(\text{in}) - \text{C}_2\text{H}_2(\text{out})] \times 100\%$, respectively.

3. Results and discussion

3.1. Catalytic performance

To investigate the sensitivity of the catalyst to pretreatment temperature, we firstly evaluated the performance of the selective hydrogenation of acetylene over the $\text{CuNi}_{0.125}/\text{SiO}_2$ and $\text{AgNi}_{0.25}/\text{SiO}_2$ catalysts reduced under different temperatures. With increasing reduction temperature from 350 to 550°C , the conversion of acetylene on the $\text{CuNi}_x/\text{SiO}_2$ catalyst increased but the selectivity to ethylene began to decrease when the reduction temperature attained 500°C (Fig. 1A and 1B). Therefore, the most proper reduction temperature should be 450°C for the $\text{CuNi}_x/\text{SiO}_2$ catalysts. The $\text{AuNi}_1/\text{SiO}_2$ catalyst exhibited the similar tendency with $\text{CuNi}_{0.125}/\text{SiO}_2$ catalyst, but was more

Fig. 1. Acetylene hydrogenation performance on $\text{CuNi}_{0.125}/\text{SiO}_2$ (A, B) and $\text{AgNi}_{0.25}/\text{SiO}_2$ (C, D) reduced at different temperatures. (a) 350°C ; (b) 400°C ; (c) 450°C ; (d) 500°C ; (e) 550°C ; (f) 300°C ; (g) 400°C ; (h) 500°C .

sensitive to the pretreatment temperature at low reaction temperatures [16]. However, the $\text{AgNi}_{0.25}/\text{SiO}_2$ catalyst was almost immune to the reduction temperature (Fig. 1C and 1D). The reduction temperature of 400 °C was selected, since the activity was slightly higher than that of the sample reduced at other temperatures. Besides, the activity of the $\text{AgNi}_{0.25}/\text{SiO}_2$ catalyst began to decrease when the reaction temperature reached 180 °C (Fig. 1C). This result was different from the behaviors of the $\text{CuNi}_{0.125}/\text{SiO}_2$ and $\text{AuNi}_1/\text{SiO}_2$ catalysts [16], over which the conversion of acetylene increased monotonously with reaction temperature. The reason might be due to the different catalytic mechanisms at high temperatures over the $\text{AgNi}_{0.25}/\text{SiO}_2$ catalyst. This will be discussed in Section 3.3.2 by testing the apparent activation energy at different ranges of temperature.

In addition to the reduction temperature, the Ni content is also an important factor that affects the interaction between the IB metal and Ni in the bimetallic nanoparticles. Therefore, we further studied the effects of the Ni/IB ratios on the catalytic performances of the IB-Ni/SiO₂ catalysts. It can be seen that the conversion of acetylene over the Cu/SiO₂ catalyst was very low even when the temperature was higher than 220 °C. With increasing atomic ratio of Ni/Cu, the catalytic activity of the $\text{CuNi}_x/\text{SiO}_2$ catalysts was significantly improved. The selectivity to ethylene began to decrease (Fig. 2B), when the Ni/Cu atomic ratio was higher than 0.125. The similar trends were obtained over the $\text{AgNi}_x/\text{SiO}_2$ (Fig. 2C and 2D) and the $\text{AuNi}_x/\text{SiO}_2$ [16] catalysts: the activity increased with the loading of Ni, but the selectivity began to decrease after an optimal ratio. For the Ni/Cu, Ni/Ag and Ni/Au, the optimal ratio was 0.125, 0.5 and 0.5, respectively. According to our previous results, the reduc-

tion of the Ni can be promoted when forming bimetallic nanoparticles with Ag and Au. The Ni with intimate interaction with the IB metals might exhibit high catalytic activity for the hydrogenation of acetylene due to its capability for the activation of the reactants. Further study by the microclariometry measurement was shown in Section 3.3.2.

