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# ARTICLE

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# Plant-mediated synthesis of AgPd/γ-Al<sub>2</sub>O<sub>3</sub> catalyst for selective hydrogenation of 1,3-butadiene at low temperature Fenfen Lu<sup>a</sup>, Daohua Sun<sup>\*<sup>b</sup></sup> and Xia Jiang<sup>b</sup> In this dissertation, silver-palladium (AgPd) bimetallic nanoparticles were synthesized by a green biosynthesized method using *Cacumen Platycladi* leaves extract, which provided both the reductive and protective agents. Then the supported AgPd/γ-Al<sub>2</sub>O<sub>3</sub> catalysts were obtained by sol-immobilization method, and the as-biosynthesized AgPd/γ-Al<sub>2</sub>O<sub>3</sub> catalysts with different particle sizes and composition were used for 1 3-butadiene hydrogenation. Ontimization of the catalysts

using *Cacumen Platycladi* leaves extract, which provided both the reductive and protective agents. Then the supported AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were obtained by sol-immobilization method, and the as-biosynthesized AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with different particle sizes and composition were used for 1,3-butadiene hydrogenation. Optimization of the catalysts preparation and selective hydrogenation parameters were tested. With the catalyst, 1,3-butadiene conversion of 98.2%, and butene selectivity of 88.1% were achieved. Durable experiment of AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was carried out for 50 h, the activity decreased slightly and the selectivity almost remains the same during the 50 h, which indicating the remarkable stability. The results of TEM and TG analysis showed that the size of AgPd nanoparticles were nearly the same before and after durable experiment, and the existence of residual biomolecules on the catalysts surface helped to prevent the agglomeration and modify the surface properties of the catalyst, which would promote desorption of the product, then avoid intensifying the level of further hydrogenation.

#### 1 Introduction

Selective hydrogenation is a very important reaction to remove alkynes or alkadienes in the stream for polymer synthesis. Palladium (Pd) catalysts have been demonstrated to be highly efficient for hydrogenation reaction, which has received considerable attention in recent decades, and become one of the important research highlights in the field of catalysis.<sup>1-4</sup> Selective hydrogenation of 1,3-butadiene is not only an important industrial process to purify the alkene streams from petroleum cracking in an excess of alkenes, but also an interesting model-reaction for unsaturated alkene hydrogenation and metal catalyst electronic structure research. Currently, there are still some problems unresolved on 1,3butadiene hydrogenation, for example, there still remains controversy on the active sites, butene further hydrogenation and the catalytic stability.<sup>5,6</sup> Selective hydrogenation of 1,3butadiene is a meaningful and challenging reaction, it is more likely to produce saturated hydrocarbons than butene from a thermodynamic point of view.<sup>7</sup> Therefore, as for 1,3-butadiene selective hydrogenation reaction system, improving the selectivity to butene is the most important factor in the selection

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- Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

of catalyst. Generally, ways to improve the selective hydrogenation include modifying the carrier, adding a second metal and changing the particle size and valence of the active metal.<sup>8,9</sup> The effect of the addition of the second metal on palladium is not yet clear, researchers generally believe that the second metal modifies the surface structure and electronic properties of Pd, improves the adsorption, diffusion and permeation of hydrogen on catalysts, changes the hydrogen species on the surface of the catalysts, and also reduces the adsorption abilities of butene, which leading to increase the selectivity of the catalyst to the single olefins.<sup>7,10</sup> Bimetallic Pb-Pd, Cr-Pd, Sn-Pd, Cu-Pd, Ag-Pd, Ni-Pd catalysts were proved to have better catalytic performance than single metal Pd catalysts.<sup>5,11</sup> Goetz et al. found that PdPb/Al<sub>2</sub>O<sub>3</sub> catalyst could maintain higher butene selectivity even when the conversion of 1,3-butadiene was high then monometallic Pd/Al<sub>2</sub>O<sub>3</sub>, which attributed to the decrease of the surface hydrogen coverage that originated from electronic interactions between the bimetallic.<sup>12</sup> Pattamakomsan et al. compared the hydrogenation performance of Pd/Al<sub>2</sub>O<sub>3</sub> and PdSn/Al<sub>2</sub>O<sub>3</sub> catalysts for 1,3-butadiene hydrogenation, and found that monometallic Pd catalysts could produce deep hydrogenation and the products of butene were easy to be isomerized. And the bimetallic catalysts could avoid the formation of butane and the proportion of 1-butene is also relatively high, by the reason that the change of the structure and electronic properties between metals.<sup>13</sup> CuPd bimetallic catalysts supported on graphite were prepared by Cooper et al. The addition of copper increased the selectivity of butene and reduced the carbon deposition of the catalysts, thus reducing the deactivation rate of the catalysts. They believed that the electronic and geometric effects between Cu and Pd improved

