

Phenol hydrogenation over Pd/ZrO₂ using ethanol as hydrogen source

Yunjie Shi^{1, a}, Bin Wang^{1, b}, Junjun Shen^{1, c} and Rongrong Miao^{1, d*}

¹Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, China

^ayunjie_shi_kmust@sina.com, ^bbinwang0913@163.com, ^cJunjun_Shen@yeah.net, ^{d*}rr.de@hotmail.com

Keywords: Ethanol, Phenol, Hydrogenation, Pd/ZrO₂

Abstract. Phenol hydrogenation over the Pd/ZrO₂ catalyst has been carried out using ethanol as hydrogen source. The reaction temperature, catalyst and ethanol quantity are found to be influencing factors for effective phenol conversion. In all cases, low quantity (5%~10%) of ethanol and high temperature is efficient for a high phenol conversion. The results show that low quantity (5%~10%) of ethanol is efficient for high cyclohexanone selectivity at low temperature (573K). However, the selectivity of cyclohexanone, cyclohexanol and cyclohexane are insensitive to the ethanol quantity at high temperature (653K). It seems that ethanol plays an important dual role: as hydrogen source and as additive to control the phenol conversion and products selectivity.

Introduction

Cyclohexanone is the key raw material for the preparation of nylon 6 and adipic acid for nylon 66 [1,2]. The industrial production of cyclohexanone commonly involves the selective catalytic hydrogenation of phenol. On the other hand, phenol is an established environmental toxin and phenol-based waste originates from a variety of industrial sources including oil refineries, petrochemical units, polymeric resin manufacturing and plastic units [7]. Therefore, catalytic hydrogenation of phenol for cyclohexanone is an important chemical process, and has been widely studied [3-10].

The selective catalytic hydrogenation of phenol to cyclohexanone usually conducted in liquid-phase, and the liquid-phase phenol hydrogenation under variable molecular hydrogen pressure offers cost and energy saving since the reaction can perform at relatively mild reaction condition [11-17]. However, the attainment of both high selectivity and high phenol conversion (>80%) is a challenge [4] because cyclohexanone can be further hydrogenated to cyclohexanol under hydrogen atmosphere. On the other hand, hydrogen (H₂) is potentially dangerous, expensive and has some limitations such as necessity of special facilities for H₂ generation, storage, and transportation [18].

In situ hydrogen generated through aqueous phase reforming (APR) of methanol on supported palladium catalysts as an alternative to molecular H₂, it has been utilized for the hydrogenation of phenol [19,20]. Formic acid (HCOOH) [21] and sodium formate (HCOONa) [22] has been also used as in situ hydrogen source for the catalytic phenol hydrogenation. However, only the pressure reactor under specific 3 bar N₂ pressure can achieve high phenol conversion of phenol hydrogenation when using formic acid as hydrogen source. Moreover, microwave effect is found to be specific and necessary for effective phenol hydrogenation using sodium formate as hydrogen donor on Pd/C. In order to make phenol hydrogenation to cyclohexanone as chemist friendly or sustainable chemical transformation, it is necessary to minimize above shortcomings. The ethanol, as a safe and chemist friendly sustainable hydrogen source, may improve the solubility of phenol in water and improve the selectivity of products.

In this study, we use ethanol as the hydrogen source for the hydrogenation of phenol under aqueous condition. On the other hand, the activity and selectivity of Pd/ZrO₂, PdCeO₂ and Pd/Al₂O₃ for the phenol hydrogenation was studied. Then the effect of ethanol quantity and temperature on phenol hydrogenation was investigated on the proper catalyst.

Experimental

The ZrO_2 , CeO_2 and Al_2O_3 were supplied by Aladdin Industrial (Shanghai) Corporation. The $\text{Pd}(\text{NO}_3)_2$ was obtained from Kunming Sino-Platinum Metals Catalysts Co., Ltd. Phenol, ethanol, cyclohexanone, cyclohexanol, cyclohexane and 2-ethy phenol were supplied by Sigma-Aldrich. The Pd/ZrO_2 , Pd/CeO_2 , $\text{Pd}/\text{Al}_2\text{O}_3$ with the mass ratio of $\text{Pd}/\text{support}=2\%$ were prepared by incipient wetness impregnation, after impregnation the catalysts were oven dried at 373 K for 10 h, and then calcined at 453 K for 4 h in 5% v/v H_2/He .