3.2. Characterization of interaction between IB metal and Ni

From the XRD patterns, the diffraction peaks of the CuO in the $\text{CuNi}_x/\text{SiO}_2$ bimetallic catalysts could be observed obviously (Fig. 3A). After the reduction, all of the $\text{CuNi}_x/\text{SiO}_2$ catalysts showed the diffraction peaks at 43.3°, 50.4° and 74.1° (Fig. 3B), which were corresponding to the crystal planes of Cu(111), Cu(200) and Cu(220), respectively. Even though the Ni/Cu atomic ratio increased to 0.5, there was still no diffraction peaks of Ni in the $\text{CuNi}_x/\text{SiO}_2$ bimetallic catalysts, indicating that the Ni might be highly dispersed on the Cu nanoparticles or it might be amorphous and could not be detected by the XRD. Although using the same preparation method, the Ag-Ni bimetallic nanoparticles of the $\text{AgNi}_x/\text{SiO}_2$ catalysts exhibited much higher dispersion than the Cu-Ni bimetallic nanoparticles. The XRD patterns of the calcined $\text{AgNi}_1/\text{SiO}_2$ catalyst only showed a very weak peak of NiO (Fig. 3C). No obvious peaks appeared when the Ni/Ag atomic ratio was lower than 0.5. After the reduction, there was still no obvious diffraction peak of Ag, only small diffraction peaks of Ni on the $\text{AgNi}_1/\text{SiO}_2$ and $\text{AgNi}_{0.5}/\text{SiO}_2$ catalysts, which demonstrated that Ni and Ag were highly dispersed on the surface of the catalysts, as reported in our previous work [17].

To further manifest the distribution of the Cu-Ni bimetallic

Fig. 2. Acetylene conversion (A, C) and ethylene selectivity (B, D) of the $\text{CuNi}_x/\text{SiO}_2$ (A, B) and $\text{AgNi}_x/\text{SiO}_2$ (C, D) catalysts. Ni/Cu atomic ratio: (a) 0; (b) 0.0625; (c) 0.125; (d) 0.25; (e) 0.5; (f) Ni (Ref. [16]). Ni/Ag atomic ratio: (g) 0; (h) 0.125; (i) 0.25; (j) 0.5; (k) 1.

Fig. 3. XRD patterns for the $\text{CuNi}_x/\text{SiO}_2$ (A, B) and $\text{AgNi}_x/\text{SiO}_2$ (C, D) catalysts after the calcination (A, C) and reduction (B, D). Ni/Cu atomic ratio: (a) 0.5, (b) 0.25, (c) 0.125, (d) 0.0625; (e) 0. Ni/Ag atomic ratio: (f) 1; (g) 0.5; (h) 0.25; (i) 0.125; (j) 0.

nanoparticles, the HAADF images were measured, as shown in Fig. 4. Two different size distributions of the nanoparticles, the largest one could attain ~ 100 nm (Fig. 4A) while the small ones could be ~ 1 nm (Fig. 4B). Thus, the XRD patterns reflected the particles with big sizes while the contribution of the small particles was covered. According to the EDS-mapping results of the big (Fig. 5A) and small (Fig. 5B) particles, one can see that the distribution of Cu and Ni was not completely the same. But the Cu and Ni seemed to be close to each other, as is similar to that of the Ag-Ni catalyst [17]. Besides, the Cu and Ag did not form obvious alloy phases with Ni according to the XRD results. Then, how could the IB metal affect the catalytic performances of the bimetallic catalysts? Further characterizations by TPR were applied to investigate the interaction between the IB metal and Ni.

