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Short Communication

Large size Pd NPs loaded on TiO_2 as efficient catalyst for the aerobic oxidation of alcohols to aldehydes

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ABSTRACT

Anti-sintering Pd/TiO_2 catalysts have been prepared by different methods and systematically characterized. Compared with the catalysts prepared by the heterogeneous deposition precipitation (HDP) method and wetness impregnation (WI) method, the catalyst prepared by the deposition precipitation (DP) method could give higher content of Pd species. Pd/TiO_2 prepared by DP method shows much higher activity than other catalysts in liquid phase oxidation of benzyl alcohol to benzyl aldehyde. The average particle size of Pd nanoparticles (NPs) is 15 nm. XPS results indicate that though Pd^{2+} species have been reduced to Pd^0 after use, the activity of catalyst is not affected, which has never been reported in the literature.

1. Introduction

The selective oxidation of alcohols to aldehydes or ketones is one of the most important transformations in organic chemistry, which has wide applications in perfumery, pharmaceutical, dyestuff and agrochemical industries [1]. In traditional methods, there are large amounts of toxic co-products produced together with aldehydes or ketones using metal oxidants, such as dichromate and chromium trioxide [2], so the methods based on toxic or expensive inorganic oxidants to greener and more atom-efficient methods which adopt recyclable catalyst and O_2 as oxidant are exigently needed [3]. Many supported noble metal catalysts have been explored for the oxidation of alcohols in liquid-phase [3], such as Pt [4], Au [5], Ru [6] and Pd [7]. Among these catalysts, Pd catalysts appear to be promising ones due to high selectivity and conversion could be obtained synchronously [7].

Despite extensive researches on Pd catalysts for alcohol selective oxidation, the active Pd species is disputed and many problems still need to be resolved. Firstly, the size of Pd NPs is smaller than 10 nm in order to achieve high activity, which is liable to be sintered. Pd species is reconstructed after used, such as Pd/Al_2O_3 or Pd/TiO_2 (the active Pd^{2+} species is reduced to Pd^0 after the reaction), which should be calcinated before the next use [7]. Furthermore, the preparation process of organic–inorganic catalyst is intricate, such as SBA-16 supported palladium–guanidine complex, and the structure of mesoporous SBA-16 is prone to be destroyed in acid or base conditions [8]. Thirdly, the selectivity is low when using coreshell catalysts, such as toluene, benzoic acid and benzyl benzoate are produced together using supported Pd{Au} core–shell NPs [9]. Lastly, Mondelli et al. find that the formation of carboxylates from benzaldehyde hydration/oxidation is largely hindered when using PdBi/Al_2O_3 as catalyst, but Pd content is 5% [10]. So it is of great importance to investigate supported Pd catalysts to overcome the problems mentioned above.

In order to solve the sintering problem, large size Pd NPs loaded on TiO_2 are prepared by different methods and characterized by XRD, XPS, ICP, CO-Chemisorption and TEM. The difference between the catalysts and the catalytic performances is also illustrated in this paper thoroughly.

2. Experimental

2.1. Materials and methods

TiO_2 was purchased from Fluka, which was calcined at 300 °C for 4 h before use. $PdCl_2$ (A. R.), Pd $(acac)_2$ (A. R.), benzyl alcohol (C. P.), 3-OMe benzyl alcohol (C. P.), 3-Cl benzyl alcohol (C. P.), n-butyl alcohol (C. P.), dibenzyl alcohol (C. P.) and benzyl ethanol (C. P.) were obtained from Sinopharm Chemical Reagent Co. Ltd. Broane tributylamine (A. R.) and oleylamine (A. R.) were purchased from Sigma-Aldrich. Other materials were supplied by local companies.

X-ray diffraction patterns (XRD) of the catalysts were performed on a Bruker D8 diffractometer with Cu-Kα radiation from 0.5° to 90° with a scan speed of 1 °/min. X-ray photoelectron spectroscopy (XPS) measurements were obtained on a PHI-5500 spectrometer with Al Kα X-ray radiation as the X-ray source for excitation. Transmission electron microscopy (TEM) was performed on a JEOL 2100F instrument

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operating at 30kV. N_2 adsorption–desorption isotherms were measured with a BELSORP mini II analyzer at liquid N_2 temperature. Surface area (S_{BET}) was calculated by the BET method, and average pore size (D) was determined from the desorption isotherms using the Barrett–Joyner–Halenda (BJH) method. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were performed on the Thermo Scientific iCAP 6300 instrument. Gas chromatography (GC) was performed on GC-2014 with Rtx-5 capillary column. CO-Chemisorption was performed on Autochem 2910 instrument.

2.2. Synthesis of the catalysts

2.2.1. WI method

Exactly 1 g TiO_2 was immersed in an aqueous solution containing 0.944 mmol $PdCl_2$ under stirring until the solution became clear. The filtrate was filtered off and washed with water. Finally, the product was dried at 60 °C for 10 h and calcined at 300 °C for 3 h. The catalyst was denoted as Pd/TiO_2-WI for short [11].

2.2.2. DP method

Exactly 1 g TiO_2 was dispersed into an aqueous solution containing 0.944 mmol $PdCl_2$ at 70 °C. Under stirring, 10 mL of aqueous solution containing 10 mmol Na_2CO_3 was added drop wise to the suspension. Finally, the catalyst was filtered off and washed with water after aging at 100 °C for 6 h, which was dried at 60 °C for 10 h and calcined at 300 °C for 3 h. The sample was abbreviated as Pd-TiO_2-DP for short [11].

