Hydrogenolysis of α-methylbenzyl alcohol to ethylbenzene over Pd/C catalyst

J Feng¹, Y H Zhong and S H Dai

Chongqing Key Laboratory of Industrial Fermentation Microorganism, College of Chemistry and Chemical Engineering, Chongqing University of Science and Technology, Chongqing 401331, China

¹ E-mail: fengjianscu@163.com

Abstract. The hydrogenolysis of α-methylbenzyl alcohol (MBA) to ethylbenzene (EB) over Pd/C catalyst was studied. The XRD and TEM results show that Pd nanoparticles are well dispersed on the carbon support with good crystallinity. There is no 1-cyclohexylethanol or ethylcyclohexane in the products, indicating that Pd/C is excellent for inhibiting the hydrogenation of the aromatic ring. Alcohol solvents are beneficial to increase the catalytic activity because of their strong polarity and good solubility.

1. Introduction

Catalytic hydrogenolysis is an important technique for the reduction of C–OH bond to the corresponding C–H bond. This transformation is widely used in organic synthesis [1-3] and biomass conversion [4-6]. In particular, the hydrogenolysis of C–OH bond in benzylic alcohols is highly desired because of the rapid development of producing value-added chemicals from lignin [7]. α-Methylbenzyl alcohol (MBA) is a typical benzylic alcohol, which is often used as a model compound to study the hydrogenolysis of C–OH bond [8]. MBA is also a byproduct in the production of propylene oxide employing the ethylbenzene hydroperoxide oxidation method [9]. If MBA can be hydrogenolyzed back to ethylbenzene (EB) with high selectivity (Scheme 1), the production of propylene oxide will achieve in a recycling process, thereby improving the economic benefit of the manufacturers.

Scheme 1. Hydrogenolysis of α-Methylbenzyl alcohol (MBA) to ethylbenzene (EB).

The hydrogenolysis of MBA has been studied over several heterogeneous catalysts [8-12], mainly including Pd, Pt, Ru and Rh. It is found that Pt, Ru or Rh based catalysts usually lead to benzene ring hydrogenation, exhibiting poor selectivity to EB [9-11]. In contrast, Pd is a superior hydrogenolysis catalyst, which can greatly lower the risk of hydrogenation of the aromatic ring [9, 11]. For example, Pd/CoO₄ was reported as a satisfactory catalyst for the hydrogenolysis of MBA by Musolino and co-workers [8]. Their results showed that a different kinetic behavior can be observed on Pd/TiO₂, Pd/SiO₂ and Pd/CoO₄. Lin et al. [12] explored a green Pd catalytic system by using CO₂-expanded
methanol and compressed CO₂/water as reaction media. CO₂ could decrease the mass transfer resistance, and increase the hydrogen solubility; however, the operating procedure was complicated and unmanageable. In addition, Pd based catalysts are also active for the transfer hydrogenolysis of MBA using hydrogen donors (formic acid and its salts) instead of molecular hydrogen [13-15]. Although the transfer hydrogenolysis approach seems safer, the cost of this process is more expensive. Furthermore, under the transfer hydrogenolysis condition, MBA often dehydrogenates to the undesired product acetophenone in a large amount because of the competing disproportionation reaction [15, 16].

In our previous work [13], we have found that Pd/C was superior to other supported Pd catalysts (Pd/Al₂O₃, Pd/NaY, Pd/SiO₂ and Pd/TiO₂) in the transfer hydrogenolysis reaction due to its moderate acid density feature. However, comparatively little research has focused on the systematically study of the traditional hydrogenolysis of MBA over Pd/C using molecular hydrogen. As a matter of fact, it is not a problem to utilize hydrogen for production in the modern industry. This inspires us to investigate the catalytic performance of Pd/C in the traditional hydrogenolysis process. The Pd/C catalyst was characterized by several techniques and evaluated by changing relevant parameters. Pd/C was found to be an efficient catalyst for the hydrogenolysis of MBA to EB under optimized conditions.