The H_2 -TPR results of the $\text{CuNi}_x/\text{SiO}_2$ catalysts are presented in Fig. 6. The monometallic Cu/SiO_2 catalyst had only one H_2 consumption peak at 232°C , corresponding to the reduction of Cu^{2+} to Cu^0 [27]. On the other hand, the monometallic Ni/SiO_2 catalyst presented a reduction peak at 330°C with a broad shoulder around 450°C . The former peak was attributed to the reduction of the nickel oxide with weak interaction with the support, and the latter was due to the highly dispersed nickel oxide, which strongly interacted with the support [28]. All of the reduction peaks of the bimetallic $\text{CuNi}_x/\text{SiO}_2$ catalysts shifted to lower temperatures. The formation of the Cu-Ni bimetallic nanoparticles made the reduction of the CuO and NiO much easier than the corresponding monometallic catalysts. This indicates that there was obvious interaction between Cu and Ni [29–32]. Besides, the consumption of hydrogen over the

Fig. 4. HAADF-STEM (A, B) and particle size distribution histogram (C) images of the $\text{CuNi}_{0.125}/\text{SiO}_2$ catalyst.

Fig. 5. STEM-EDS mapping (A, B) images of the CuNi_{0.125}/SiO₂ catalyst.

CuNi_x/SiO₂ catalysts obtained by the TPR results was in good agreement with the stoichiometric results, as shown in Table 2. This demonstrates that the Cu and Ni in the bimetallic catalysts could be reduced completely when the reduction temperature was 450 °C. The sensitivity of the activity to the pretreatment temperature over the catalysts described in Section 3.1 could be ascribed to the changes of structure or distribution of metallic Ni on the surface of the bimetallic nanoparticles. The formation of the Cu-Ni bimetallic nanoparticles made the reduction of the CuO and NiO much easier than the corresponding monometallic catalysts. This indicates that there was obvious interaction between Cu and Ni. As to the AgNi_x/SiO₂ [17] and AuNi_x/SiO₂ [16] catalysts, the interactions between Au/Ag and Ni were previously proved by the TPR and *in situ* CO-DRIFT.

Fig. 6. TPR profiles of the (a) Cu/SiO₂, (b) CuNi_{0.125}/SiO₂, (c) CuNi_{0.5}/SiO₂ and (d) Ni/SiO₂ catalysts.

Table 2
Hydrogen consumption of the CuNi_x/SiO₂ catalysts.

Catalyst	Nominal H ₂ consumption (μmol/g)	Actual H ₂ consumption (μmol/g)
CuNi _{0.5} /SiO ₂	850.2	813.9
CuNi _{0.125} /SiO ₂	663.1	627.2
Cu/SiO ₂	552.3	544.4

After the introduction of IB metals, NiO_x might preferentially interact with IB metals other than silica, which weakened the interaction between the NiO_x and silica, and further promoted their reduction.

3.3. Comparison of IB-Ni/SiO₂ catalysts

3.3.1. Catalytic activity and stability

The optimal catalytic performance of the IB metals and Ni bimetallic catalysts is shown in Fig. 7. We found that the reaction activity over the AuNi_{0.5}/SiO₂ catalyst was obviously higher than those over CuNi_{0.125}/SiO₂ and AgNi_{0.5}/SiO₂ catalysts at 100 °C. From 100 to 180 °C, the three catalysts showed similar behavior with temperature. Their activity followed the following order: AuNi_{0.5}/SiO₂ > AgNi_{0.5}/SiO₂ > CuNi_{0.125}/SiO₂, but ethylene selectivity followed a reversed order. With the reaction temperature rising, the three catalysts all arrived at their highest activity at the temperature range from 180 to 220 °C. But further increasing the reaction temperature, the acetylene conversion of the AgNi_{0.5}/SiO₂ decreased obviously, which was different from the performance over the CuNi_{0.125}/SiO₂ and AuNi_{0.5}/SiO₂ catalysts. For this phenomenon, we speculated that the segregation of Ag on the surface of the nanoparticles covered part of the active sites due to the small surface energy of Ag [33–35].

The stability of the three catalysts at 160 °C was studied under the same reaction condition. As shown in Fig. 8, the acetylene conversion over the CuNi_{0.125}/SiO₂ catalyst was still higher than 93.4% after 24 h. Meanwhile, the ethylene selectivity could keep at 61.9%. Over the AgNi_{0.5}/SiO₂ catalyst, the conversion of acetylene decreased to about 80% from 100% after 24 h. In sharp contrast, very quick deactivation happened over the AuNi_{0.5}/SiO₂ catalyst: the conversion of acetylene decreased to 14.9% from 81.5% after 200 min. Because of its poor stability, its apparent activation energy cannot be attained accurately.

