



## Effects of Heat Treatment Temperatures on the Performance of Au/TiO<sub>2</sub> Catalyst for Liquid Phase Selective Hydrogenation of Phthalic Anhydride

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A series of Au/TiO<sub>2</sub> catalysts with the same gold loading were prepared by deposition-precipitation method followed by calcination and reduction at different temperatures and applied into the hydrogenation of phthalic anhydride. The effects of heat treatment temperatures on their performances were investigated. It was observed that higher calcination temperature and reduction temperature led to an increase in the gold particle size and a collapse of mesoporous structure, which was accompanied by the decrease in the catalytic performance. Among the Au/TiO<sub>2</sub> catalysts investigated, the one calcined at 300 °C and reduced at 200 °C, with smaller gold particle size (3.1 nm), exhibited the best catalytic performance with 94.7 % conversion and 94.2 % selectivity to phthalide.

**Key Words:** Gold catalyst, Heat treatment, Phthalic anhydride, Hydrogenation, Phthalide.

### INTRODUCTION

Phthalide and its derivatives are important industrial intermediates for pharmaceuticals, fine chemicals and organic synthesis. The liquid phase selective hydrogenation of phthalic anhydride is one of the most promising technologies for producing phthalide, owing to its reduced pollutant production and high yield. Usually, Raney Ni or supported nickel catalysts are used for the hydrogenation of phthalic anhydride and show high activity<sup>1-3</sup>. Nevertheless, the process usually needs higher hydrogen pressure (above 4 MPa) and the selectivity of the nickel catalysts to phthalide is low (<89 %), with varying amounts of hydrogenation byproducts such as *o*-toluic acid, aromatic ring-hydrogenated derivatives of the components of the reaction mixture and *o*-phthalic acid. It is therefore desirable to develop an efficient catalyst with high activity and selectivity to phthalide.

Recently, supported gold catalysts have received extensive attentions as efficient catalysts for the selective hydrogenation of oxygen-containing unsaturated groups such as nitro group in the presence of other reducible functional groups<sup>4-14</sup> and carbonyl group in the  $\alpha,\beta$ -unsaturated aldehydes and ketones<sup>15-24</sup>, due to their special selectivity toward the reduction of oxygen-containing unsaturated groups. In our previous work, we studied the liquid phase hydrogenation of phthalic anhydride to phthalide using Au/TiO<sub>2</sub> catalysts with different gold loadings and found that this is highly promising due to high product

yield<sup>25</sup>. The aim of this study is to investigate systematically the effect of the calcination temperature and the reduction temperature on the catalytic performances of Au/TiO<sub>2</sub> catalyst for the liquid phase selective hydrogenation of phthalic anhydride to phthalide.

### EXPERIMENTAL

All chemicals were obtained from commercial suppliers and used without further purification. TiO<sub>2</sub> ( $S_{\text{BET}} = 220 \text{ m}^2\text{g}^{-1}$ ) was supplied by Hongsheng Material Co. Ltd.

**Catalyst preparation:** The Au/TiO<sub>2</sub> catalyst was prepared by deposition-precipitation method<sup>25</sup> with modifications as follows: the sample was calcined at 250, 300, 350 and 400 °C in air for 4 h and reduced at 150, 200, 250 and 400 °C in hydrogen flow for 3 h. The gold loading was 1.4 wt %, measured by an Elan DRC-e ICP-MS instrument of PE Inc. USA.

**Catalyst characterization:** X-ray diffraction patterns of the catalysts were measured with a Thermo X'TRA X-ray diffractometer using CuK $\alpha$  radiation. High-resolution transmission electron microscopy (HRTEM) was measured using a JEM-1200EX equipment. BET specific surface areas and pore structures were measured by pulsed nitrogen adsorption-desorption method at -196 °C using a Micromeritics ASAP 2010 instrument.

**Catalytic activity test:** The liquid phase hydrogenation of phthalic anhydride was carried out in a 100 mL stainless steel autoclave equipped with magnetic stirring. The reaction

conditions were as follows: phthalic anhydride 5.0 g,  $\gamma$ -butyrolactone 50 mL, catalyst 1.0 g, stirring rate 1000 rpm, reaction temperature 180 °C and pressure 3.0 MPa H<sub>2</sub>. The reaction products were analyzed using a gas chromatograph equipped with a HP-5 capillary column and a flame ionization detector.

## RESULTS AND DISCUSSION

**Effect of calcination temperature:** Structural parameters for Au/TiO<sub>2</sub> catalysts calcined at different temperatures are listed in Table-1. It is clearly seen that with the increase in the calcination temperature the BET surface area and the pore volume decreased, whereas the pore size increased. This may be due to the collapse of mesoporous structure when calcination at higher temperature.