2. Experimental
The Pd/C (5%) catalyst was prepared by impregnation technique [13]. MBA (98%) was purchased from Aladdin. Other reagents were commercially obtained as analytical reagent samples and used as received. BET surface area of Pd/C was measured on an auto adsorption/desorption analyzer (ZXF-6, Northwest Chemical Industry). Powder X-ray diffraction (XRD) measurements were performed on a diffractometer (Philips) equipped with a Cu Kα radiation source (λ = 0.15406 nm). Transmission electron microscopy (TEM) images were obtained by JEM-1200EX. The hydrogenolysis of MBA was carried out in a 20 mL autoclave batch reactor. The catalyst was pre-activated in the same autoclave before each reaction test. A typical run was performed as follows. Pd/C (0.1 g), MBA (1 g) and ethanol (5 mL) were added to the autoclave. The reactor was sealed and purged repeatedly with hydrogen to eliminate air, and then pressurized to the necessary hydrogen pressure. The reaction mixture was stirred when it was heated to the desired temperature. After the reaction, the products were analyzed by gas chromatograph (Agilent 6890N, Agilent Technologies).

3. Results and discussion
The BET surface area of the Pd/C catalyst was determined to be 585 m²/g, a little lower than the carbon support (620 m²/g, provided by the supplier). Figure 1 shows the XRD pattern of the Pd/C catalyst. The major phase presented in the diffractogram is amorphous carbon, which is accompanied by some graphite phase at 2θ = 26.4° and 50.4° (JCPDS Card #41-1487). The diffraction peaks at 2θ = 40.1°, 46.7°, 68.1°, 82.1° and 86.6° are attributed to metallic Pd (JCPDS Card #05-0681). These sharp peaks indicate that the crystallinity of the Pd nanoparticles is good. According to the Scherrer equation, the mean Pd particle size was 13.0 nm. A representative TEM image of the Pd/C catalyst is shown in figure 2. The Pd nanoparticles are dispersed evenly over the carbon hosts, with a mean size of 11.3 nm. However, the size distribution is a bit wide, as shown by the histograms (± 1.9 nm). The mean Pd particle size determined by TEM is lower than that of XRD, possibly because some small Pd particles can't be detected by XRD.

As was mentioned above, an undesired side reaction in the hydrogenolysis of MBA is the hydrogenation of the aromatic ring [9-11]. In this work, EB is always the main product when the reaction is performed on Pd/C. A small amount of styrene and acetophenone are formed as the major byproducts. Styrene is produced by the dehydration of MBA on the acidic sites of the support [9, 17]. The formation of acetophenone is attributed to the dehydrogenation of MBA on the Pd active sites [13, 16]. No 1-cyclohexylethanol or ethylcyclohexane is detected in the products, suggesting that Pd/C is excellent for suppressing the hydrogenation of the benzene ring.
Figure 1. XRD pattern of Pd/C catalyst.

Figure 2. TEM image and particle size distribution of Pd/C catalyst.

Figure 3 presents the effect of reaction temperature on the MBA conversion and the product selectivity. As the temperature increased from 30 °C to 70 °C, there was a uniform increase in the MBA conversion from 66.8% to 99.9%. The reaction can proceed nearly completed at 70 °C. This temperature is even lower than that used in the transfer hydrogenolysis of MBA over Pd/C [13,15]. The selectivity to EB reached up to 97.1% at 50 °C, and it changed slightly even if the reaction temperature continued to increase. The high selectivity to EB is of great importance because it will enable the recycling process of the propylene oxide production to become really feasible and quite simple [13].

Figure 4 shows the effect of hydrogen pressure on the catalytic performance of Pd/C. The hydrogen pressure had a significant impact on the MBA conversion when it was below 1 MPa, after which the conversion changed slightly. This is consistent with the results obtained by the Pd/HMOR90 catalyst [9]. It is known that the solubility of hydrogen is proportional to the pressure [18]. Therefore, the increasing MBA conversion may be owing to the enhanced hydrogen concentration in the solution with increasing pressure. However, the concentration of hydrogen probably reached a certain limit and did not increase obviously when the pressure was higher than 1 MPa. Interestingly, the product selectivity showed little changes as the hydrogen pressure increased, but lower pressures (<1 MPa) can ensure an excellent selectivity to EB.
Figure 3. Effect of reaction temperature on the hydrogenolysis of MBA over Pd/C. EB: ethylbenzene; SE: styrene; AP: acetophenone.

Figure 4. Effect of hydrogen pressure on the hydrogenolysis of MBA over Pd/C.

Shown in figure 5 is the reaction profile for the hydrogenolysis of MBA over Pd/C. It appears that as the conversion of MBA neared completion, the hydrogenation of styrene became difficult, which results in the decrease of EB selectivity. It has been revealed that styrene is an intermediate product in the hydrogenolysis process, and it can be hydrogenated to EB on the metal sites [9]. As the reaction progress, the carbon deposition may occur on the catalyst, leading to the blocking of Pd sites for hydrogenation. This is a reasonable explanation for the variation tendency of the product selectivity in figure 5.

