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New palladium catalysts prepared by glow discharge plasma for the selective hydrogenation of acetylene

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Abstract

For the selective hydrogenation of acetylene, the novel Pd/α-Al_2O_3 catalysts prepared by plasma method were investigated. The influence of the preparation method, content of Pd active component, catalyst promoter and reaction temperature has been investigated. It was found that the conversion and selectivity of the catalysts prepared by glow discharge plasma were superior to those obtained from the conventional catalysts. The acetylene conversion of 100% and the selectivity of 71.3% in C_2H_4 were obtained at 50 °C over the plasma-prepared sample (0.15 wt.% Pd), while the plasma-prepared catalyst was stable during the long-time test for more than 20 h.

Keywords: Palladium catalyst; Plasma technique; Acetylene; Selective hydrogenation; Ethylene

1. Introduction

Plasma chemistry is an interesting field spring up from last 20 years, as an effective molecule activation approach. Connecting the plasma technique with catalysis leads to a new application field: preparation and amelioration of catalysts under the non-equilibrium state [1–6]. Vissokov and coworkers [5] prepared the catalyst of ammonia synthesis with higher dispersion at a higher surface area using arc low temperature plasma. Recently, Dalai et al. [6] reported that Fe/Co catalysts prepared had an uniformity via plasma treatment. There are many highly vivacious species in the plasma chamber, i.e., high-energy ions, electrons, activated atoms, and radicals. Ohshima and Yumura [7] tested the catalytic performance of Fe, Ni, Co and Mo ultra-fine catalyst prepared by carbon arc plasma, and discovered that the plasma treatment could enhance the activity of bi-metallic catalyst.

The selective hydrogenation of acetylene to ethylene is an important process used to purify ethylene streams [8–15] containing trace amount of acetylene, for the production of polyethylene. It is desirable that the abundant ethylene component remains intact during the acetylene hydrogenation. Typically, supported palladium catalysts have been employed for this process due to its good activity and selectivity and the convenient desorption property of ethylene on the catalyst surface. The ethylene molecule formed on the surface would be substituted by acetylene molecule in the near gas phase because of the chemisorption strength of acetylene on the catalyst surface was much higher than that of ethylene, which reduced the possibility of further hydrogenation. During long-time investigations, the researchers have found the sequence of catalytic activity is Pd > Pt > Ni; Rh > Co > Fe > Cu/Au in the reaction of selective hydrogenation of acetylene. Alumina supported low Pd content catalyst is widely used [8–15].

The present study was undertaken in an attempt to determine the effect of plasma preparation method on the catalytic performance of palladium catalysts for selective hydrogenation of acetylene.

2. Experimental

The catalysts applied in this work were prepared by the conventional impregnation method and the glow discharge plasma preparation method, for a comparison purpose.

Impregnation method [16–18]. The alpha-alumina was impregnated with a magnesium nitrate aqueous solution, then dried and calcined at 500 °C for 5 h to form a MgO (5 wt.%) modified support. The modified α-Al_2O_3 was impregnated with a proper volume of $PdCl_2$ solution, subsequently dried at 80 °C in water bath and 110 °C in a drying

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Table 1
List and characteristics of catalyst samples by plasma or impregnation

Sample	Pd (wt.%)	Preparation method
Plas-1	0.30	Plasma
Plas-2	0.15	Plasma
Plas-3	0.10	Plasma
Plas-4	0.05	Plasma
Imp-1	0.30	Impregnation
Imp-2	0.15	Impregnation
Imp-3	0.10	Impregnation
Imp-4	0.05	Impregnation

oven, calcined in air at 450 °C for 5 h and then reduced in hydrogen to give supported palladium sample with 0.3, 0.15, 0.10, 0.05 wt.% of palladium. These samples were nominated as the Imp-1, Imp-2, Imp-3 and Imp-4, respectively.

The glow discharge plasma method [1–4,19]. The catalyst support was impregnated at first using the same process as the above. The precursor was put into the discharging tube and decomposed in nitrogen, when its visual color turned to dark brown, the gas feed was switched from N_2 to H_2 for reducing it on maintaining the operation for 40 min. All the processing is under a glow discharge plasma. The plasma generator is of GP06-DL3 type coupled with a high-frequency plasma generator. The discharge parameters are as follows: frequency 13.56 MHz, discharge voltage 100 V, anodic current 100 mA, total time of plasma treatment 85 min and a vacuum between 2 and 200 Pa. The prepared catalysts were nominated as the Plas-1, Plas-2, Plas-3 and Plas-4, respectively, and they were listed in Table 1.

