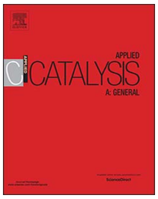
Applied Catalysis A, General 545 (2017) 90–96

Contents lists available at ScienceDirect

Applied Catalysis A, General

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



Research Paper

# Selective hydrogenation of acetylene in an ethylene-rich stream over silica supported Ag-Ni bimetallic catalysts

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## ARTICLE INFO

*Keywords:*
Ni
Ag
Acetylene
Selective hydrogenation
Excess ethylene

## ABSTRACT

Semi-hydrogenation of acetylene in an ethylene-rich stream is an industrially important process. Recent work on the purification of ethylene mainly focuses on the modification of Pd catalysts; little attention has been paid to the development of alternative catalysts with low-cost metals. Herein, a series of Ag-Ni/$SiO_2$ bimetallic catalysts, with varied Ni/Ag atomic ratios, were prepared by wetness co-impregnation method. Their activity for the selective hydrogenation of acetylene in an ethylene-rich stream was evaluated, which showed that the introduction of Ag decreased the formation of both ethane and methane, thus increased the ethylene selectivity. The ethylene selectivity over the $AgNi_{0.25}/SiO_2$ catalyst was increased by > 600% when compared with the corresponding monometallic $Ni_{0.25}/SiO_2$ as well as the simple physical mixture of the monometallic Ag/$SiO_2$ and $Ni_{0.25}/SiO_2$ catalysts. As was verified by a combination of the X-ray diffraction, high angular annular dark field scanning transmission electron microscopy, energy-dispersive X-ray spectroscopy under scanning transmission electron microscopy results, decreased Ni content induced the sintering of the bimetallic nanoparticles while with uniform dispersion. Temperature-programmed reduction results demonstrated that, compared with the corresponding monometallic catalysts, both the reduction of $AgO_x$ and $NiO_x$ were promoted in the Ag-Ni/$SiO_2$ bimetallic catalysts. *In-situ* Fourier-transform infrared spectroscopy results also illustrated obvious interaction between Ag and Ni. The contact between Ag and Ni may account for the enhanced ethylene selectivity.

## 1. Introduction

Ethylene is one of the most important products of the petrochemical industry; it always comes from the pyrolysis of hydrocarbons, such as cracking of naphtha and ethane [1–3]. Among this process, small amount of acetylene is one of the most undesired by-products, which is poisonous to the polymerization catalysts and must be diminished to meet an acceptable level [4–6]. The most preferred method to remove acetylene is selective hydrogenation of acetylene to ethylene, which will be beneficial to lowering the content of acetylene and increasing the amount of ethylene.

Traditionally, Pd-based catalysts are chosen for this process for their high acetylene conversion; however the selectivity to ethylene is low [7–9]. To improve the selectivity to ethylene, another element (Au, Ag, Cu, Ga, Si, Zn, C, S, *etc.*) is always introduced to Pd [10–20]. Group IB metals (Au, Ag, Cu) are among the most widely studied partner of Pd [10–12,20–27], especially for Cu and Ag. For example, Anderson et al. did a lot of work on Cu-Pd bimetallic catalysts for the semi-hydrogenation of acetylene [21–24]. While Ag modified Pd catalysts are widely used under an ethylene rich-stream, and have long been recognized as the preferred choice in industry [1,3,11]. Our previous work also demonstrated that Ag alloyed Pd single-atom catalyst is efficient and durable for the semi-hydrogenation of acetylene in excess ethylene [25]. As the commercially used catalyst, Pd is identified as the active element for this reaction, but it is one of the noble metals with high price. Besides lowering the concentration and making efficient use of Pd atoms, a cost-effective way is to substitute Pd with another low-cost metal to achieve satisfactory catalytic performance.

