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Au/FeO_x-TiO₂ as an efficient catalyst for the selective hydrogenation of phthalic anhydride to phthalide

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Abstract

Au/FeO_x-TiO₂, prepared by deposition-precipitation method, is an efficient and stable catalyst for the liquid phase selective hydrogenation of phthalic anhydride to phthalide under mild reaction conditions. © 2010 Xiao Nian Li. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

Keywords: Au/FeOx-TiO2 catalyst; Phthalic anhydride; Liquid phase hydrogenation; Phthalide

Phthalide is an important industrial intermediate for pharmaceuticals, fine chemicals and organic synthesis. It can be produced by several methods, such as the reaction of phthalimide and sodium hydroxide, and the chemical reduction of phthalic anhydride. Nevertheless, these processes are of low yield and serious environmental pollution. Now it is highly desirable to produce phthalide by the selective hydrogenation of phthalic anhydride in liquid phase with H_2 . Usually, Raney Ni or supported nickel catalysts are used for the hydrogenation reaction and show high activity [1–4]. However, the selectivity of the nickel catalysts to phthalide is low. It is therefore desirable to develop an efficient heterogeneous catalyst with high activity and high selectivity for the selective hydrogenation of phthalic anhydride to phthalide.

Supported gold catalysts show unique catalytic performance for many reactions and have attracted more and more considerable attention [5,6]. Recently, it is found that gold catalysts exhibit a remarkable selectivity for the hydrogenation of oxygen-containing unsaturated groups such as nitro group [7], and carbonyl group [8]. In our previous work, we studied the liquid phase hydrogenation of phthalic anhydride to phthalide using Au/TiO₂ catalyst and found that the catalyst had high activity and selectivity for this reaction, but deactivated rapidly [9]. Herein, we report that Fe_2O_3 -modified TiO₂ supported gold catalyst can enhance the stability of Au/TiO₂ catalyst, and can efficiently and selectively catalyze the liquid phase hydrogenation of phthalic anhydride to phthalide.

1. Experimental

 TiO_2 (Hongsheng Material, 220 m²/g) supported Au catalyst was prepared by deposition-precipitation method according to [9]. Metal oxide (Fe₂O₃, Sm₂O₃ CeO₂ or MgO) modified TiO₂ supported gold catalysts were prepared as

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follows. A calculated amount of metal oxide precursor (metal nitrate, analytical reagent) was dissolved in distilled water, and TiO₂ was added and impregnated for 12 h at room temperature. Then, the sample was dried at 110 °C for 12 h and calcined at 500 °C for 4 h. The resulting metal oxide-modified TiO₂ supported gold catalysts were prepared by the method as Au/TiO₂. The catalysts were dried at 100 °C for 12 h, calcined at 300 °C in air for 4 h and reduced at 200 °C in hydrogen flow for 3 h. The metal oxide content was 5 wt.% and Au content was 2 wt.%. The morphology and the gold particle size of the catalysts were obtained by high-resolution transmission electron microscopy (HRTEM), in a JEM-1200EX equipment. Au loading in the catalysts was measured by an Elan DRC-e ICP-MS instrument of PE Inc. USA.

Experiment of the liquid phase hydrogenation of phthalic anhydride was carried out in a 100 mL stainless steel autoclave equipped with magnetic stirring at 180 °C and 3.0 MPa H₂. The following conditions were applied: phthalic anhydride 5.0 g, solvent γ -butyrolactone 50 mL and catalyst 1.0 g. The reaction products were analyzed using a gas chromatograph equipped with a HP-5 capillary column and a flame ionization detector. Product identification was performed with an Agilent 6890 gas chromatograph equipped with an Agilent 5973 mass selective detector.

2. Results and discussion

Table 1 shows the hydrogenation results of phthalic anhydride over several metal oxides modified TiO₂ supported gold catalysts as well as Au/TiO₂. All the supported gold catalysts used in this work gave >91% selectivity to phthalide, with only traces of *o*-toluic acid and *o*-phthalic acid (formed from unconverted phthalic anhydride and water of reaction) byproducts, and without any aromatic ring-hydrogenated derivatives which were usually detected when nickel catalysts were used [10]. The results indicated clearly that further hydrogenation of the desired product phthalide usually observed over nickel-based catalysts, could be successfully inhibited over the supported gold catalysts. Compared with Au/TiO₂, the addition of Sm₂O₃, MgO and CeO₂ decreased the activity of the catalyst. It was excited that the addition of Fe₂O₃ increased the activity and the selectivity of Au/TiO₂, giving 97.6% conversion and 95.2% selectivity to phthalide. To the best of our knowledge, Au/FeO_x-TiO₂ is the most selective and active catalysts for the liquid phase hydrogenation of phthalic anhydride up to now. From HRTEM results of the two catalysts (Fig. 1a and b) it can be seen that the gold nanoparticles were evenly dispersed on the surfaces of the supports, with diameters