Calcination temperature (°C)	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>total</sub> (cm <sup>3</sup> g <sup>-1</sup> )	D <sub>pore</sub> (nm)	d (nm) TEM
250	108.5	0.21	6.05	3.0
300	100.4	0.16	6.39	3.1
350	90.2	0.14	9.43	-
400	72.0	0.10	13.05	6.3

Fig. 1 shows the XRD patterns of Au/TiO<sub>2</sub> catalysts calcined at different temperatures. Diffraction peaks of both anatase and rutile phases in TiO<sub>2</sub> were observed on all the samples. Calcination at high temperature (above 350 °C) decreased the crystallization of the anatase phase. No significant signals attributed to gold species were observed for all the samples, indicating that gold particles are too small to be detected.

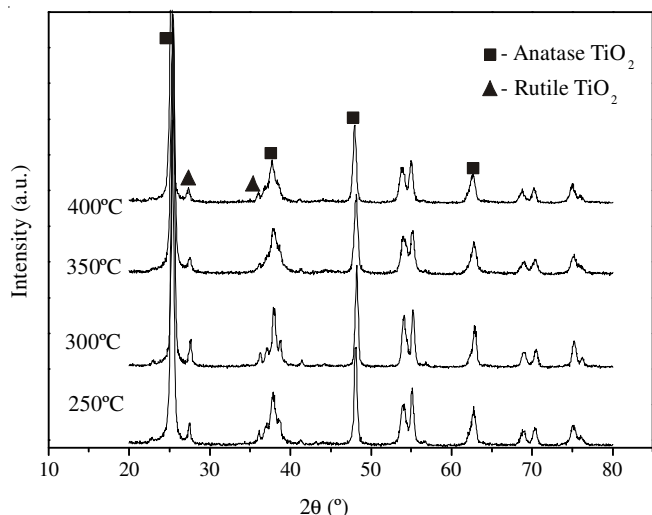


Fig. 1. XRD patterns of Au/TiO<sub>2</sub> catalysts calcined at different temperatures

Fig. 2. shows the HRTEM images of the gold catalysts calcined at different temperatures. Gold particles are seen as dark contrasts on the surface of TiO<sub>2</sub> particles. The average gold particle sizes are listed in Table-1. The average gold particle size was almost the same for the samples calcined at 250 °C and 300 °C; gold particles were evenly dispersed on the support, with an average size of about 3.0 nm (Fig. 2a and

2b). However, gold particles on the sample calcined at 400 °C were much larger and showed a much broader size distribution, as shown in Fig. 2c. Many gold particles with larger size than 10 nm were seen after calcination at this temperature and no particles with size below 3 nm were observed. This suggested that the large particles were formed by aggregation of small particles after calcination at higher temperature. In addition, it can be seen from Fig. 2 that the structure of the support TiO<sub>2</sub> was destroyed when the catalyst was calcined at 400 °C, which is in agreement with BET results.

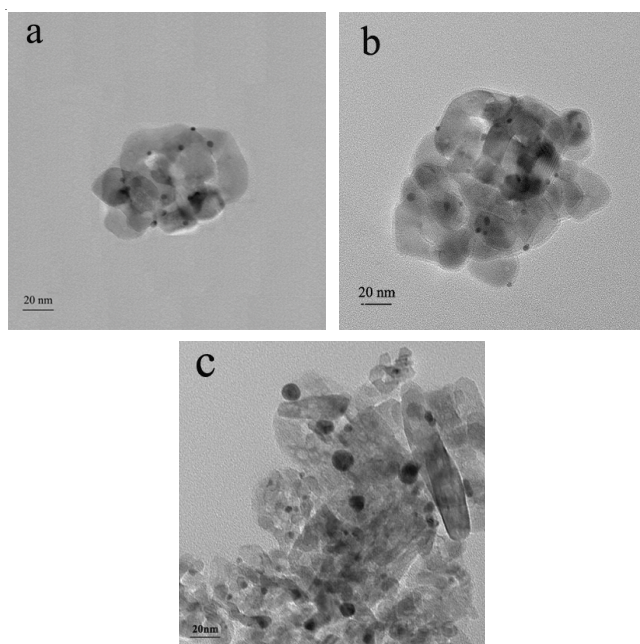


Fig. 2. HRTEM images of Au/TiO<sub>2</sub> catalysts calcined at (a) 250 °C, (b) 300 °C and (c) 400 °C