As another element in the same group of VIII as Pd, nickel showed high activity for a series of hydrogenation reactions due to the relatively low barrier for hydrogen dissociation [28–32]. It has also been identified as an active element for alkyne hydrogenation in industry [29]. Similar to Pd, though with high acetylene conversion, the monometallic Ni catalyst displays poor selectivity to ethylene for the selective hydrogenation of acetylene, the modification of other elements will tune both the activity and selectivity simultaneously [33–35]. For example, by screening a series of less expensive bimetallic compounds, Studt et al. identified that, compared with the

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http://dx.doi.org/10.1016/j.apcata.2017.07.041
Received 21 June 2017; Received in revised form 17 July 2017; Accepted 25 July 2017
Available online 26 July 2017
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monometallic Ni catalyst, NiZn alloy supported on $MgAl_2O_4$ spinel exhibited much higher selectivity to ethylene at low pressures, and the catalytic performance would surpass that of the Ag-Pd system [35]. Pérez-Ramírez et al. did a lot of work on alkyne hydrogenation [36–38], they found that the ternary system (Cu-Ni-Fe) with appropriate metal ratios displayed outstanding ethylene selectivity, while the reaction was under pure acetylene and $H_2$ conditions. Moreover, compared with the Pd-based catalysts, high operating temperatures (523 K, *etc.*) were needed for this process [36]. The DFT results from Yang et al. demonstrated that, compared with pure Ni, the ethylene selectivity was improved through the formation of the bimetallic surfaces of Au/Ni (111) and Ag/Ni(111) [39]. Despite of the above mentioned efforts to seek for the low-cost catalysts, little attention has been paid to the design of novel alternative catalysts for the selective hydrogenation of acetylene in an ethylene-rich stream. Especially for the possibility of the replacement of the commercially recognized Ag-Pd system with Ag-Ni bimetallic catalyst, to the best of our knowledge, till now there are few reports on this catalyst being used in this process.

Herein, aimed at the investigation of the substitution of Ni for Pd and the effect of Ag on the Ni catalyst for the selective hydrogenation of acetylene in an ethylene-rich stream, we prepared a series of silica gel supported Ag-Ni bimetallic catalysts by employing simple incipient wetness co-impregnation method. Their catalytic performance for the selective hydrogenation of acetylene in excess ethylene was investigated. Combined with the characterization results of XRD, HAADF-STEM, STEM-EDS, their geometric structure was analyzed. The interaction between Ag and Ni was further verified by TPR, *in-situ* FT-IR. Thus, the relationship between the catalytic performance and the structure of the catalysts was clarified.

## 2. Experimental

### 2.1. Catalyst preparation

A series of catalysts with different Ni:Ag atomic ratios were prepared by incipient wetness co-impregnation. First, silica gel (Qingdao Ocean Chemical Plant with a Brunauer-Emmett-Teller (BET) surface area of 463 $m^2\ g^{-1}$) was impregnated with a mixture of $Ni(NO_3)_2·6H_2O$ and $AgNO_3$ solutions to obtain a nominal Ag loading of 5 wt% and different Ni:Ag atomic ratios. The samples were subsequently dried at 80 °C for 10 h, followed by calcination in air at 400 °C for 2 h. The as-prepared catalysts are denoted as $AgNi_x/SiO_2$, with x denoting the Ni:Ag atomic ratio. To make a comparison with the corresponding monometallic Ni catalyst, $Ni_{0.25}/SiO_2$ and $Ni_1/SiO_2$ catalysts were prepared by the same method, with the similar Ni contents to the $AgNi_{0.25}/SiO_2$ and $AgNi_1/SiO_2$ catalysts.

### 2.2. Catalyst characterizations

The actual metal loadings of all the as-prepared catalysts were quantified by inductively coupled plasma spectrometry (ICP-AES) on a Thermo IRIS Intrepid II XSP instrument. The results were shown in Table 1.

**Table 1**
Metal loadings determined by inductively coupled plasma spectrometry (ICP-AES).

| Catalysts | Ag:Ni atomic ratios | Actual loading (wt%) | |
|---|---|---|---|
| | | Ag | Ni |
| $Ag/SiO_2$ | – | 4.92 | – |
| $AgNi_1/SiO_2$ | 1 | 4.71 | 2.77 |
| $AgNi_{0.5}/SiO_2$ | 2 | 5.22 | 1.63 |
| $AgNi_{0.25}/SiO_2$ | 4 | 4.90 | 0.81 |
| $AgNi_{0.125}/SiO_2$ | 8 | 4.82 | 0.37 |
| $Ni_{0.25}/SiO_2$ | – | – | 0.66 |

X-ray diffraction (XRD) patterns were obtained on a PW3040/60 X' Pert Pro Super (PANalytical) diffractometer, operating at 40 kV and 40 mA using a Cu Kα radiation source ($\lambda = 0.15432$ nm). The scanning angle (2θ) was from 10° to 80°.

