Contents lists available at ScienceDirect

ELSEVIER





journal homepage: www.elsevier.com/locate/catcom

Short Communication

Selective hydrogenation of 3,3-dimethylbutanoyl chloride to 3,3-dimethylbutyraldehyde with silica supported Pd nanoparticle catalyst

Sifang Li*, Guoqin Chen, Lan Sun

Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

A R T I C L E I N F O

Article history: Received 24 November 2010 Received in revised form 21 January 2011 Accepted 25 January 2011 Available online 3 February 2011

Keywords: Hydrogenation 3,3-dimethylbutyraldehyde Catalysis Pd nanoparticle

ABSTRACT

A novel method for selective hydrogenation of 3,3-dimethylbutanoyl chloride (DMBC) to 3,3-dimethylbutyraldehyde (DMBA) with silica supported Pd nanoparticle catalyst (Pd/SiO₂) is developed. The catalysts were characterized by Fourier transform infrared spectroscopy, X-ray powder diffraction, N₂ physisorption and transmission electron microscopy. The performance of the Pd/SiO₂ catalyst was compared with Pd/C and Pd/BaSO₄ catalysts with or without being pretreated by quinoline–sulfur. The Pd/SiO₂ catalyst activated at 80 °C by bubbling hydrogen in cyclohexane for 1 h showed the highest yield of DMBA. For 3 wt.% Pd/SiO₂, the yield of DMBA reached 84.6%, which exhibited much higher value than Pd/C and Pd/BaSO₄ catalysts.

© 2011 Published by Elsevier B.V.

1. Introduction

3,3-Dimethylbutyraldehyde (DMBA) is an important intermediate for the preparation of neotame which is known as an extremely potent sweetener because its sweetening potency has been reported to be 8000 times that of sucrose [1]. In addition, DMBA is also used to produce pharmaceuticals such as pyrone derivatives [2]. DMBA can be synthesized by the following methods: (a) oxidation of 1-chloro-3, 3-dimethylbutane with DMSO [3]; (b) hydrolysis of 1,1-dichloro-3, 3-dimethylbutane [4]; (c) oxidation of 3,3-dimethylbutanol with 2,2,6,6-tetramethyl-1-piperidinyloxy and a free radical [5]; (d) reduction of 3,3-dimethylbutyric acid with palladium acetate and trip-tolyphosphine [6]. Each of these reported protocols suffered from the use of expensive reagents or low product yields. Therefore, the development of simple, convenient and economical approaches for the synthesis of DMBA is still needed.

Aldehydes can be synthesized by Rosenmund reduction of the corresponding acid chlorides in the presence of a supported Pd catalyst. Pospisek and Blaha [7] reported preparation of DMBA by hydrogenation of 3,3-dimethylbutanoyl chloride (DMBC) in the presence of Pd/BaSO₄ catalyst. It is known that a suitable catalyst poison such as quinoline–sulfur is often used to prevent successive hydrogenation of aldehyde to alcohol in Rosenmund reduction [8–15]. Catalyst poison deactivates the catalyst for undesired reaction but causes much difficulty in purification of the aldehyde and reuse of the

catalyst. Therefore, attempts to dispense with the use of catalyst poisons acquire considerable significance. It is known to control the structure [16], particle size [17] and pore size [18] of a metal oxide by using organic compounds in sol–gel method. Ethylene glycol and acetylacetone were used in the preparation of Pd/SiO₂ catalyst [19]. Residual organics in the catalyst promoted the selectivity in the hydrogenation of benzoyl chloride [20].

The aim of this research is to develop a method for synthesis of DMBA by selective hydrogenation of DMBC in the presence of silica supported Pd nanoparticle catalyst. Polyethylene glycol (PEG 200) and tetrahydrofuran were used in the preparation of the catalyst via sol–gel method. X-ray powder diffraction (XRD), transmission electron microscope (TEM), N₂ physisorption and Fourier transform infrared spectroscopy (FT-IR) were used to characterize the catalysts. The selectivity of the Pd/SiO₂ was compared with Pd/C and Pd/BaSO₄. The effect of activation conditions on the catalytic activity was investigated.