Table-2 shows the results of the liquid phase hydrogenation of phthalic anhydride over Au/TiO<sub>2</sub> catalysts calcined at different temperatures. All the catalysts were reduced at 200 °C for 3 h prior to reaction. It can be seen that the catalytic performance of Au/TiO<sub>2</sub> was remarkably affected by the calcination temperature. The sample calcined at 300 °C exhibited the best catalytic performance, with 94.7 % conversion of phthalic anhydride and 94.2 % selectivity to phthalide. The lower activity of the catalyst calcined at 250 °C may be due to incomplete decomposition of the catalyst precursor. With increasing the calcination temperature above 300 °C (*i.e.* at 350 °C and 400 °C), the catalytic performance of Au/TiO<sub>2</sub> obviously decreased. Combined with the characterization results of the catalysts as mentioned above, it can be seen that the catalytic performance of Au/TiO<sub>2</sub> catalyst for the hydrogenation of phthalic anhydride is mainly affected by the size of gold particles. The Au/TiO<sub>2</sub> catalysts with small gold particles are preferred for the hydrogenation of phthalic anhydride. It has been accepted that the activity of gold nanoparticles is determined by the number of low coordinated gold atoms in corner or edge positions, which increases with decreasing the gold particle size<sup>26,27</sup>.

**Effect of reduction temperature:** The effect of reduction temperature on the catalytic performance of Au/TiO<sub>2</sub> catalyst calcined at 300 °C was investigated. The results are listed in

TABLE-2  
CATALYTIC ACTIVITY AND SELECTIVITY OF Au/TiO<sub>2</sub>  
CATALYSTS CALCINED AT DIFFERENT TEMPERATURES  
FOR 4 h AND REDUCED AT 200 °C FOR 3 h<sup>a</sup>

Calcination temperature (°C)	Conversion (%)	Selectivity (%)	
		Phthalide	Others <sup>b</sup>
250	79.3	94.1	5.9
300	94.7	94.2	5.8
350	54.9	86.2	13.8
400	40.1	78.8	21.2

<sup>a</sup>Reaction conditions: 1.0 g catalyst, 180 °C, 5.0 g phthalic anhydride in 50 mL  $\gamma$ -butyrolactone, 3.0 MPa H<sub>2</sub>, 9 h. <sup>b</sup>Other products are *o*-toluic acid and *o*-phthalic acid

Table-3. It can be obviously seen that the reduction temperature had a notable influence on the performance of the catalyst. The unreduced catalyst showed low activity, with only 39.3 % conversion of phthalic anhydride. The catalysts reduced at 150 °C and 200 °C had high catalytic performance, being the latter the more active. Generally, the ionic gold species are reduced at about 200 °C<sup>28</sup>. The results suggest that Au<sup>0</sup> is the active site for the hydrogenation of phthalic anhydride. The unreduced catalyst contained most of ionic gold species, showed low activity. It can be seen that with the reduction temperature increased to 400 °C, the catalytic activity and selectivity to phthalide obviously decreased. These differences in catalytic performances could be ascribed to differences in the gold particle size and in the reduction extent of the gold precursor. From Fig. 3 it can clearly be seen that higher reduction temperature could result in the increase in the gold particle size, which led to a decrease in the activity and selectivity to phthalide. The moderate reduction temperature is 200 °C.

TABLE-3  
CATALYTIC ACTIVITY AND SELECTIVITY OF Au/TiO<sub>2</sub>  
CATALYSTS CALCINED AT 300 °C FOR 4 h AND  
REDUCED AT DIFFERENT TEMPERATURES FOR 3 h<sup>a</sup>

Reduction temperature (°C)	Conversion (%)	Selectivity (%)	
		Phthalide	Others
Unreduced	39.3	93.5	6.5
150	91.7	95.4	4.6
200	94.7	94.2	5.8
250	87.8	93.3	6.7
400	59.8	88.6	11.4

<sup>a</sup>Reaction conditions are the same as Table-2

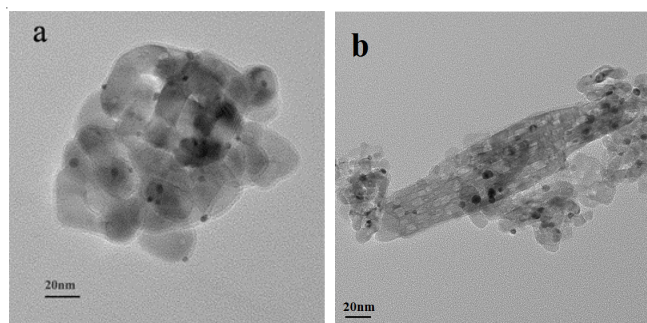


Fig. 3. HRTEM images of Au/TiO<sub>2</sub> catalysts reduced at (a) 200 °C and (b) 400 °C.

## Conclusion

From present data, the activity and selectivity of Au/TiO<sub>2</sub> catalyst for the liquid phase hydrogenation of phthalic anhydride to phthalide were strongly affected by the heat treatment. Higher calcination temperature and reduction temperature resulted in the increase in the gold particle size and a collapse of mesoporous structure, leading to the decrease in the activity and selectivity to phthalide. In this work, the best catalytic performance were obtained when Au/TiO<sub>2</sub> was calcined at 300 °C and reduced at 200 °C.

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