Table 1

Catalytic results of phthalic anhydride hydrogenation over different gold catalysts ^a .	- \$	180 °C, 3 MPa H ₂ γ-butyrolactone	
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Catalyst	Conversion (%)	Selectivity (%)		
		Phthalide	Others ^b	
Au/FeO _x -TiO ₂	97.6	95.2	4.8	
Au/Sm ₂ O ₃ -TiO ₂	89.1	93.2	6.8	
Au/CeO ₂ -TiO ₂	85.5	95.5	4.5	
Au/MgO-TiO ₂	87.5	91.3	8.7	
Au/TiO ₂	94.7	94.2	5.8	

^a Reaction conditions: 1.0 g catalyst, 180 °C, 5.0 g phthalic anhydride in 50 mL γ -butyrolactone (solvent), 3.0 MPa H₂, and reaction time 9 h. ^b *o*-Toluic acid and *o*-phthalic acid.



Fig. 1. HRTEM images of (a) fresh Au/TiO₂, (b) fresh Au/FeO_x-TiO₂, (c) used Au/TiO₂ and (d) used Au/FeO_x-TiO₂ catalysts.

Table 2								
Stability of	f Au/FeO _x -TiO ₂ a	nd Au/TiO ₂	catalysts fo	r the selec	tive hydroge	nation of	phthalic a	nhydride ^a .

Catalyst	Cycle	Conversion (%)	Selectivity (%)	Au loading (wt.%) ^b
Au/TiO ₂	1	97.9	92.9	1.35
	2	89.1	88.6	_
	3	84.0	86.4	_
	4	81.3	93.6	-
	5	79.9	94.1	0.87
Au/FeO _x -TiO ₂	1	98.2	94.6	1.48
	2	92.3	92.9	-
	3	87.8	93.2	_
	4	88.0	93.2	-
	5	87.2	92.4	1.04

^a Reaction conditions: 1.0 g catalyst, 180 °C, 5.0 g phthalic anhydride in 50 mL γ -butyrolactone (solvent), 3.0 MPa H₂, and 11 h. ^b Obtained by ICP-MS.

in the range of 2–4 nm. In addition, the addition of Fe_2O_3 increased the dispersion degree of gold particles, which may be the reason for the increase in the catalytic performance of Au/TiO₂.

The stability of Au/FeO_x-TiO₂ as well as Au/TiO₂ in phthalic anhydride hydrogenation was checked. The hydrogenation reaction was performed for 11 h to ensure an almost complete substrate conversion and the catalyst was recovered, filtered and washed with γ -butyrolactone. As can be seen in Table 2, Au/TiO₂ showed continued loss of activity after each reuse. In contrast, Fe₂O₃-modified TiO₂ supported gold catalyst exhibited a much better stability for the reaction. After having reused five times, Au/FeO_x-TiO₂ catalyst still kept high activity and selectivity, with 87.2%conversion of phthalic anhydride and 92.4% selectivity to phthalide. The results suggested that Fe_2O_3 significantly improved the stability of the gold catalyst. As can be seen from the HRTEM image of the used Au/TiO₂ and Au/FeO_x-TiO₂ catalysts (Fig. 1c and d), the amounts of gold particles on the surface of the used catalysts decreased compared with the fresh catalysts (Fig. 1a and b). ICP-MS results (Table 2) showed that the gold content decreased from 1.35% to 0.87% for Au/TiO₂ and from 1.48% to 1.04% for Au/FeO_x-TiO₂ after five cycles. It suggested a leaching of gold from the catalyst, which might contribute to the decay of the catalyst activity. On the other hand, the HRTEM and ICP-MS results showed that the percentage of gold leaching from Au/FeO_x-TiO₂ was smaller than that from Au/TiO₂, suggesting that Fe_2O_3 promoter could inhibit the loss of gold from the catalyst, which could be well explained by the HRTEM characterization results of the two catalysts. As shown in Fig. 1b, the addition of Fe₂O₃ produces locally clustered Fe₂O₃ film on TiO₂, and this film and TiO₂ jointly anchor the gold particles, which can improve the gold binding energy [11], and therefore increase the stability of gold particles. This result was similar to the early work of Carrettin et al. [12] in which iron presented near the interfaces between the gold clusters and the TiO₂ support and improved the activity and stability of the gold catalyst for CO oxidation.

3. Conclusion

In conclusion, we successfully achieved the liquid phase hydrogenation of phthalic anhydride using gold catalysts. Fe_2O_3 -modified TiO₂ supported gold catalyst with highly dispersed gold nanoparticles has a catalytic activity and selectivity to phthalide superior to those of the most active catalysts yet reported [1–4]. This gold catalyst is expected to find wide applications in other hydrogenation reactions, especially in selective hydrogenations under mild conditions.

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