2. Experimental section

2.1. Materials

3 wt.% Pd/BaSO₄ was prepared according to reference [21], 3 wt.% Pd/C was procured from Baoji Rock Nonferrous Metal CO. Ltd., China. Dinitrodiamminepalladium, 3,3-dimethylbutyric acid, thionyl chloride, benzene, tetraethylorthosilicate (TEOS), ethanol, PEG 200, tetrahydrofuran and cyclohexane were of analytical grade. H₂ and N₂ (both purities were more than 99.99%) were obtained from Linde Gases CO. Ltd., China.

^{*} Corresponding author. Tel./fax: +86 592 2186195. *E-mail address:* sfli@xmu.edu.cn (S. Li).

^{1566-7367/\$ -} see front matter © 2011 Published by Elsevier B.V. doi:10.1016/j.catcom.2011.01.025

2.2. Synthesis of DMBC

In a 500 ml three-necked flask equipped with reflux condenser, magnetic stirrer and thermometer, 100 ml of thionyl chloride was added dropwise to 3,3-dimethylbutyric acid (117 g). The mixture was refluxed at 80 °C in an oil bath for 3 h. Sulfur dioxide and hydrogen chloride escaping from the condenser were absorbed in the alkali solution. After the completion of the reaction, the residual thionyl chloride was removed under vacuum. Then 20 ml of anhydrous benzene was added, and the mixture of benzene and thionyl chloride was removed under vacuum. This process was repeated 3 times. Finally, DMBC was distilled under reduced pressure (20 kPa) at 79–81 °C.

2.3. Catalyst preparation

3 wt.% Pd/SiO₂ catalysts were prepared via sol–gel method. Dinitrodiamminepalladium and TEOS were used as precursors for palladium and silica. PEG 200 and tetrahydrofuran were employed as the Pd-dispersant. The catalyst was prepared as follows: 0.13 g of dinitrodiamminepalladium was added into a mixture of PEG 200 (7 ml) and tetrahydrofuran (1.5 ml) at 80 °C under vigorous stirring. Then the solution was added to 7.3 ml of TEOS dissolved in ethanol (4.5 ml) and stirred for 1 h at 80 °C. A mixture of deionized water (2 ml) and ethanol (2 ml) was added and the resulting viscous solution was aged at 80 °C for 24 h to turn into a gel. The gel was dried at 80 °C in vacuum for 8 h. Prior to hydrogenation reaction, some catalysts were activated in an atmosphere of hydrogen at different temperatures (80 °C, 160 °C and 200 °C) for 4 h, while some other samples were activated in cyclohexane by bubbling hydrogen into the solution at 80 °C for 1 h. The Pd/C and Pd/BaSO₄ catalysts with or without quinoline–sulfur were also used for comparison. The inhibited catalyst was prepared by adding 20 μ l of quinoline–sulfur (containing quinoline 85.7 g/l and sulfur 14.3 g/l) for 1 g catalyst to the reaction mixture.

2.4. Catalyst characterization

Fourier transform infrared spectroscopy (FT-IR) of the catalysts was measured by KBr pellet method on a Nicolet Nexus FT-IR spectrophotometer in the wave number range 4000–450 cm⁻¹. X-ray powder diffraction (XRD) of the samples was recorded on an X'Pert PRO X-ray diffractometer with Cu K α radiation (λ =0.15406 nm)



Fig. 1. TEM images of 3 wt.% Pd/SiO₂ catalysts activated at different conditions: (a) activated at 80 °C in cyclohexane; (b) activated at 80 °C; (c) activated at 160 °C; (d) activated at 200 °C.

with a scanning angle (2θ) range from 10° to 60°, voltage and current of 40 kV and 30 mA. Surface areas calculated by the BET method were determined from nitrogen adsorption–desorption isotherms at liquid nitrogen temperature by using a Micromeritics TriStar 3000 instrument. The morphologies of the catalysts were characterized by a TECNAI F30 HRTEM transmission electron microscope (TEM).