To explore the reason for the deactivation of the catalysts, the TGA and XRD tests were carried out on the CuNi_{0.125}/SiO₂,

Fig. 7. Acetylene conversion (A) and ethylene selectivity (B) over $\text{CuNi}_{0.125}/\text{SiO}_2$ (a), $\text{AgNi}_{0.5}/\text{SiO}_2$ (b) and $\text{AuNi}_{0.5}/\text{SiO}_2$ (c) catalysts reduced at 450 °C (the $\text{AuNi}_{0.5}$ data derived from the reference [16]).

$\text{AgNi}_{0.5}/\text{SiO}_2$ and $\text{AuNi}_{0.5}/\text{SiO}_2$ catalysts after the stability tests for 24 h. The results are shown in Figs. 9 and 10. In Fig. 9, the weight loss below 120 °C was ascribed to the water evaporation, and over 600 °C, the weight loss was negligible. Thus, the amount of coke on the catalyst surface was calculated based on the weight loss between 120 and 600 °C. The results showed

Fig. 8. Acetylene conversion and ethylene selectivity with time on stream at 160 °C over $\text{CuNi}_{0.125}/\text{SiO}_2$ (a), $\text{AgNi}_{0.5}/\text{SiO}_2$ (b) and $\text{AuNi}_{0.5}/\text{SiO}_2$ (c) catalysts (solid for conversion; hollow for selectivity).

Fig. 9. TGA results of the $\text{CuNi}_{0.125}$ (a), $\text{AgNi}_{0.5}$ (b) and $\text{AuNi}_{0.5}$ (c) catalysts after the stability tests for 24 h.

that the weight loss of the $\text{CuNi}_{0.125}/\text{SiO}_2$, $\text{AgNi}_{0.5}/\text{SiO}_2$ and $\text{AuNi}_{0.5}/\text{SiO}_2$ catalysts was 6.44%, 6.01% and 11.12%, respectively. Comparing to the $\text{AuNi}_{0.5}/\text{SiO}_2$ catalyst, the amount of coke formation on the surface of $\text{CuNi}_{0.125}$ and $\text{AgNi}_{0.5}$ catalysts was significantly less. Therefore, we speculated that extremely poor stability over the $\text{AuNi}_{0.5}/\text{SiO}_2$ catalyst was mainly caused by the coke deposition, which could cover the active sites on the surfaces of the catalyst. Over the $\text{AgNi}_{0.5}/\text{SiO}_2$ catalyst, the decreasing of reaction activity was partly caused by segregation of Ag on the surface of metallic Ni [36,37]. Moreover, the XRD results (Fig. 10) indicated that the structure of these catalysts had no obvious change after the stability tests, which further confirmed that the deactivation of the catalysts was mainly caused by the coke deposition.

3.3.2. Apparent activation energy and microcalorimetric result

In order to understand the essential reasons for their difference in reaction activity, the apparent activation energy for the acetylene hydrogenation in the low and high temperature ranges was studied. Here, the apparent activation energy of the $\text{AuNi}_{0.5}/\text{SiO}_2$ catalyst was not given because of its poor stability.

Fig. 10. XRD results of the $\text{CuNi}_{0.125}/\text{SiO}_2$ (a), $\text{AgNi}_{0.5}/\text{SiO}_2$ (b) and $\text{AuNi}_{0.5}/\text{SiO}_2$ (c) catalysts after the stability tests for 24 h.

Fig. 11. Arrhenius plots for acetylene conversion over the $\text{AgNi}_{0.5}/\text{SiO}_2$ (a, b) and $\text{CuNi}_{0.125}/\text{SiO}_2$ (c, d) catalysts at low (a, c) and high (b, d) temperature ranges.