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#### ARTICLE

the active surface and surface hydrogen species of Pd catalysts.<sup>14</sup>

The method by using natural plants to synthesize nanomaterials is a new and eco-friendly technique.<sup>15-19</sup> In recent years, our research group have successfully combine the bioreduction technology of metal nanoparticles with preparation of supported metal catalysts, and realized that the preparation and loading of metal nanoparticles under mild conditions.<sup>20-22</sup> In this work, the selectivity of butene in 1,3butadiene hydrogenation reaction was enhanced by adding a second active metal silver (Ag). And the bimetallic AgPd/y-Al<sub>2</sub>O<sub>3</sub> was obtained by the sol-immobilization method, with the mediating of plant extract of Cacumen platycladi leaves. The structure of the AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was characterized by the analysis of X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), transmission electron microscopy (TEM), CO chemisorption measurement techniques, thermogravimetry (TG), atomic absorption spectroscopy (AAS) and Fourier transform infrared spectroscopy (FTIR). Besides, the influences of various catalyst parameters and catalytic reaction conditions on the bimetallic catalytic performance were investigated.

#### **2** Experimental Sections

#### 2.1 Materials

Silver nitrate (Ag(NO)<sub>3</sub>) was purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Palladium nitrate (Pd(NO<sub>3</sub>)<sub>2</sub>) was purchased from Aladdin Reagent Co., Ltd. (China). Aluminium oxide ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) was supplied by Cener Tech Tianjin Chemical Research and Design Institute Co., Ltd. The sundried *Cacumen platycladi* leaves in the previous study<sup>17</sup> were used in this work.

#### 2.2 Catalyst preparation

1.0 g of the milled *Cacumen platycladi* leaves powder was dispersed into 100 mL deionized water with a 250 mL conical flask, and then kept in a water bath shaker at 30 °C and 150 rpm for 2 h. Then, the aqueous mixture was filtered to remove the residual insoluble biomass and obtain the extract, and the achieved extract was stored in the refrigerator for later use.

First, a certain ratio of Pd(NO<sub>3</sub>)<sub>2</sub>(75.08 mM) and AgNO<sub>3</sub>(58.87 mM) solutions were added into 100 mL conical flask, then deionized water were added to keep the total volume 10 mL. The mixture was then placed in an oil-bath with constant stirring rate. When the temperature reach the specified value, 10 mL of the Cacumen platycladi leaves extract was added. After 1 h constant stirring, AgPd colloid was achieved, then the pH value of as-synthesized AgPd colloid was acidified at 2 with nitric acid, and then certain amount of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support (to keep the metal concentration 0.5 wt%) was added to the AgPd colloid with vigorous stirring. After another 1 h, the suspension was filtered using a cellulose filter membrane of pore size 0.8 mm, and the retained solid was washed totally with deionized water, and then dried at 50  $\,$   $^{\circ}$ C in a vacuum oven for 12 h, and the corresponding catalyst was labelled as  $AgPd/\gamma - Al_2O_3$ .

