Effect of IB-metal on Ni Catalyst for Selective Hydrogenation of Acetylene

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Abstract: As one of the most important products of the petrochemical industry, ethylene is the main material for synthesis of polyethylene. However, the impurity of little amount of acetylene is poisonous for the catalysts to produce the polyethylene. Similar to monometallic Pd catalyst, non-precious metal Ni catalyst also shows the excellent activity and the poor selectivity for ethylene in selective hydrogenation of acetylene. Herein, effect of IB-metal on the Ni catalyst in selective hydrogenation of acetylene was systematically studied. The results obtained by XAFS, TPR, and *in situ* DRIFT demonstrated there was interaction between the IB-metal and Ni. This interaction may contribute to the improvement of ethylene selectivity.
Keywords: non-precious metal Ni, IB-Ni, interaction.

1. Introduction

Ethylene is mostly produced by the cracking of naphtha. It contains about 1% acetylene impurity, which must be diminished to lower than 5 ppm because a very small amount of acetylene will poison the catalyst used in the process of producing polyethylene [1, 2]. At present, the Pd-based catalysts in the selective hydrogenation of acetylene has been systematically and in-depth studied [3-5], but how to improve their poor selectivity for ethylene caused by the over hydrogenation of acetylene still remains a challenging issue. In addition, as a noble metal, the high cost of Pd also limits its widespread use in industry. Therefore, how to develop low cost catalysts with good catalytic performances becomes research hotspot. Through theoretical calculation, Yang et al.[6] demonstrated that the addition of Au and Ag to Ni improved the selectivity of ethylene, while the addition of Cu had no obviously promotion to the selectivity of ethylene. Pei et al.[7] also demonstrate Ag-Ni catalysts improves ethylene selectivity by experiment. But, so far, the systematic experimental research on the IB-Ni bimetallic catalysts has not reported yet. Here, we systematically compared the IB-Ni bimetallic catalysts for the selective hydrogenation of acetylene to ethylene. This work may provide a new perspective for further understanding the catalytic behavior of Ni-based catalysts for hydrogenation reactions.

2. Experimental

All the IB-metal loading of the IB-Ni bimetallic catalysts was fixed. The loading of Ni was determined by calculation according to the certain Ni/IB atomic ratio.

3. Results and discussion

Firstly, we investigated the effect of reduction temperature on the catalytic performance of the $CuNi_x/SiO_2$ and $AgNi_x/SiO_2$ catalysts (x denoted the Ni/IB atomic ratio). And then, we fixed the optimal reduction temperature and studied the influence of IB/Ni atomic ratio on the catalytic performance. The catalysts with the optimal IB/Ni atomic ratio at the optimal reduction temperatures were picked out. Flowingly, we compared their catalytic performances for the selective hydrogenation of the acetylene. As shown in Figure 1, below 220 ºC, with increasing reaction temperature, the conversion over the three catalysts were increased linearly. But over 220 ℃, the acetylene conversion over the $CuNi/SiO_2$ and $AuNi/SiO_2$ catalysts was close to 100% and kept stable at the reaction temperature ranging from 220 ºC to 300 ºC while the ethylene selectivity was gradually increased. As the reaction temperature rises, acetylene conversion and ethylene selectivity of the $AgNi/SiO_2$ catalyst sharply decreased. From the above results, we speculated that the effect of the IB metal on the catalytic activity of the Ni-based catalysts may be the same at the temperature ranging from 100 to 180 ºC. Their difference mainly occurs in the high reaction temperature zone (> 180 ºC). Our experimental results were somewhat different from the DFT results reported in literatures.[6] To investigate the origin of the differences among them, we investigated the

activation energy, the interaction between the IB-metal and Ni and the nature of the surfaces of the catalysts at the low and high temperature regions, respectively. Besides, the stability and the amount of coking after the duration test were also investigated over the three catalysts.

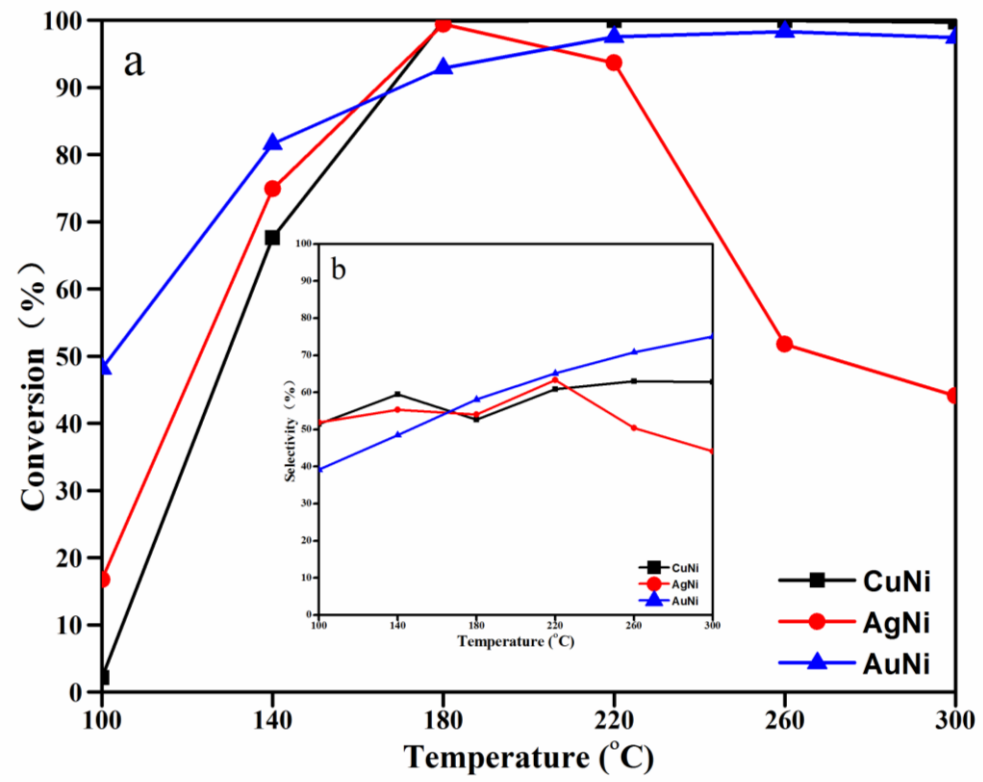

Figure 1. Acetylene conversion (a) and ethylene selectivity (b) of the CuNi /SiO_2, AgNi / SiO_2 and AuNi /SiO_2 catalysts reduced at their optimal temperature.

4. Conclusions

This study systematically studied the effect of the IB metal on the Ni-based catalysts in selective hydrogenation of acetylene. The results may play an important role in the further study of nickel-based catalysts for the selective hydrogenation of acetylene.

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