The liquid phase hydrogenation of phenol into cyclohexanone was carried out in a 4ml stainless steel reactor (Swagelok Co. Ltd.). 0.0408g phenol, 0.0408g catalysts, 2ml ultrapure water and ethanol in demand volume ratio was loaded in the reactor. Repeatedly charging and venting with helium was used to displace air. A Techne fluidized sand bath (model SBL-2) was used to keep the reactor at the desired temperature. After heating for the desired time, the reactor was removed and cooled to room temperature by a fan. Diluted by acetone the hydrogenous products were analyzed by an Agilent Technologies model 7820A gas chromatograph with a flame ionization detector (FID) using DB-WAX column (J&W Scientific).

The overall fractional conversion of phenol (X_{phenol}) and reaction selectivity in terms of products (S_{product}) is given by

$$X_{\text{phenol}} = \frac{n_0 - n_{\text{phenol}}}{n_0} \times 100\% \quad (1)$$

$$S_{\text{product}} = \frac{n_{\text{product}}}{n_0 - n_{\text{phenol}}} \times 100\% \quad (2)$$

n_0 , n_{phenol} , n_{product} refer to the molar quantity of phenol before reaction, the molar quantity of phenol after reaction, the molar quantity of products (cyclohexanone, cyclohexanol, cyclohexane and 2-ethy phenol) respectively.

Results and discussion

The hydrogenation of phenol over three different catalysts Pd/ZrO_2 , Pd/CeO_2 and $\text{Pd}/\text{Al}_2\text{O}_3$ is carried out at the temperature of 653K first.

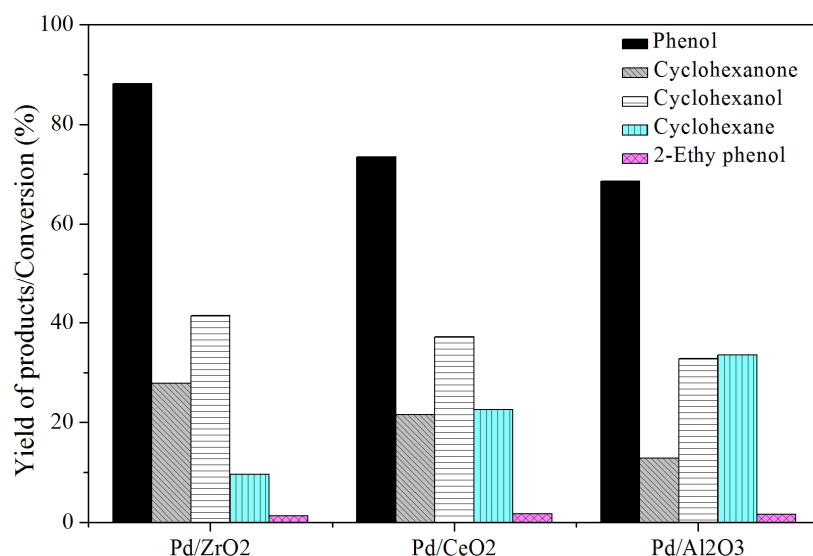


Fig. 1, The phenol conversion and product distributions during phenol hydrogenation using different catalysts in water at 653K. Reaction condition: Phenol(0.0408g), Catalyst(0.0408g), Water(2ml), Ethanol(0.3ml), Reaction Time(180min).

As shown in Fig. 1, cyclohexanone, cyclohexanol, and cyclohexane are the dominate products of phenol hydrogenation using ethanol as hydrogen source. In addition, a small quantity of 2-ethy phenol (<1.8%) is also detected. According to Fig. 1, it can be seen that the Pd/ZrO₂ catalyst shows the highest phenol conversion (88.21%) and the best selectivity of cyclohexanone (27.82%) compare with Pd/CeO₂ (X_{phenol}=73.48%, S_{cyclohexanone}=21.56%) and Pd/Al₂O₃ (X_{phenol}=68.58%, S_{cyclohexanone}=12.82%). The high activity and selectivity of the Pd/ZrO₂ may be attributed to the character of the support which possess acid–base as well as redox properties. For ZrO₂, the acid sites are relatively weaker than the basic sites. Hence, phenol predominantly adsorbed on basic sites in non-polar fashion and this produces cyclohexanone with high selectivity [23]. Therefore, the effect of ethanol quantity on phenol hydrogenation is investigated on Pd/ZrO₂.