#### 2.3 Catalyst characterization

The dried as-synthesized  $AgPd/\gamma$ - $Al_2O_3$  catalysts were analysed by XRD using an X-ray diffractometer3 (Idlinina 787) Rigaku) with Cu Ka radiation (40 kV, 30 mA). TEM characterization was performed on an electron microscope (Tecnai F30, Netherlands) with an accelerating voltage of 300 kV. The sizes of the AgPd nanoparticles were obtained based on the statistical average from TEM images. XPS characterization was obtained to determine the valence state on a PHI-Quantum 2000 spectrometer (Physical Electronics, America), the powder samples were characterized by X-ray equipped with a hemispherical electron analyzer and a Al K $\alpha$ (1486.6 eV) X-ray source. The binding energy was calibrated by C 1s as the reference energy (C 1s = 284.6 eV). The actual metal loadings of the samples were determined by AAS (GFA-6880, Japan). TG studies were carried out on a SDT Q600 (NETZSCH, Germany) thermo balance under flowing air atmosphere at a heating rate of 10 °C/min. The in-situ FTIR experiments were performed using a home-built in-situ IR cell with quartz lining and CaF<sub>2</sub> windows in a FTIR spectrometer (N6700, Nicolet) using an MCT/A detector. Prior to the adsorption experiment, the samples were dried and pretreated in situ at 35 °C in a vacuum for 1 h. The spectra prior to the

adsorption experiment were used as background.

#### 2.4 Catalyst testing

The measurements of prepared catalysts were tested in the hydrogenation of 1,3-butadiene reaction, which carried out at 35 °C in a fixed-bed flow stainless reactor (i.d. Six mm) under atmospheric pressure. The reaction system consists of a glass tube covered Cr-Al thermocouple located in the center of the catalyst bed to measure the reaction temperature. In a typical experiment under gas-phase conditions, the sample (50 mg) was placed into the reaction tube. A mixture of gases based on 1,3-butadiene (2.15%),  $H_2$  (4.30%), and  $N_2$  (balance gas), previously prepared in a gas cylinder, was injected into the reactor, and the feed flow rate was adjusted to 13.5 mL/min with mass flow meter (Sevenstar Electronics). The performance of catalysts were monitored on line using a gas chromotograph (GC) coupled with an Al<sub>2</sub>O<sub>3</sub> column and an FID detector, and the product stream was sampled every 20 min and analysed. Conversions of 1,3-butadiene and selectivity of butene were obtained from the GC areas corresponding to the reactant (1,3butadiene), main products (1-butene, cis-2-butene and trans-2butene) and by product (butane).

#### 3 Results and Discussion

#### 3.1 Characterization of catalysts

#### 3.1.1 Transmission electron microscopy (TEM) studies

The monometallic and bimetallic catalysts prepared by immobilization of the as-prepared nanoparticles with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support were examined by TEM, which were performed to examine the particle mean size and the size distribution of catalysts. As shown in Fig. 1, it is obvious that the assynthesized nanoparticles were close to spherical particle. The correlations between the particles mean size and the Pd molar fraction is shown in Fig. 1F, clearly, the size of particles became larger with increasing Pd molar ratio. Under the same

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59 60 ARTICLE

Journal Name



Fig. 1 TEM images and size histograms (inlet) of biosynthesized monometallic and bimetallic catalysts: (A)  $Ag/\gamma - Al_2O_3$ , (B)  $Ag_3Pd_1/\gamma - Al_2O_3$ , (C)  $Ag_1Pd_1/\gamma - Al_2O_3$ , (D)  $Ag_1Pd_3/\gamma - Al_2O_3$ , (E)  $Pd/\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (F) particle mean size versus Pd molar fraction.

synthesizing condition, the bimetallic nanoparticle size (10.5±1.4 nm, 8.5±0.8 nm, 7.6±0.8 nm) were all in between the monometallic particle size of Ag (21.1±3.8 nm) and Pd (6.9±0.6 nm), which suggesting that the molar ratio of bimetallic has obvious influence on the particle size, and the size of bimetallic nanoparticles decrease with increasing Pd ratio.