In the low temperature range from 100 to 180 °C (Fig. 11), the apparent activation energy of the $\text{CuNi}_{0.125}/\text{SiO}_2$ and $\text{AgNi}_{0.5}/\text{SiO}_2$ catalysts was close to each other with the value of 54.5 and 52.8 kJ/mol, respectively. This result indicated that these two catalysts exhibited similar catalytic mechanisms or similar active sites in the low temperature range. In the high temperature range from 180 to 300 °C, the apparent activation energy of the $\text{CuNi}_{0.125}/\text{SiO}_2$ catalyst was 21.9 kJ/mol, which was obviously lower than that in the low temperature range. This result indicated that the reactants might be much easier to be activated over the $\text{CuNi}_{0.125}/\text{SiO}_2$ catalyst at high temperatures. As for the $\text{AgNi}_{0.5}/\text{SiO}_2$ catalyst, its apparent activation energy became negative at temperatures higher than 180 °C. We speculated that metallic Ag might be segregated on the surface of metallic Ni caused by much lower surface energy of Ag than Ni [36,37] at high temperatures, which led to the change of structure of the active sites and reaction mechanisms. Further study is still needed to make it clear.

To further study the origin of the activity over the

IB-Ni/ SiO_2 catalysts, microcalorimetric measurements of acetylene were undertaken over the Ni/SiO_2 , $\text{CuNi}_{0.125}/\text{SiO}_2$, $\text{AgNi}_{0.5}/\text{SiO}_2$ and $\text{AuNi}_{0.5}/\text{SiO}_2$ catalysts. Microcalorimetry can provide important information on both of the number of active sites and the adsorption strength for probe molecule as a function of the coverage on the surface of the samples. The initial adsorption heats of acetylene over the $\text{CuNi}_{0.125}/\text{SiO}_2$, $\text{AgNi}_{0.5}/\text{SiO}_2$, $\text{AuNi}_{0.5}/\text{SiO}_2$ and $\text{Ni}_{0.5}/\text{SiO}_2$ catalysts were 187, 196, 304, and 103 kJ/mol, respectively (Fig. 12A); that was, their initial acetylene adsorption strength followed the order: $\text{AuNi}_{0.5}/\text{SiO}_2 > \text{AgNi}_{0.5}/\text{SiO}_2 > \text{CuNi}_{0.125}/\text{SiO}_2 > \text{Ni}_{0.5}/\text{SiO}_2$. The surface coverage of acetylene on these catalysts also followed the same sequence. These observations demonstrated that acetylene adsorption over the Ni/SiO_2 catalysts was strongly enhanced by the interaction between Ni and the IB metals. This result was in accordance with the TPR and *in situ* CO-DRIFT results [16,17]. The effect of Au on Ni/SiO_2 was the most significant, and Cu followed. This result could well decipher their catalytic activity at low temperatures (Fig. 7A).

4. Conclusions

The effect of IB metals on the Ni catalyst in the selective hydrogenation of acetylene was systematically studied under the same reaction conditions. The addition of the IB metals greatly enhanced the catalytic activity of the Ni/SiO_2 catalyst. The TPR and *in situ* CO-DRIFT results demonstrated that there was interaction between the IB metals and Ni, which might contribute to the improvement of the catalytic performance. The microcalorimetric measurements of acetylene unveiled that the addition of IB metals significantly enhanced the acetylene adsorption on the Ni-based catalysts. The initial adsorption energy followed the same order as the reaction activity of the three catalysts: $\text{AuNi}_{0.5}/\text{SiO}_2 > \text{AgNi}_{0.5}/\text{SiO}_2 > \text{CuNi}_{0.125}/\text{SiO}_2$. Finally, it was demonstrated that the deactivation of the catalysts was mainly caused by coke formation rather than the change of the nanoparticle size, evidenced by the results of TGA and XRD. This work may provide a new perspective for further design of the Ni-based catalysts for hydrogenation reactions.