Catalysts were investigated for the selective hydrogenation of acetylene using a continuous quartz micro-reactor with an internal diameter of 4 mm. The schematic diagram of experiment apparatus is shown in Fig. 1. And the feedstock was introduced into the reactor from its top and hydrogenated over the catalyst (200 mg). The feed was $C_2H_2/H_2/N_2 = 1/2/6$ (v/v), total flowing at 110 ml/min. The effluent was analyzed at every half-an-hour using an online gas chromatograph equipped with a flame ionization detector (FID).

Table 2
Reaction results of two catalysts prepared by plasma or impregnation[a]

Sample	Pd content (wt.%)	$X_{C_2H_2}$ (%)		$S_{C_2H_4}$ (%)	
		50 °C	90 °C	50 °C	90 °C
Imp-2	0.15	0.96	20.57	4.22	7.76
Plas-2	0.15	100.00	100.00	71.27	50.08

[a] Reaction conditions: $C_2H_2/H_2/N_2$ (v/v) = 1/2/6; total flow = 110 ml/min.

3. Results and discussion

3.1. Role of plasma method on the catalytic performance

The experimental results indicated that the catalysts prepared by a glow discharge plasma exhibited significant enhancements in the catalytic performances compared with those of catalysts prepared by impregnation. The activity and selectivity over catalysts prepared by plasma exhibit a significant increase, compared with the conventional samples, especially at lower reaction temperature.

Plasma processing is quick, clean and easy to be controlled. Meanwhile, it is worth to point out that especially for the 0.15 wt.% Pd catalyst prepared by plasma, the conversion increased from a value of 0.96–100% and the selectivity was promoted greatly at 50 °C (see Table 2). Besides, on the catalysts prepared by plasma, the oligomers (green oil) formation and coke-forming reactions were suppressed. The results of long-time test were shown in Fig. 2. It was found that this sample kept a high conversion of acetylene for a quite long time (>20 h) after a short induced period.

The surface of supported palladium catalyst was undertaken the actions of high-energy atoms, electrons and ions during the plasma treatment. It resulted in a decreasing of the decomposition temperature and also that of reduction, and then the dispersion of active Pd component could be improved. The enhanced selectivity was related to that the chemisorption of ethylene was much weaker on plasma treated sample, and the adsorbed ethylene could be replaced by acetylene molecule more easily. Thus, the treatment by

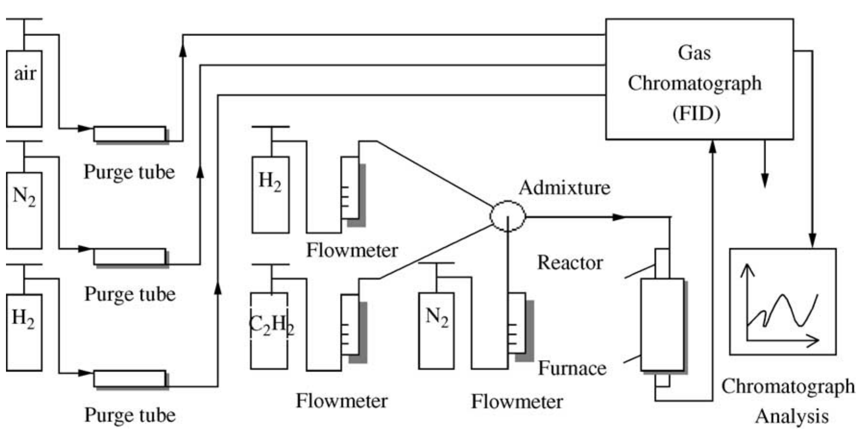

Fig. 1. Schematic diagram of the reaction apparatus for the selective hydrogenation.

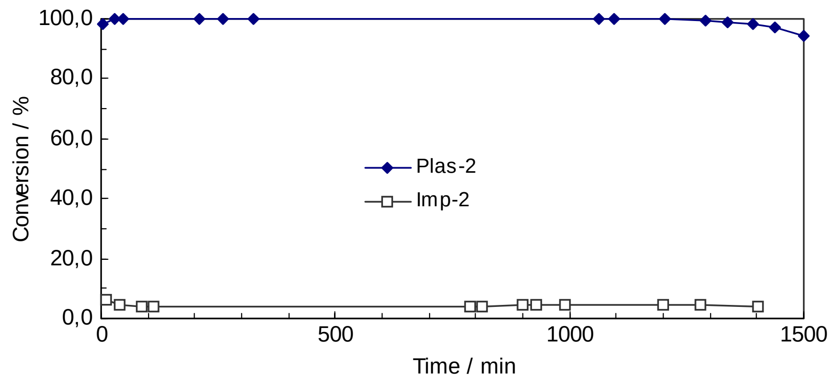

Fig. 2. Conversion versus reaction time on the samples by plasma or impregnation.

the glow discharge plasma, as a new kind of surface modification technique, could change effectively the interaction between metal and support, obtaining new active materials with higher reaction performances [1–3].