#### 3.1.2 X-ray diffraction (XRD) studies

Fig. 2 shows the powder XRD patterns of the AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with different initial Ag/Pd ratios (3:1, 1:1, 1:3), Ag/y-Al<sub>2</sub>O<sub>3</sub> and Pd/y-Al<sub>2</sub>O<sub>3</sub> catalysts. The characteristic peak of Ag catalyst at 20 position 38.1° pertains to (111) plane (ref. code: 04-0783), which was covered up by the diffraction of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (19.3°, 37.5°, 39.3°, 45.7°, 60.5°, 66.6°, ref. code: 50-0741), and the specific absorbing peak of Pd catalyst at 40.1° corresponds to (111) plane (ref. code: 46-1043). Clearly, the metal diffraction peaks of bimetallic catalysts all around 39.5° located between 38.1°(Ag(111))and 40.1°(Pd(111)) is assigned to the obvious alloying structure with fcc crystal form,<sup>18,23</sup> and the intensity increased with the increasing Pd fraction. Since  $\gamma\text{-}Al_2O_3$  has many obvious characteristic absorption peaks, no other peaks were found among the range of  $2\theta$  from 30 to  $90^{\circ}$ .



Fig. 2 XRD patterns of Ag/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts pretreated with different Ag/Pd molar ratio: (a)  $\gamma$ - $AI_2O_3$ , (b)  $Ag/\gamma - AI_2O_3$ , (c)  $Ag_3Pd_1/\gamma - AI_2O_3$ , (d)  $Ag_1Pd_1/\gamma - AI_2O_3$ , (e)  $Ag_1Pd_3/\gamma$ - $Al_2O_3$ , (f)  $Pd/\gamma$ - $Al_2O_3$ .

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# 3.1.3 X-ray photoelectron spectroscopy (XPS) studies Article Online

XPS elemental analysis was used to quantify other ward to analysis was used to quantify other ward to analysis was used to quantify other ward to be a set of the set surface chemical composition and the chemical state of supported catalysts.<sup>24-26</sup> Fig. 3 and Table 1 show the X-ray photoelectron spectroscopic patterns and binding energy of Ag and Pd elements in monometallic and bimetallic catalysts with different initial metal molar ratios. It is obviously that, Ag was in metallic state in these catalysts, while Pd was in the presence of metallic state and oxidation state.<sup>23,27</sup> The coexistence of a small amount of the oxidation state of Pd was beneficial for 1,3-butadiene hydrogenation.<sup>17</sup> In the case of strong interaction between metal nanoparticles and metal oxide support, their Fermi energy levels are compromised to a new value. As a result, immobilization led to lower the core-level binding energy of Ag, Pd and AgPd bimetallic, which also become a proof of the interaction between oxide support and supported metal.

Moreover, the positions of the AgPd bimetallic metal peaks are close to those of the monometallic Ag and Pd peaks. The metal peaks of AgPd bimetallic samples has revealed a tiny negative binding energy shift of Ag 3d core level binding energy in AgPd samples as compared to monometallic Ag sample, as shown in Fig. 3, Which has been previously reported in AgPd alloys both experimentally and theoretically.<sup>28-30</sup> While the binding energy of Pd 3d electrons was positively shifted for AgPd samples as compared to that for monometallic Pd sample, this positive shift may be caused by the partial electron transfer from Ag to Pd atoms.<sup>31</sup> The shifts of core level binding energy for Ag and Pd elements consistent with the former reports.<sup>31,32</sup>

3.1.4 Fourier Transform Infrared Spectroscopy (FTIR) studies To explicit the metal active sites, we focused on in-situ FTIR study of CO adsorption on the supported catalysts. Fig. 4 shows in situ FTIR spectra of CO absorbed on the Ag/y-Al2O3, Pd/y- $Al_2O_3$  and  $AgPd/\gamma$ - $Al_2O_3$  catalysts prepared with different Ag/Pd molar ratio. According to previous reports, 13,33 the linear CO species can be observed at around 2100 cm<sup>-1</sup>, and IR band