High angular annular dark field scanning transmission electron microscopy (HAADF-STEM) images were obtained on a JEM-2100F instrument equipped with STEM dark-field (DF) detector operating at 200 kV. Elemental distribution of the catalysts was analyzed by energy-dispersive X-ray spectroscopy (EDS) under scanning TEM (STEM) mode. Prior to observation, a small amount of the reduced (at 400 °C) catalysts was ultrasonically dispersed by ethanol, and several drops of the suspension placed on copper microgrid covered with carbon polymer, then dried at room temperature. The particle size distributions of as-prepared catalysts were collected by measuring more than 200 particles from different areas. Elemental distribution analysis was undertaken over relatively large particles.

Temperature-programmed reduction (TPR) experiments were conducted on a Micromeritics AutoChem II 2920 automated characterization system. First, about 100 mg of the calcined sample was loaded into a U-shaped quartz reactor and pretreated with air at 150 °C for 30 min to remove the adsorbed water. After cooling to 50 °C, the flowing gas was switched to 10 vol% $H_2$/Ar, and the catalyst was heated to 500 °C at 10 °C $min^{-1}$.

Fourier-Transform Infrared Spectra (FT-IR) were carried out on a Bruker EQUINOX 55 infrared spectrometer with a DTGS detector. Prior to the CO chemisorption, the as-prepared samples were reduced at 400 °C under flowing 80 vol% $H_2$/He (20 mL $min^{-1}$) for 1 h, followed by evacuation at 400 °C for 0.5 h, then cooled to room temperature. An initial background spectrum was collected before the introduction of CO to the surface of the sample, and subtracted automatically from subsequent spectra. CO adsorption experiments were undertaken sequentially. After introduction of the similar amount of CO and followed by evacuation for 5 min, the spectra were collected.

### 2.3. Activity test

Selective hydrogenation of acetylene in an ethylene-rich stream was carried out in a quartz reactor. Prior to the activity tests, 30 mg of catalysts were reduced under flowing 80 vol% $H_2$/He (20 mL $min^{-1}$) at 400 °C for 1 h followed by purging with He (20 mL $min^{-1}$) at the same temperature. After cooling to room temperature, a gas mixture with 1.0 vol% $C_2H_2$, 20.0 vol% $H_2$ and 20.0 vol% $C_2H_4$ balanced with He was introduced into the reactor. The gas hourly space velocity (GHSV) was 60, 000 $mL_{gas}\ g_{catalyst}^{-1}\ h^{-1}$. With the feed gas purities of $H_2$ (UHP, 99.999%), He (UHP, 99.999%), $C_2H_2$ and $C_2H_4$ (mixture of 4.76 vol.% $C_2H_2$ in $C_2H_4$, with the impurity of about 50 ppm amount of $C_2H_6$ and 10 ppm amount of $CH_4$ from Dalian Special Gases Co., LTD.). Mass flow controllers were used to control all gas flows. The temperature was held constant for 25 min before ramping to the next temperature point. We checked that the conversion/selectivity could reach steady state within 25 min. Both the inlet and outlet gas composition were analyzed by on-line gas chromatography (Agilent Technologies 6890N) equipped with a flame ionization detector (FID).

As $C_2H_4$ and $C_2H_6$ were the only C2 products detected by GC, accompanied by ppm amount of $CH_4$. Negligible oligomers were formed during the hydrogenation process, due to the large excess of hydrogen in the feed gas [22–24] and the short contact time. Thus, based on the inlet and outlet volume concentrations of the feed gas and products, the conversion and selectivity were calculated as follows:

$$C_2H_2\ \text{conversion} = \frac{[C_2H_2]_{in} - [C_2H_2]_{out}}{[C_2H_2]_{in}} \times 100\% \tag{1}$$

$$C_2H_4\ \text{selectivity} = \left(1 - \frac{([CH_4]_{out} - [CH_4]_{in})/2 + [C_2H_6]_{out} - [C_2H_6]_{in}}{[C_2H_2]_{in} - [C_2H_2]_{out}}\right) \times 100\% \tag{2}$$

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