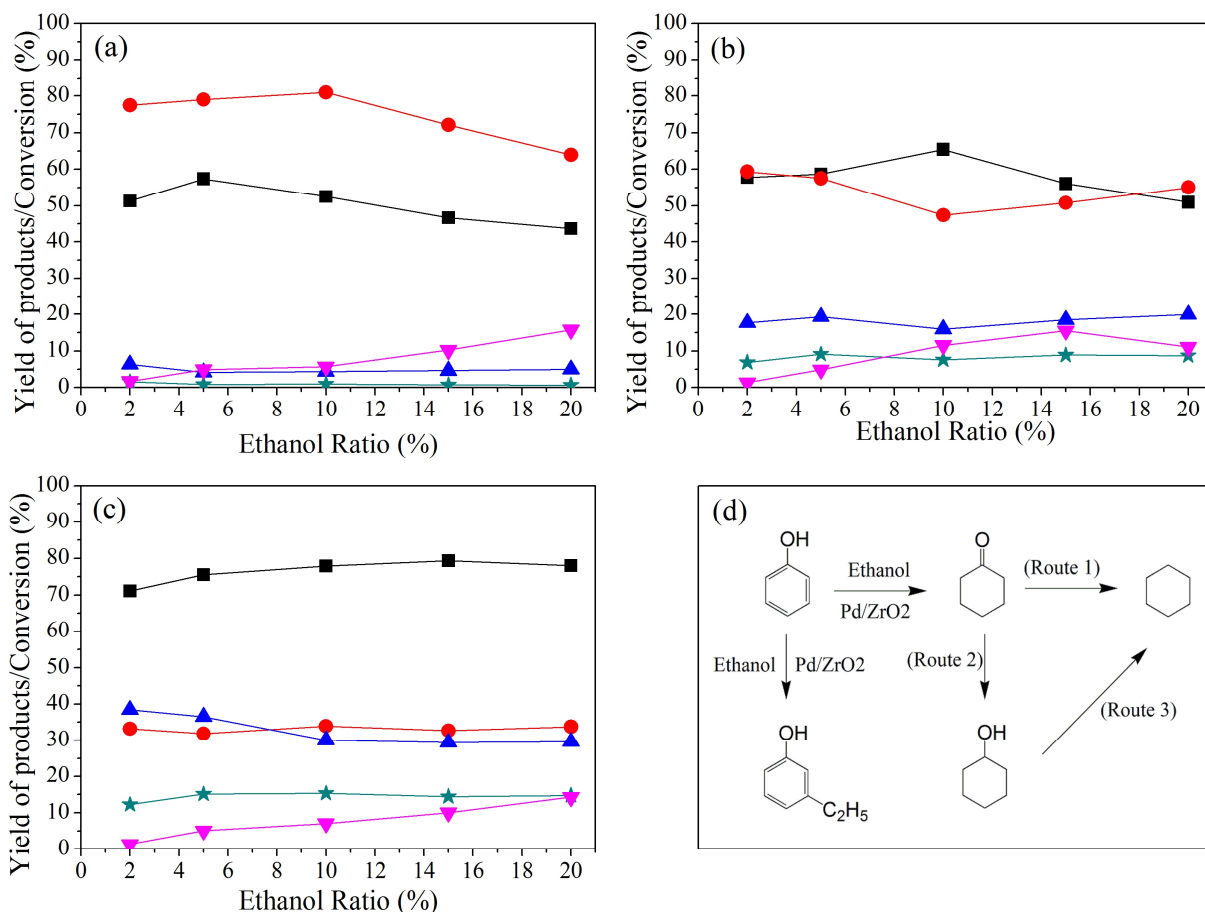


Fig. 2, Effect of ethanol volume ratio on the phenol conversion and selectivity during the hydrogenation of phenol using Pd/ZrO₂ in water at different temperature: (a)573K, (b)623k, (c)653k. Reaction condition: Phenol(0.0408g), Catalyst(0.0408g), Water(2ml), Reaction Time(60min).