Fig. 3 XPS patterns of Ag and Pd elements in Ag/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Pd/ $\gamma$ - $Al_2O_3$  and  $AgPd/\gamma$ - $Al_2O_3$  catalysts: (A) Ag 3d regions of  $Ag/\gamma$ - $Al_2O_3$ , (B) Pd 3d regions of Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (C) Ag 3d regions of AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (D) Pd 3d regions of AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

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#### ARTICLE

Table 1 XPS peak positions of Ag and Pd elements in Ag/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.  $Pd/\gamma$ -Al<sub>2</sub>O<sub>3</sub> and AgPd/\gamma-Al<sub>2</sub>O<sub>3</sub> catalysts.

| AgNO <sub>3</sub> /Pd(NO <sub>3</sub> ) <sub>2</sub><br>(mol/mol) | Biding energy (eV) |                   |                   |                   |  |
|---|--------------------|-------------------|-------------------|-------------------|--|
|   | Ag                 |                   | Pd                |                   |  |
|   | 3d <sub>5/2</sub>  | 3d <sub>3/2</sub> | 3d <sub>5/2</sub> | 3d <sub>3/2</sub> |  |
| 1:0   | 367.6              | 373.6             |                   |                   |  |
| 3:1   | 367.4              | 373.4             | 335.6             | 340.8             |  |
| 1:1   | 367.2              | 373.2             | 335.6             | 340.7             |  |
| 1:3   | 367.0              | 373.0             | 335.5             | 340.7             |  |
| 0:1   |                    |                   | 335.4             | 340.6             |  |



Fig. 4 In situ FTIR spectra of CO absorbed on the Ag/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,  $Pd/\gamma$ -Al<sub>2</sub>O<sub>3</sub> and AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts prepared with different Ag/Pd molar ratio: (a)  $Ag/\gamma-Al_2O_3$ , (b)  $Ag_3Pd_1/\gamma-Al_2O_3$ , (c)  $Ag_1Pd_1/\gamma - Al_2O_3$ , (d)  $Ag_1Pd_3/\gamma - Al_2O_3$ , (e)  $Pd/\gamma - Al_2O_3$ .

below 2000 cm<sup>-1</sup> are ascribed to the bridge CO species consisting of isolated bridged species, compressed bridged species and three-metal bridged species. The result reveals that the bridge bonded species dominate for catalysts with increasing Pd content. The peaks intensity of the bimetallic catalyst decreased with increasing Ag content, this is probably the consequence of some Ag dilution affect associated with the formation of AgPd alloy.

#### 3.2 Catalyst activity studies

#### 3.2.1 Effect of the Ag/Pd molar ratio

According to the early reports, <sup>34, 35</sup> the relative proportion of the bimetallic metals is important for the performance of the catalysts, since the composition of bimetallic metals affects their surface composition and exhibits different catalytic properties. Thus, AgPd/y-Al2O3 bimetallic catalysts with different initial Ag/Pd ratios and monometallic catalysts (Ag/y- $Al_2O_3$  and  $Pd/\gamma$ - $Al_2O_3$ ) with 0.75% loading were tested, respectively. The best 1,3-butadiene hydrogenation performance was obtained with the initial Ag/Pd ratio of 1:3 (Fig. 5), the conversion of 1,3-butadiene was up to 100% and the butene selectivity was 68.1%. However, the catalysts with the initial Ag/Pd ratio of 3:1 and 1:1 showed low activity, and  $Ag/\gamma - Al_2O_3$  was hardly active for this reaction. As for catalyst Pd/y-Al<sub>2</sub>O<sub>3</sub>, the activity was up to 100%, but the butene selectivity was only 32.3%. Clearly, the addition of Ag dilutes Pd active sites, which supress the further hydrogenation to some degree, and leading to better catalytic activity.



Fig. 5 Catalytic performance of monometallic catalysts (Ag/ $\gamma$ - $Al_2O_3$ ,  $Pd/\gamma$ - $Al_2O_3$ ) and bimetallic catalysts (AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) with different initial Ag/Pd ratios.