2.5. Hydrogenation of DMBC

A three-necked flask (250 ml) equipped with reflux condenser, mechanical stirrer and thermometer was used as the reactor. 100 g of cyclohexane was charged into the reactor, and 2 g of the catalyst was suspended in the cyclohexane via vigorous stirring under a nitrogen atmosphere. The mixture was heated up to 80 °C by immersing the reactor in a thermostatic oil bath. Then 20 g of DMBC was added and hydrogen saturated with the solvent vapor in advance was bubbled through the mixture at a steady flow rate at atmospheric pressure. Hydrogen chloride from the reaction was trapped in a water sink. The conversion of DMBC was measured by titrating the hydrogen chloride absorbed in the water with NaOH solution. Samples of the reaction mixture were withdrawn periodically for analysis. The yield of DMBA was determined by mixing 0.5 g sample with saturated 2,4-dinitrophenylhydrazine solution to form a yellow precipitate of 2,4dinitrophenylhydrazone which was collected, dried and weighed [12,22].

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows TEM images of 3 wt.% Pd/SiO₂ activated at 80 °C in cyclohexane as well as 80 °C, 160 °C and 200 °C without the solvent. The TEM images reveal the dispersion of Pd nanoparticles on silica. The Pd particle size and distribution were found to vary depending on the activation conditions employed in the preparation process (Fig. 2). Pd/SiO₂ activated at 80 °C in cyclohexane shows the narrowest particle distribution. As the Pd/SiO₂ was activated at 80 °C in cyclohexane, the particles were suspended in the liquid, which avoided the aggregation of palladium due to good mass and heat transfer. The average Pd particle size increases from 3.4 nm to 7.0 nm with the elevation of the activation temperature from 80 °C to 200 °C. This is probably because the organic residues in the surface of the catalyst decrease during the heating and result in aggregation of palladium particles. It is worth mentioning that Pd/C has similar Pd

Fig. 2. Particle size distribution of catalysts activated at different conditions.

Table 1	
Physical property of Pd/Si	O_2 catalysts.

Catalyst	Activation temperature (°C)	BET surface area (m²/g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
Pd/SiO ₂	80 ^a	264	0.43	27.96
	80	251	0.57	26.22
	160	296	0.63	25.19
	200	317	0.64	25.07
Pd/C	80 ^a	930	0.62	22.04
$Pd/BaSO_4$	80 ^a	127	0.46	29.13

^a Catalyst was activated in cyclohexane.

particle size and distribution to Pd/SiO_2 , but $Pd/BaSO_4$ has larger Pd particle size and wider distribution than Pd/SiO_2 .

Table 1 shows the surface areas of 3 wt.% Pd/SiO₂ activated at 80 °C, 160 °C and 200 °C, which were calculated by the BET method. Pd/SiO₂ activated at 80 °C in cyclohexane shows slightly larger surface area than that activated at the same temperature without the solvent. As the temperature is elevated, surface areas and pore volumes of the catalysts increase, while the average pore diameters decrease. The increase of the surface areas can be attributed to the loss of organics on the surface of the catalyst.

Fig. 3 shows the XRD patterns of the support silica and Pd/SiO₂ catalysts activated under different conditions. From XRD, peaks due to metallic palladium (for example, Pd (111) and (200) around $2\theta = 40.6$ and 47, respectively) become a little sharper with an elevation of the activation temperature, indicating that the palladium particles grow. The average size of palladium particles, which is calculated from the full width at half maximum of the XRD peak at $2\theta = 40.6$ using the Scherer equation [23], increases from 4 nm to 9 nm with the elevation of the activation temperature from 80 °C to 200 °C. These XRD observations are roughly consistent with the TEM results.

FT-IR spectra of the Pd/SiO₂ catalysts were recorded (Fig. 4). The FT-IR spectra showed the typical vibration modes from silica, namely: v_{as} Si—O—Si at 1088 cm⁻¹, v Si—O (H) at 969 cm⁻¹, v_s Si—O—Si at 795 cm⁻¹ and δ Si—O—Si at 463 cm⁻¹. In addition, the corresponding vibrations are due to the presence of organic compounds in the catalysts. For example, v_{as} CH₃ and v_{as} CH₂ at 2955 and 2886 cm⁻¹ could be identified, respectively. The presence of the organic residues in the studied samples could be correlated to the organics used in the sol–gel process. Even after seven runs, the catalyst still shows organic residues from FT-IR curves in Fig. 4(d). Thus, it can be concluded that organic residues could be stable embedded in the silica gel matrices.