(■)Conversion of phenol and selectivity to (●)Cyclohexanone; (▲)Cyclohexanol; (★)Cyclohexane; (▼)2-Ethyl Phenol.

The effect of the ethanol volume ratio (range of 2%~20%) on phenol conversion and the product distributions at different temperature are presented in Fig. 2. It can be seen that, the conversion of phenol increases with increasing temperature. And the impact of ethanol volume ratio on phenol conversion is different under different temperature. As shown in Fig. 2(a), the phenol conversion decreases from 57.38% for the ethanol volume ratio of 5% to 43.65% for the ethanol volume ratio of 20% at low temperature (573K). What's more, it can be seen from Fig. 2(b) that the phenol conversion decreases from 65.42% for the ethanol volume ratio of 10% to 50.91% for the ethanol volume ratio of 20% at 623K. At 653K as shown in Fig. 2(c), however, the phenol conversion decreases slightly with increasing ethanol quantity after reaches a maximum (77.89%) at the ethanol

volume ratio of 10%. And it also indicates that the phenol conversion becomes insensitive to the ethanol volume ratio at high temperature.

The products distribution of phenol hydrogenation shows different trend under various temperature. As shown in Fig. 2(a), cyclohexanone are the dominant products and show the similar trend as the phenol conversion at 573K. And the high selectivity of cyclohexanone decreases from 80.93% to 63.93% when the ethanol volume ratio increases from 10% to 20%. However, the selectivity of cyclohexanol (4.17%~6.34%) and cyclohexane (0.69%~1.54%) keep in a low level, and the selectivity of cyclohexanol and cyclohexane is insensitive to the ethanol quantity. In addition, the selectivity of 2-ethyl phenol (4.94%~15.75%) increases obviously with increasing ethanol volume ratio (2%~20%), and it seems that the decrease in cyclohexanone selectivity is compensated for by an increase in the selectivity of 2-ethyl phenol. In the case of 623K, it is established by the Fig. 2(b) that the selectivity of cyclohexanone (47.35%~59.32%) decreases significantly due to the rise of temperature. On the other hand, the selectivity of cyclohexanol (15.95%~19.95%) and cyclohexane (6.90%~9.10%) increases slightly. In addition, the selectivity of 2-ethyl phenol (1.41%~15.53%) increases obviously as observed at the temperature of 573K. As shown in Fig. 2(c), the selectivity of cyclohexanone (31.88%~33.92%) decreases significantly when the temperature rise to 653K. Nevertheless, the selectivity of cyclohexanol (29.34%~36.49%) and cyclohexane (14.46%~15.37%) shows the reverse trend and become the main products. Furthermore, the selectivity of 2-ethyl phenol (5.03%~14.31%) increases obviously with increasing ethanol volume ratio (2%~20%) as observed at the temperature of 573K and 623K.

Obviously, the results show that the phenol conversion and the products selectivity influenced by temperature and ethanol quantity strongly. This phenomenon may be explained by the interaction of ethanol with the Pd surface [24]. That it is to say, the absorption of ethanol on the Pd surface may strongly influence on the catalyst activity. Therefore, more ethanol occupy the active site of catalyst with increasing ethanol quantity. As a result, the conversion of phenol decreases with increasing ethanol quantity under low temperature (573K). However, at high temperature, most of the ethanol is existed as gas phase and the absorption capacity become weaker on Pd at high temperature (653K). Thus, it can be seen from the experiment that the phenol conversion is insensitive with the ethanol quantity at high temperature. The selectivity of phenol hydrogenation prefer to cyclohexanone at low temperature. However, it seems that cyclohexanone converts into cyclohexanol and cyclohexane at high temperature. In conclusion, high temperature promoting the process of route 1, route 2 and route 3 as shown in Fig. 2(d).