### 3.2.2 Effect of Cacumen platycladi concentration

Adjusting the reactant concentration was an effective way to regulate the reaction rate, and then accordingly control the size of as-synthesized nanoparticles. Therefore, a series of catalysts prepared with different concentration of Cacumen platycladi were studied (Fig. 6). It is obvious that the conversion of 1,3butadiene firstly increases and then decreases with increasing Cacumen platycladi concentration, clearly, 5.0 g/L was the best concentration for the catalyst performance. It was observed from TEM analysis (Fig. 7) result that nanoparticle size was inversely proportional to the concentration of Cacumen platycladi, since lower concentration (eg. 1.25 g/L and 2.5 g/L) was insufficient to fully reduce the metal ions, when the concentration gradually increase to 7.5 g/L and 10 g/L, there were too much biomolecule residues on the catalysts, which may cover the active sites and lead to the lower catalytic activity. Thus, the concentration of 5.0 g/L achieved the best catalytic performance.

#### 3.2.3 Effect of preparation temperature

The influence of preparation temperature on the performance of 1,3-butadiene hydrogenation was studied and shown in Fig. 8. The conversion of 1,3-butadiene increased with increasing of preparation temperature, when the temperature increased to 90°C, the conversion was 100%, while the butene selectivity decreased slightly to 84.9%. Since the higher preparation temperature could get higher reduction rate of metal precursor, accordingly the yield of bimetallic nanoparticles and the active site increased, which lead to the higher catalytic performance.





 Journal Name



Fig. 7 TEM images and size histograms (inlet) of biosynthesized AgPd nanoparticles under different *Cacumen platycladi* concentration: (A) 2.5 g/L, (B) 5.0g/L, (C) 7.5g/L, (D) 10g/L.



Fig. 8 1,3-butadiene hydrogenation over AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with different preparing temperature.

Therefore, the 1,3-butadiene conversion and butene selectivity both take into account, higher preparation temperature is benefit for 1,3-butadiene hydrogenation.

#### 3.2.4 Effect of calcination temperature

The influence of calcination temperature on the catalytic performance was studied and showed in Fig. 9. It can be seen from the diagram that when the calcination temperature was under 250 °C, the catalytic activity remained almost unchanged, and the butene selectivity gradually decreased with the increasing calcination temperature; when the calcination temperature continues to increase to 275 °C, the catalytic activity decreased sharply and remained only about 2%. When the calcination temperature further increased to 300 °C, the catalyst hardly shows activity.

Herein, to figure out the possible reasons for the influence of calcination temperature, TEM and XRD analysis has been studied. Fig. 10 shows the TEM diagram of bimetallic catalysts with different calcination temperatures and the corresponding particle size distribution diagram. It is obviously that when calcination temperature was less than or equal to 250 °C, the particle size of nanoparticles was basically unchanged, and the dispersion of nanoparticles shows good. When the calcination temperature continues to rise to 275 °C and 300 °C, the diameter of the nanoparticles was relatively poor. Thus, bimetallic particle agglomeration in higher calcination temperature resulted in the deactivation of catalysts; Fig. 11 was the XRD diagram of bimetallic catalysts with different







Fig. 10 TEM images and size histograms (inlet) of AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with different calcination temperature: (A) Ag<sub>1</sub>Pd<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (B) 100-Ag<sub>1</sub>Pd<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (C) 200-Ag<sub>1</sub>Pd<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (D) 225-Ag<sub>1</sub>Pd<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (E) 250-Ag<sub>1</sub>Pd<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (F) 275-Ag<sub>1</sub>Pd<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (G) 300-Ag<sub>1</sub>Pd<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.



Fig. 11 XRD patterns of AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with different calcination temperature: (a) Ag<sub>1</sub>Pd<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (b) 100-Ag<sub>1</sub>Pd<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (c) 200-Ag<sub>1</sub>Pd<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (d) 225-Ag<sub>1</sub>Pd<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (e) 250-Ag<sub>1</sub>Pd<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (f) 275-Ag<sub>1</sub>Pd<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (g) 300-Ag<sub>1</sub>Pd<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Journal Name

#### ARTICLE

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#### 3.2.5 Effect of metal loading

The dosage of AgPd bimetallic catalyst is an important factor for its catalytic performance. The AAS analysis was carried by measuring the total amount of metals in the catalyst filtrate, and then the actual loading of bimetallic catalysts was calculated. Table 2 showed that the actual loading and theoretical loading of bimetallic catalysts were similar when the catalyst dosage increased from 0.2% to 1.0%.