Fig. 3. XRD patterns of 3 wt.% Pd/SiO₂ catalysts treated under different conditions: (a) support; (b) activated at 80 °C in cyclohexane; (c) activated at 80 °C; (d) activated at 160 °C; (e) activated at 200 °C.

Fig. 4. FT-IR spectra of 3 wt.% Pd/SiO₂ catalysts: (a) activated at 80 °C in cyclohexane; (b) activated at 160 °C; (c) activated at 200 °C; (d) after seven runs.

3.2. Catalytic activity

In the hydrogenation over a supported Pd catalyst, mass transfer resistance may be serious [24,25]. In order to overcome the mass transfer resistance, the effects of stirring rate and hydrogen flow rate were studied. Above the stirring rate of 1000 rpm and the hydrogen flow rate of 120 ml/min, there were no significant changes in the conversions of DMBC, which indicates the absence of mass transfer resistance.

It is known that the nature of a support have a significant effect on the catalytic performance [26,27]. In Rosenmund reduction, the most common supports used are activated carbon and barium sulfate. The performance of Pd/SiO₂ catalyst in the hydrogenation of DMBC to DMBA was compared with Pd/C and Pd/BaSO₄ catalysts. Results are summarized in Table 2. Pd/SiO₂ catalyst exhibits much higher selectivity and yield of DMBA than Pd/C and Pd/BaSO₄ catalysts with or without catalyst poison. The main by-product is 3,3dimethylbutanol, which is formed by the subsequent reduction of DMBA. It is evident that a suitable catalyst poison such as guinolinesulfur will enhance the selectivity with a lower conversion.

Table 3 shows the results of hydrogenation of DMBC over 3 wt.% Pd/SiO₂ catalysts activated under different conditions. The catalyst performance was remarkably affected by the activation conditions. The catalyst activated in cyclohexane at 80 °C for 1 h showed the highest catalyst performance. Increase of the activation temperature of the catalyst was accompanied with the decrease of selectivity to DMBA. The yield of DMBA dramatically decreased for the catalyst activated at 200 °C, which was attributed to the growth and aggregation of palladium particles as shown in Fig. 1.

Reuse of the catalyst is of great industrial relevance, therefore, 3 wt.% Pd/SiO₂ activated at 80 °C in cyclohexane was used to test the reusability of the catalyst. The Pd/SiO₂ catalyst was subjected to seven consecutive runs under the same conditions as Table 3. The conversion was still above 90% and the surface area of the catalyst

ole 2

Hydrogenation	of	DMBC	using	various	Pd	cataly	/sts
Invulogenation	UI.	DIVIDC	using	various	1 U	catan	/ 313

Catalysts	Reaction time (h)	Conversion (%)	Selectivity (%)	Yield (%)
Pd/SiO ₂ Pd/C Pd/BaSO ₄ Pd/C ^a	6 6 10	93 89 86 81	91 75 74 88	84.6 66.8 63.6 71.3
Pd/BaSO ₄ ^a	10	80	84	67.2

DMBC 20 g; catalyst dosage, 10 wt.% based on DMBC; solvent, cyclohexane, 100 g; temperature, 80 °C; hydrogen flow rate, 120 ml/min; stirring rate, 1000 rpm. ^a Catalysts with quinoline-sulfur.

Table 3

Activation temperature (°C)	Conversion (%)	Selective (%)	Yield (%)
80 ^a	93	91	84.6
80	92	87	80.0
160	94	80	75.2
200	95	75	71.3

Effect of activation conditions on the hydrogenation of DMBC.

DMBC 20 g; catalyst dosage, 10 wt.% based on DMBC; solvent, cyclohexane, 100 g; temperature, 80 °C; hydrogen flow rate, 120 ml/min; stirring rate, 1000 rpm; reaction time, 6 h.

Catalyst was activated in cyclohexane.

was measured to be $259 \text{ m}^2/\text{g}$ after seven cycles of reaction, which showed no significant changes.