Fig. 12. Differential heat of adsorption (A) and surface coverage (B) of acetylene over the $\text{CuNi}_{0.125}/\text{SiO}_2$ (a), $\text{AgNi}_{0.5}/\text{SiO}_2$ (b), $\text{AuNi}_{0.5}/\text{SiO}_2$ (c) and Ni/SiO_2 (d) catalysts.

Graphical Abstract

Chin. J. Catal., 2020, 41: 1099–1108 doi: 10.1016/S1872-2067(20)63568-9

Effect of IB-metal on Ni/SiO₂ catalyst for selective hydrogenation of acetylene

Hua Liu, Mengqian Chai, Guang Xian Pei, Xiao Yan Liu*, Lin Li, Leilei Kang, Aiqin Wang, Tao Zhang *

Dalian Institute of Chemical Physics, Chinese Academy of Sciences; University of Chinese Academy of Sciences

The IB-Ni bimetallic catalysts exhibited much higher activity than the monometallic Ni/SiO₂, which could be contributed to the different adsorption energy of C₂H₂ on the surfaces of the catalysts.

References

- [1] W. T. McGown, C. Kemball, D. A. Whan, M. S. Scurrall, *J. Chem. Soc., Faraday Trans. 1*, **1977**, 73, 632–647.
- [2] W. Huang, J. R. McCormick, R. F. Lobo, J. G. Chen, *J. Catal.*, **2007**, 246, 40–51.
- [3] A. Borodziński, G. C. Bond, *Catal. Rev. Sci. Eng.*, **2006**, 48, 91–144.
- [4] A. Borodziński, G. C. Bond, *Catal. Rev. Sci. Eng.*, **2008**, 50, 379–469.
- [5] K. Georgios, M. B. Boucher, A. D. Jewell, E. A. Lewis, T. J. Lawton, A. E. Baber, H. L. Tierney, F. S. Maria, E. C. H. Sykes, *Science*, **2012**, 335, 1209–1212.
- [6] A. Marc, K. Kirill, B. Malte, T. Detre, G. Yuri, S. G. Robert, *J. Am. Chem. Soc.*, **2010**, 132, 14745–14747.
- [7] G. X. Pei, X. Y. Liu, A. Wang, A. F. Lee, M. A. Isaacs, L. Li, X. Pan, X. Yang, X. Wang, Z. Tai, K. Wilson, T. Zhang, *ACS Catal.*, **2015**, 5, 3717–3725.
- [8] G. X. Pei, X. Y. Liu, A. Wang, L. Li, Y. Huang, T. Zhang, *New J. Chem.*, **2014**, 38, 2043–2051.
- [9] G. X. Pei, X. Y. Liu, X. Yang, L. Zhang, A. Wang, L. Li, H. Wang, X. Wang, T. Zhang, *ACS Catal.*, **2017**, 7, 1491–1500.
- [10] M. Armbruster, M. Friedrich, M. Heggen, R. Cardoso-Gil, *J. Am. Chem. Soc.*, **2011**, 133, 9112–9118.
- [11] H. Zhou, X. Yang, L. Li, X. Liu, Y. Huang, X. Pan, A. Wang, J. Li, T. Zhang, *ACS Catal.*, **2016**, 6, 1054–1061.
- [12] A. J. McCue, C. J. McRitchie, A. M. Shepherd, J. A. Anderson, *J. Catal.*, **2014**, 319, 127–135.
- [13] W. A. van Barneveld, V. Poncet, *Rec. Trav. Chim.*, **1974**, 93, 243–246.
- [14] G. A. Martin, J. A. Dalmon, *J. Catal.*, **1982**, 75, 233–242.
- [15] A. G. Boudjahem, M. Chettibi, S. Monteverdi, M. M. Bettahar, *J. Nanosci. Nanotechnol.*, **2009**, 9, 3546–3554.