The effect of metal loading on the performance of selective hydrogenation of 1,3-butadiene was shown in Fig. 12. Clearly, the best performance of catalysts were achieved at loading of 0.4%, namely, 1,3-butadiene conversion of 98.2%, and butene selectivity of 88.1% were obtained. Furthermore, it can be seen from the diagram that the hydrogenation selectivity decreases gradually with the increase of metal loading, while the conversion of 1,3-butadiene reached 100% at loading of 0.5%, and remains unchanged at 100% thereafter. Comparing the XRD spectra of AgPd bimetallic catalysts with different loadings (Fig. 13), the diffraction peaks of catalysts were not obvious when the loadings was less than 0.5%, indicating that the bimetallic nanoparticles are uniformly distributed on the surface of the support. With increasing of metal loading, the characteristic peak intensity of (111) crystal face (39.6°) of AgPd bimetallic nanoparticles increased gradually. At lower metal loading, the catalyst usually showed lower activity since the insufficient number of metal active sites; while the catalyst with higher metal loading has more active sites, it was easy to make the catalyst further hydrogenation, which leads to the decrease of selectivity of butene.



Fig.12 1,3-butadiene hydrogenation over  $AgPd/\gamma-Al_2O_3$  catalysts at different metal loading.

Table 2 Determination of actual AgPd loading on AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.

| Samples  | Actual AgPd loading (%) |  |  |
|--|-------------------------|--|--|
| $0.2\%$ AgPd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> | 0.20                    |  |  |
| $0.4\%$ AgPd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> | 0.40                    |  |  |
| $0.5\%$ AgPd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> | 0.50                    |  |  |
| 0.6% AgPd/y-Al <sub>2</sub> O <sub>3</sub>             | 0.59                    |  |  |
| $1.0\%$ AgPd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> | 0.99                    |  |  |



Fig. 13 XRD patterns of AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with different AgPd loadings: (a)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (b) 0.2%Ag<sub>1</sub>Pd<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (c) 0.4%Ag<sub>1</sub>Pd<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (d) 0.5%Ag<sub>1</sub>Pd<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (e) 0.6%Ag<sub>1</sub>Pd<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (f) 1.0%Ag<sub>1</sub>Pd<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

#### 3.6 Durability of the catalysts

Whether the catalyst can run stably for a long time is one of the most important factors to be considered in industrial production. In many cases, the biggest obstacle to popularize the high-efficiency catalyst studied experimentally to actual production is the stability problem, clearly, the stability testing and research is very necessary. In this section, the stability of AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst prepared by plant reduction method with 0.4% metal loading was investigated. As shown in Fig. 14, the conversion of 1,3-butadiene stayed close to 100% for the first 12 h, then decrease slightly to 96% for another 24 h, and slowly decreased to 90% at 50 h. But the butene selectivity remains basically unchanged for 50 h.

From the TEM diagram of the catalyst before and after the stability testing (Fig. 15), the particle size of nanoparticles on



Fig. 14 1,3-butadiene hydrogenation over  $AgPd/\gamma$ - $Al_2O_3$  catalyst as a function of time-on-stream.



Fig. 15 TEM images and size histograms (inlet) of  $AgPd/\gamma$ - $Al_2O_3$  catalyst: (A) before testing, (B) after testing.