Conclusion

This work explores the phenol hydrogenation using ethanol as hydrogen source. By comparing the catalytic activity of Pd/ZrO₂, Pd/CeO₂ and Pd/Al₂O₃, Pd/ZrO₂ is found to have the best activity and selectivity in this reaction system. In the ethanol volume ratio range studied (2%~20%). The results show that the main products are cyclohexanone at low temperature, and cyclohexanone, cyclohexanol, cyclohexane are the main products at high temperature. It can be seen that low quantity (5%~10%) of ethanol and high temperature is efficient for a high phenol conversion. On the other hand, high cyclohexanone selectivity achieves in a low quantity (5%~10%) of ethanol at low temperature, but it becomes insensitive to ethanol quantity at high temperature. These results show that ethanol play an important dual role: as hydrogen source and as additive to control the phenol hydrogenation process.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (21307049 and U1137603), the High Technology Talent Introduction Project of Yunnan in China (2010CI110) and the Science and Technology Major Project of Yunnan Province (2012ZB002).

References

- [1] I.Dodgson, K.Griffen, G.Barberis, F.Pignataro, G.Tauszik: submitted to Chemical Industry (1989)
- [2] M.Howe-Grant, Ed: submitted to Kirk-Othmer Encyclopedia of Chemical Technology (1991)
- [3] K. Weissmehl and H. J. Arpe: submitted to Industrial Organic Chemistry (1993)
- [4] J. F.Van Peppen, W.B. Fisher and C. H.Chan: submitted to Catalysis of Organic Reactions (1980)
- [5] W. B. Fisher and J. F. van Peppen: submitted to US Patent (1978)
- [6] S. Scire, S. Minico and C. Crisafulli: submitted to Applied Catalysis: B (2002)
- [7] S.G. Shore, E. Ding and C. Park et al: submitted to Catalysis Communications (2002)
- [8] N. Mahata, K.V.Raghavan and V.Vishwanathan et al: submitted to Physical Chemistry (2001)
- [9] V.Vishwanathan, N.Mahata and M.A.Keane: submitted to Reaction Kinetics and Catalysis Letters (2001)
- [10] H.Liu, T.Jiang, B.Han, S.Liang, Y. Zhou: submitted to Science (2009)
- [11] M.L.Buil, M.A.Esteruelas, S.Niembro, M.Oliván, L.Orzechowski, C.Pelayo and A.Vallriber: submitted to Organometallics (2010)
- [12] X.Yang, S.J. Liao, J.H. Zeng and Z.X.Liang: submitted to Applied Surface Science (2011)
- [13] X.Yang, L.Du, S.J.Liao, Y.X.Li and H.Y.Song: submitted to Catalysis Communications (2012)
- [14] X.Yang, X.Yu, L.Z.Long, T.J.Wang, L. L.Ma, L.P.Wu, Y.Bai, X.J. Li and S. J. Liao: submitted to Chemical Communication (2014)
- [15] D.M.Zhang, Y.J.Guan, E.J.M.Hensen, L.Chen and Y.M.Wang: submitted to Catalysis Communications (2013)
- [16] J.F.Zhu, G.H.Tao, H.Y.Liu, L.He, Q.H.Sun and H.C.Liu: submitted to Green Chemistry (2014).
- [17] Y.J.Guan, D.M. Zhang and Y.M.Wang: submitted to Catalysis Letters (2012)
- [18] J.Zhong, J.Chen, L.Chen: submitted to Catalysis Science & Technology (2014)
- [19] Y.Z.Xiang, X.N. Li, C.S. Lu, L. Ma, J.F.Yuan, F.Feng: submitted to Industrial & Engineering Chemistry Research (2011)
- [20] Y.Z. Xiang, L.N.Kong, C.S.Lu, L.Ma, X.N.Li: submitted to Reaction Kinetics Mechanisms and Catalysis (2010)
- [21] D.Zhang, F.Ye, T.Xue, Y.Guan, Y.M.Wang: submitted to Catalysis Today (2014)
- [22] H.Cheng, R.Liu, Q.Wang, C.Wu, Y.Yu, F. Zhao: submitted to New Journal of Chemistry (2012)
- [23] S.Velva, M.P.Kapoorb, S.Inagakib, K.Suzukia: submitted to Applied Catalysis A: General (2003)
- [24] J.Y.He, C.Zhao, Johannes A. Lercher: submitted to Journal of catalysis(2014)