2.2.3. HDP method

Exactly 1 g TiO_2 was added into an aqueous solution containing 10 mmol of urea and 0.944 mmol $PdCl_2$. The suspension was transferred into an oil bath preheated to 100 °C, and held at this temperature for 6 h. The filtrate was filtered off and washed with water. Finally, the product was dried at 60 °C for 10 h and calcined at 300 °C for 3 h. The sample was designated as Pd/TiO_2-HDP [11].

2.2.4. Collide method

As motioned in other literature [12], 0.25 mmol $Pd(acac)_2$ was mixed with 15 mL oleylamine under argon flow. The solution was heated to 60 °C and 3.45 mmol broane tributylamine complex was added to the system. The temperature was raised to 90 °C at 1 °C/min. The solution was cooled room temperature and 30 mL ethanol was added, and the product was separated by centrifugation. Pd NPs were dispersed into pentane.

10 mg Pd NPs were added to TiO_2 and sonicated for 2 h. After evaporation of pentane, 20 mL acetic acid was added to the mixture and stirred for 8 h. Finally, the product was filtered and dried at 60 °C for 10 h, which was calcined at 300 °C for 3 h. The catalyst was denoted as Pd/TiO_2-C for short.

Table 1
Oxidation of benzyl alcohol catalyzed by Pd/TiO_2.

Entry	Catalyst	Conv. (%)	Sel. (%)	Metal loadings (wt%)[g]
1[a]	Pd/Al_2O_3-WI	35	85	–
2[a]	Pd/SiO_2-WI	3	93	–
3[a]	Pd/TiO_2-WI	30	95	0.22
4[a]	Pd/TiO_2-DP	65	96	0.72
5[a]	Pd/TiO_2-HDP	34	94	0.20
6[a]	Pd/TiO_2-C	60	96	0.75
7[b]	Pd/TiO_2-DP	63	96	0.72
8[c]	Pd/TiO_2-DP	62	96	0.72
9 [13][d]	PdAu/MSNs	98	95	2.88
10 [14][e]	Pd@Ni/MWCNTs	94	90	20
11[f]	Pd/TiO_2-DP	64	96	0.72
12	–	3	98	0

[a] Catalyst (50 mg), benzyl alcohol (46.3 mmol), O_2 bubbling rate (20 mL/min), temperature 120 °C, 3 h.

[b] The catalyst reused.

[c] The reused catalyst calcined in air at 300 °C.

[d] $m_{BzoH}/m_{Metal} = 1000/1$, 90 °C, O_2 pressure: 5 atm, 1 h.

[e] Benzyl alcohol 2 mmol, K_2CO_3 6 mmol, catalyst (Pd: 0.2 mmol), water, H_2O_2 6 h, K_2CO_3: 100 °C, 8 h.

[f] The catalyst was reduced with H_2 at 300 °C.

[g] The metal loading was detected by ICP-AES.

Table 2
Catalytic properties of Pd/TiO_2 using various substrates.

Entry	Substrate	Conv. (%)	Sel. (%)
1	3-OMe benzyl alcohol	46	99
2	3-Cl benzyl alcohol	35	99
3	n-Butylalcohol	2	98
4	di-Benzyl alcohol	51	98
5	Benzyl ethanol	3	98

Reaction conditions: catalyst (50 mg), benzyl alcohol (46.3 mmol), O_2 bubbling rate (20 mL/min), and temperature (120 °C).

2.3. The test of catalytic activity

The oxidation of benzyl alcohol over heterogeneous Pd/TiO_2 catalysts was performed in 10 mL bottle using molecular oxygen as oxidant. In each experiment, 50 mg catalyst was added into 46.3 mmol benzyl alcohol. The mixture was heated to 120 °C for 3 h with oxygen bubbled in at a flow rate of 20 mL/min. After the system cooled to room temperature, the catalyst was removed from the reaction mixture by centrifugation and the products were analyzed by GC. The catalyst was washed with ethanol and dichloromethane for 3 times and dried at 60 °C in vacuum for the next use.

3. Results and discussion

3.1. Oxidation of benzyl alcohol using Pd/TiO_2 prepared by different methods

Catalytic performance and the amount of Pd loadings of Pd/TiO_2 prepared by different methods were shown in Table 1. Conversion of benzyl alcohol and selectivity of benzyl aldehyde catalyzed by the catalyst Pd/TiO_2, Pd/SiO_2 and Pd/Al_2O_3 prepared by WI method were 30%, 95%, 3%, 93%, 35% and 85% respectively (Table 1, entries 1–3). Given that the acid property of Al_2O_3 that may accelerate the reaction rate of side reactions, TiO_2 was chosen as support. Pd/TiO_2-DP showed much higher conversion compared with Pd/TiO_2-WI and Pd/TiO_2-HDP (Table 1, entries 3–5). Pd–TiO_2–C also exhibited similar conversion (Table 1, entry 6), but the preparation procedure was long and tedious. Conversion was unchanged whether the reused catalyst Pd/TiO_2 was calcined or not (Table 1, entries 7 and 8). Metal loadings of Pd/TiO_2 prepared by the methods mentioned above were lower than that of PdAu/MSNs [13] and Pd@Ni/MWCNTs [14]. The oxygen pressure in these catalysts was 5 atm and H_2O_2 was used as an oxidant (Table 1, entries 9 and 10). The conversion of benzyl alcohol was nearly unchanged when the Pd/TiO_2 was reduced (Table 1, entry 11). The conversion was low when no catalyst was added to the system (Table 1, entry

Table 3
Catalytic reusability of Pd/TiO_2 for the oxidation of benzyl alcohol.

Run	1	2	3	4	5
Con. (%)	65	63	65	62	66
Sel. (%)	96	95	96	95	96

Reaction conditions: catalyst (50 mg), benzyl alcohol (46.3 mmol), O_2 bubbling rate 20 mL/min, temperature 120 °C, 3 h.