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the surface of the catalyst remained almost unchanged, indicating that the active center of the catalyst does not change during the durability test. Also, from XPS (Fig. 16) and XRD (Fig. 17) analysis of the AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst before and after testing, the results showed that the metallic state basically considered maintaining invariable, thus this may responsible for the good catalytic stability. From the TG diagram of Fig. 18, it is obviously the quality of the catalyst decreased with increasing temperature. A weightlessness peak appeared around 100 °C for all samples, which was caused by the presence of a small amount of free water desorption. The apparent mass loss peaks near 300 °C indicated that the residual biomass molecules are mainly decomposed by combustion at this temperature. Meanwhile, TG analysis showed that the residual biomass of Cacumen platycladi leaves on AgPd/y-Al<sub>2</sub>O<sub>3</sub> catalyst was approximately 3.6%. We assume that the 3.6% residual biomass molecules have a positive impact on promoting the catalytic reaction and maintaining the stability of the catalyst. On the one hand, the residual plant biomass molecules on the catalyst surface protect nanoparticles from agglomeration and growth during the catalytic reaction. Besides, the residual plant biomass molecules play a role in modifying the catalyst, which is more conducive to the timely desorption of butene from the catalyst surface, thereby reducing the probability of deep hydrogenation of butene. Furthermore, taking the metal loading and turnover frequency into consideration, Table 3 lists the rough comparison of catalytic performance in selective hydrogenation of 1,3-butadiene. Among the catalysts, the turnover frequency of AgPd/y-Al2O3 is relatively high, while the metal loading and testing temperature are low. Hence, the 88.1% butenes selectivity and 98.2% 1,3-butadiene conversion were obtained at relatively low temperature and metal loading.



Fig. 16 XPS patterns of Ag and Pd elements in of AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst: (A) Ag 3d regions of AgPd/y-Al2O3, (B) Pd 3d regions of  $AgPd/\gamma - Al_2O_3$ .

Table 3 A rough comparison of catalytic performance in hydrogenation of 1,3-butadiene.

| Catalyst                              | loading | Reaction  | Con. | TOF <sup>a</sup> | Ref  |
|---------------------------------------|---------|-----------|------|------------------|------|
|                                       | (wt.%)  | temp.(°C) | (%)  | $(s^{-1})$       | Rei. |
| Pd/Al <sub>2</sub> O <sub>3</sub>     | 0.3     | 25        | 100  | 0.101            | 1    |
| $Pd/\gamma$ - $Al_2O_3$               | 0.5     | 35        | 100  | 0.092            | 17   |
| PdCu/Mn <sub>2</sub> O <sub>3</sub>   | 1.0     | 35        | 100  | 0.102            | 36   |
| PdNi/γ-Al <sub>2</sub> O <sub>3</sub> | 0.91    | 70        | 90   | 0.149            | 35   |
| $AgPd/\gamma$ - $Al_2O_3$             | 0.4     | 35        | 100  | 0.153            | This |
|                                       |         |           | 100  |                  | work |

<sup>a</sup> Calculation of TOF (s<sup>-1</sup>) after 1h of reaction.





Fig. 17 XRD patterns of AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (a) before testing, (b) after testing.



Fig.18 TG profiles of support  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (a), AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (b).

#### 4 Conclusions

In this paper,  $AgPd/\gamma$ - $Al_2O_3$  catalysts were prepared by sol-gel method using Cacumen platycladi leaves extract. Then the catalysts were characterized by XRD, UV-Vis, FTIR, TEM and TG analysis. The performance of the as-synthesized catalysts was evaluated by selective hydrogenation of 1,3-butadiene. The influence of preparation conditions (including the molar ratio of silver to palladium, the concentration of Cacumen platycladi leaves extract, preparation temperature, the loading of catalysts) and durability experiment were investigated. The result showed that the AgPd/y-Al2O3 bimetallic catalyst exhibited good stability for the hydrogenation of 1,3-butadiene. The activity of the catalyst decreased a bit and the butene selectivity remained basically unchanged for 50 h. The changeless particle size, invariable metallic state and the residual biomass molecules may be responsible for the good performance of AgPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.

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# Graphic abstract:

Plant-mediated synthesis of bimetallic  $AgPd/\gamma$ - $Al_2O_3$  catalyst for selective hydrogenation of low-temperature 1,3-butadiene was reported.