Solvent choice is known to be important for the hydrogenolysis of lignin [19, 20]. Considering that benzylic alcohols are abundant functional group in lignin [7], we believe that solvent has a significant effect on the hydrogenolysis of MBA. Therefore, a series of commonly used solvents, including methanol, ethanol, n-propanol, n-hexane, and cyclohexane were evaluated. As illustrated in figure 6, all the tested solvents showed good selectivity to EB (> 90%), and the best results were achieved with methanol and ethanol (both were about 97%). As for the MBA conversion, the reactions conducted in alcohol solvents were obviously better than that in n-hexane or cyclohexane. Generally, the polarity and solubility are two main factors that can influence the solvent effect on the hydrogenolysis reaction [20]. Methanol, ethanol and propanol are excellent polar solvents. The interaction between alcohol solvents and the hydroxyl group of MBA can increase the substrate solubility, thereby facilitating its
contact with the catalyst. From the viewpoint of its low toxicity and cost, ethanol is the best solvent for the hydrogenolysis of MBA to EB.

![Figure 5. Reaction profile for the hydrogenolysis of MBA over Pd/C.](image)

![Figure 6. Hydrogenolysis of MBA in different solvents over Pd/C.](image)

4. Conclusions
The efficient hydrogenolysis of MBA to EB was achieved over Pd/C catalyst. The reaction temperature, hydrogen pressure, reaction time and solvent can significantly influence the catalytic performance of Pd/C. Under optimized conditions (5 mL ethanol, 50 °C, 1 MPa, 1 h), the conversion of MBA and the selectivity to EB can be high up to 94.0% and 97.1%, respectively. The successful transformation of MBA to EB makes the production of propylene oxide can be realized in a recycling process.

Acknowledgments
This work was supported by the Scientific and Technological Research Program of Chongqing Municipal Education Commission (No. KJ1601309), and the Open Fund of Chongqing Key Laboratory of Industrial Fermentation Microorganism, Chongqing University of Science and Technology (No. LIFM201708).
References

[1] Ranade V S and Prins R 2000 Chem. Eur. J. 6 313
[2] Muzart J 2005 Tetrahedron 61 9423
[3] Thakar N, Polder N F, Djanashvili K, Bekkum H, Kapteijn F and Moulijn J A 2007 J. Catal. 246 344
[4] Schlaf M 2006 Dalton Trans. 39 4645
[5] Corma A, Iborra S and Velty A 2007 Chem. Rev. 107 2411
[6] Feng J and Xu B 2014 Prog. React. Kinet. Mech. 39 1
[7] Zakzeski J, Bruijnincx P C A, Jongerius A L and Weckhuysen B M 2010 Chem. Rev. 110 3552
[8] Musolino M G, Mauriello F, Busacca C and Pietropaolo R 2015 Top. Catal. 58 1077
[9] Kwak B S, Kim T J and Lee S I 2003 Appl. Catal. A 238 141
[10] Sanders D K, Lin S D and Vannice M A 1994 J. Catal. 147 375
[11] Sato T, Sato O, Arai K, Mine E, Hiyoshi N, Rode C V and Shirai M 2006 J. Supercrit. Fluids 37 87
[12] Lin H W, Yen C H, Hsu H and Tan C S 2013 RSC Adv. 3 17222
[13] Feng J, Yang C F, Zhang D L, Wang J B, Fu H Y, Chen H and Li X J 2009 Appl. Catal. A 354 38
[14] Mao H, Liao X P and Shi B 2011 Catal. Commun. 12 1177
[15] Sawadjoon S, Lundstedt A and Samec J S M 2013 ACS Catal. 3 635
[16] Keresszegi C, Mallat T and Baiker A 2001 New J. Chem. 25 1163
[17] Kwak B S and Kim T J 1999 Appl. Catal. A 188 99
[18] Feng J, Zhang Y Q, Xiong W, Ding H and He B 2016 Catalysts 6 51
[19] Wang X Y and Rinaldi R 2012 ChemSusChem 5 1455
[20] Shu R Y, Zhang Q, Ma L L, Xu Y, Chen P R, Wang C G and Wang T J 2016 Bioresour. Technol. 221 568