- [16] M. Chai, X. Liu, L. Li, G. Pei, Y. Ren, Y. Su, H. Cheng, A. Wang, T. Zhang, *Chin. J. Catal.*, **2017**, 38, 1338–1346.
- [17] G. X. Pei, X. Y. Liu, A. Wang, Y. Su, L. Li, T. Zhang, *Appl. Catal. A*, **2017**, 545, 90–96.
- [18] Y. Liu, J. Zhao, J. Feng, Y. He, Y. Du, D. Li, *J. Catal.*, **2018**, 359, 251–260.
- [19] S. A. Nikolaev, V. V. Smirnov, A. Y. Vasil'kov, V. L. Podshibikhin, *Kinet. Catal.*, **2010**, 51, 375–379.
- [20] Y. Chai, G. Wu, X. Liu, Y. Ren, W. Dai, C. Wang, Z. Xie, N. Guan, L. Li, *J. Am. Chem. Soc.*, **2019**, 141, 9920–9927.
- [21] F. Studt, F. Abild-Pedersen, T. Bligaard, R. Z. Sørensen, C. H. Christensen, J. K. Nørskov, *Science*, **2008**, 320, 1320–1322.
- [22] F. Studt, F. Abild-Pedersen, T. Bligaard, R. Z. Sørensen, C. H. Christensen, J. K. Nørskov, *Angew. Chem.*, **2008**, 120, 9439–9442.
- [23] B. Blaise, P. R. Javier, *J. Am. Chem. Soc.*, **2010**, 132, 4321–4327.
- [24] B. Yang, R. Burch, C. Hardacre, P. Hu, P. Hughes, *Catal. Sci. Technol.*, **2017**, 7, 1508–1514.
- [25] B. Yang, R. Burch, C. Hardacre, G. Headdock, P. Hu, R. Burch, *ACS Catal.*, **2012**, 2, 1027–1032.
- [26] H. Wei, X. Wei, X. Yang, G. Yin, A. Wang, X. Liu, T. Zhang, *Chin. J. Catal.*, **2015**, 36, 160–167.
- [27] Q. Zheng, M. D. Wales, M. G. Heidlage, M. Rezac, H. Wang, S. H. Bossmann, *J. Catal.*, **2015**, 330, 222–237.
- [28] M. T. Tsay, F. W. Chang, *Appl. Catal. A*, **2000**, 203, 15–22.
- [29] S. D. Robertson, B. D. McNicol, J. H. D. Baas, S. C. Kloet, J. W. Jenkins, *J. Catal.*, **1975**, 37, 424–431.
- [30] P. P. Upare, M.-G. Jeong, Y. K. Hwang, D. H. Kim, Y. D. Kim, D. W. Hwang, *Appl. Catal. A*, **2015**, 491, 127–135.
- [31] C. Fang, S. Kuboon, P. Khemthong, T. Butburee, P. Chakthranont, V. Itthibenchapong, *Int. J. Hydrogen Energy*, **2019**, DOI: /10.1016/j.ijhydene.2019.03.272.
- [32] J. Zelin, S. A. Regenhart, C. I. Meyer, H. A. Duarte, V. Sebastian, A. J. Marchi, *Chem. Eng. Sci.*, **2019**, 206, 315–326.

- [33] R. Arnaldo, R. Giulia, F. Riccardo, F. Alessandro, B. C. Curley, L. D. Lloyd, *J. Chem. Phys.*, **2005**, 122, 277–308. L742–L748.
[34] G. Treglia, B. Legrand, *Phys. Rev. B*, **1987**, 35, 4338–4344. [36] Q. Fu, T. Wagner, *Surf. Sci. Rep.*, **2007**, 62, 431–498.
[35] S. Mukherjee, J. L. Morán-López, *Surf. Sci. Lett.*, **1987**, 188, [37] A. V. Ruban, H. L. Skriver, J. K. Nørskov, *Phys. Rev. B*, **1999**, 59, 15990–16000.