3.2. Effect of Pd content

The content of supported active component is a key parameter on the catalytic performance. Activities of these two series of samples behave a similar variation trend with the increasing palladium content. On the conventional low Pd loading samples (Imp-2 to Imp-4), the conversions are close to 3.5% at 70 °C and that of the sample containing 0.3 wt.% palladium is 14.3% at 70 °C. When the temperature increased to 90 °C, the conversions on the above three low loading samples increased to a value from 11 to 20%, respectively; however, it was augmented to 100% for the 0.3 wt.% catalyst (Imp-1). For the performances of catalysts by plasma at 70 °C, the conversion was about 8% on the two less loading palladium catalysts (Plas-3 and Plas-4). For the plasma catalysts containing more Pd, the conversion of 100% have been achieved on Plas-2 and Plas-1 at 70 °C. When the temperature is more than 90 °C, the acetylene conversion could reach 100% for all these four catalysts prepared by plasma. These two series of catalysts prepared by plasma or impregnation were characterized by XRD and TPR. The results indicated that there was a favorable dispersion of active component in the catalyst by plasma. For those catalysts with relatively higher content of palladium, there were more active centers on the catalyst surface which was favorable for the catalytic activity.

3.3. Influence of the reaction temperature

Unlike the variation of conversion, the temperature for an optimum selectivity over the samples is related to the palladium content and the prepared method. In the catalytic activity testing with different catalysts by plasma, the conversion reached a high level (100%) at a temperature beyond 90 °C (shown in Fig. 3), indicating that at a higher temperature, the rate of C_2H_2 activation on the catalytic surface was enhanced significantly. Samples by impregnation with low Pd loading gave a stable selectivity about 10%; a maximal selectivity was achieved over 0.3 wt.% Pd loading sample. When the temperature was risen from 50 to 150 °C, it was at 90 °C that the better selectivity was achieved.

Temperature rising improved the desorption of formed ethylene which would be in favor of higher selectivity, but rising to a higher range (>110 °C), the velocity of deep hydrogenation increased also, even much faster. As a result, the ethylene selectivity decreased again. When the desorption/adsorption properties of ethylene on the catalyst surface was in good correlation with the change of reaction rate, a stable selectivity could be obtained sequentially.

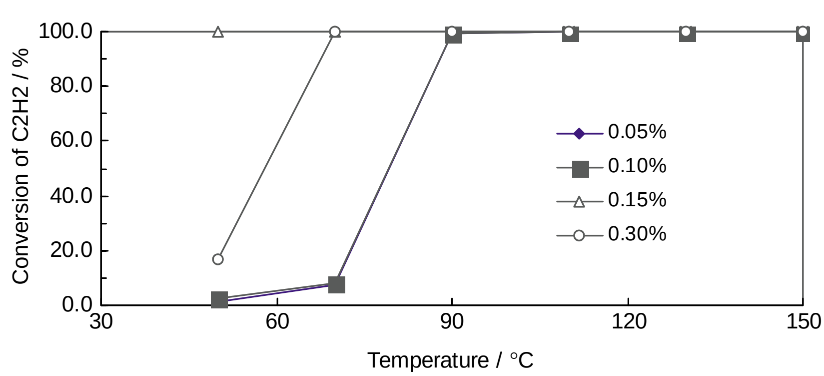

Fig. 3. Acetylene conversion versus reaction temperature on plasma samples.

4. Conclusions

Based on the above experimental results, the catalysts by plasma processing exhibited the obvious advantages in catalytic performance at low temperature (<110 °C), compared to the samples prepared by conventional impregnation. The acetylene conversion of 100% with a selectivity of 71.3% for ethylene were obtained on the palladium catalyst Plsm-2 (0.15 wt.%) prepared by plasma. This selectivity is several times of that for the conventional sample containing the same Pd content. This catalyst was stable during a test for more than 20 h.

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