4. Conclusions

DMBA was synthesized with high yields via selective hydrogenation of DMBC using Pd/SiO₂ catalyst prepared by sol-gel method. TEM and XRD indicate that Pd nanoparticles were highly dispersed on the silica. Narrow particle size distribution was observed for Pd/SiO₂ catalyst activated at 80 °C by bubbling hydrogen in cyclohexane. FT-IR demonstrates the presence of the organic residues in the catalyst. The yield of DMBA could achieve 84.6% by 3 wt.% Pd/SiO₂ catalyst, which showed much higher catalytic activity than Pd/C and Pd/BaSO₄ catalysts.

Acknowledgement

The authors thank Xiamen Fine Chemical Technology Company for the financial support of this study.

References

- [1] C. Nofre, J.M. Tinti, Food Chem. 69 (2000) 245-257.
- [2] J. Domagala, M. Pyrone, US 5,808,062 (1998).
- [3] Z. Guo, R. Sawyer, I. Prakash, Synth. Commun. 31 (2001) 3395-3399.
- [4] I. Prakash, H. Estates, Z. Guo, US 5,994,593 (1999).
- I. Prakash, WO 2,005,082,825 (2005). [5]
- I. Prakash, L.A. Robert, K.S. Tanielyan, US 7,030,281 (2006). [6]
- [7] J. Pospisek, K. Blaha, Coll. Czech. Chem. Commun. 52 (1987) 514-521.
- [8] K.W. Rosenmund, F. Zetzsche, Ber. Dtsch. Chem. Ges. 51 (1918) 585-594.
- E.B. Hershberg, J. Cason, Org. Synth. 21 (1941) 84-88. [9]
- [10] T. Ito, K. Watanabe, Bull. Chem. Soc. Jpn. 41 (1968) 419-423.
- A.W. Burgstahler, L.O. Weigel, C.G. Shaefer, Synthesis 11 (1976) 767-768. [11]
- [12] S. Affrossman, S.J. Thomson, J. Chem. Soc. 5 (1962) 2024-2029. [13]
 - J.A. Peters, H.V. Bekkum, Recl. Trav. Chim. Pays-Bas 100 (1981) 21-24.
- [14] J.A. Peters, H.V. Bekkum, Recl. Trav. Chim. Pays-Bas 90 (1971) 1323-1325.
- [15] A.I. Rachlin, H. Gurien, D.P. Wagner, Org. Synth. 51 (1971) 8-9.
- [16] C.M. Liu, X.T. Zu, Q.M. Wei, L.M. Wang, J. Phys. D: Appl. Phys. 39 (2006) 2494-2497
- M. Galceran, M.C. Pujol, M. Aguiló, F. Díaz, J. Sol-Gel Sci. Technol. 42 (2007) 79-88. [18] R. Linacero, M.L. Rojas-Cervantes, J.D. López-González, J. Mater. Sci. 35 (2000) 3269-3278
- [19] S. Tanaka, F. Mizukami, S. Niwa, M. Toba, K. Maeda, H. Shimada, K. Kunimori, Appl. Catal. A 229 (2002) 165-174.
- [20] S. Tanaka, F. Mizukami, S. Niwa, M. Toba, G. Tasi, H. Shimada, K. Kunimori, Appl. Catal. A 229 (2002) 175-180.
- [21] A.I. Vogel, Vogel's Textbook of Practical Organic Chemistry, 5th ed.Longman, London, 1989.
- [22] X. Jia, X. Liu, J. Li, P. Zhao, Y. Zhang, Tetrahedron Lett. 48 (2007) 971-974.
- [23] M. Bhagwat, P. Shah, V. Ramaswamy, Mater. Lett. 57 (2003) 1604-1611.
- [24] V.G. Yadav, S.B. Chandalia, Org. Proc. Res. Dev. 1 (1997) 226-232.
- [25] J.A. Bennett, R.P. Fishwick, R. Spence, J. Wood, J.M. Winterbottom, S.D. Jackson, E. H. Stitt, Appl. Catal. A 364 (2009) 57-64.
- [26] J. Panpranot, K. Pattamakomsan, J.G. Goodwin, P. Praserthdam, Catal. Commun. 5 (2004) 583-590
- [27] A. Quintanilla, J.J.W. Bakker, M.T. Kreutzer, J.A. Moulijn, F. Kapteijn, J. Catal. 257 (2008) 55-63.