IB金属对Ni/SiO₂催化剂乙炔选择性加氢反应性能的影响

刘 华^{a,b}, 柴梦倩^{a,b}, 裴广贤^{a,b}, 刘晓艳^{a,*}, 李 林^a, 康磊磊^a, 王爱琴^a, 张 涛^{a,b#}

^a中国科学院大连化学物理研究所, 中国科学院航天催化材料重点实验室, 辽宁大连116023

^b中国科学院大学, 北京100049

摘要: 乙烯是合成聚乙烯的原料, 其主要来源是石油裂解气, 其中少量的乙炔杂质会严重毒化生产聚乙烯的催化剂, 因此需要将其去除。对于乙炔选择加氢反应, 传统工业上使用的是Pd基催化剂, 尽管其乙炔转化率很高, 但对乙烯的选择性很低。我们前期的研究发现, IB族金属(Au, Ag和Cu)与Pd形成的合金单原子催化剂可以有效地提高乙烯的选择性。作为与Pd同组的非贵金属, Ni催化剂在多种催化加氢反应中显示出优异活性, 而在乙炔选择加氢反应中, Ni是否能够替代贵金属Pd尚无定论。本文系统地研究了IB金属对Ni/SiO₂催化剂乙炔选择性加氢性能的影响。与Pd/SiO₂催化剂不同, 单金属Ni/SiO₂催化剂在低温下不具有活性。将IB金属添加到Ni/SiO₂催化剂中, 可以显著提高其催化活性以及对乙烯的选择性。其中, AuNi_x/SiO₂和CuNi_x/SiO₂催化剂的催化活性随还原温度升高而提高, 而AgNi_x/SiO₂催化剂对预处理温度不敏感。通过调变IB/Ni原子比和还原温度优化了催化剂的催化性能, 发现优化后的三种催化剂(CuNi_{0.125}/SiO₂、AgNi_{0.5}/SiO₂和AuNi_{0.5}/SiO₂)的活性和选择性随反应温度升高表现出相似的变化趋势。催化稳定性考察结果显示, CuNi_{0.125}/SiO₂催化剂表现出最高选择性和稳定性; 尽管AuNi_{0.5}/SiO₂的初始活性最高, 但是稳定性最低。

采用XRD、TPR和微量吸附量热等表征手段对不同IB金属对Ni基催化剂性质的影响进行了系统考察。以Cu-Ni_x/SiO₂催化剂为例, H₂-TPR测试结果表明, Cu-Ni双金属纳米颗粒的形成使得还原温度低于相应的单金属催化剂, 表明铜和镍之间存在明显的相互作用。此外, 通过TPR获得的CuNi_x/SiO₂催化剂上的氢气消耗量与理论耗氢量相吻合, 表明在还原处理的过程中双金属催化剂中的CuO和NiO可以被完全还原。乙炔的微量吸附量热结果表明, 在CuNi_{0.125}/SiO₂、AgNi_{0.5}/SiO₂、AuNi_{0.5}/SiO₂和Ni_{0.5}/SiO₂催化剂上的初始吸附热分别为187, 196, 304和103 kJ/mol, 即它们的初始乙炔吸附强度顺序为AuNi_{0.5}/SiO₂ > AgNi_{0.5}/SiO₂ > CuNi_{0.125}/SiO₂ > Ni_{0.5}/SiO₂。该结果与三者的初始催化活性顺序一致, 表明IB金属的加入可以增强乙炔在催化剂表面的吸附, 从而提高催化活性。

关键词: 乙炔; 乙烯; 选择加氢; Ni; IB金属

收稿日期: 2019-10-12. 接受日期: 2019-12-09. 出版日期: 2020-07-05.

*通讯联系人. 电话: (0411)84379416; 传真: (0411)84685940; 电子信箱: xyliu2003@dicp.ac.cn

#通讯联系人. 电子信箱: taozhang@dicp.ac.cn

基金来源: 国家重点研发计划(2016YFA0202801); 中国科学院战略性先导科技专项(XDB17020400); 国家自然科学基金(21776271); 中国博士后科学基金(2017M621171).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).