



Gas-phase hydrogenation of maleic anhydride to butyric acid over Cu/TiO₂/γ-Al₂O₃ catalyst promoted by Pd

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Received 12 February 2002; accepted 27 February 2003

Abstract

The promoter effect of palladium on the Cu/TiO₂/γ-Al₂O₃ catalyst was investigated for the gas-phase selective hydrogenation of maleic anhydride to butyric acid at atmospheric pressure. The results show that Pd is added rarely into the Cu/TiO₂/γ-Al₂O₃ catalyst for the hydrogenation of maleic anhydride, the higher selectivity to butyric acid can be obtained. In the absence of Pd (or Cu) in the Cu–Pd/TiO₂/γ-Al₂O₃ catalyst, the selectivity to butyric acid (BA) is nearly zero. Using the Cu–Pd/TiO₂/γ-Al₂O₃ (Pd/Cu = 3/100 (atom)) catalyst, 56.2% selectivity to BA and 100% conversion of maleic anhydride were obtained at 280 °C.

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Keywords: Supported Cu–Pd catalyst; Selective hydrogenation; Maleic anhydride; Butyric acid; Promoter of Pd

1. Introduction

Butyric acid (BA) is a very useful chemical intermediate to produce butyrates [1,2], cellulose derivatives of butyric acid [3,4], and used directly as a protecting material and so on [5]. BA is produced commercially by the oxidation of butanol or the fermentation of starch [6–8]. BA can be also prepared by the oxidation of aldehyde [9] and biotransformation of alcohol [10–12]. In this paper, a novel synthesis route of butyric acid by selective hydrogenation of maleic anhydride (MA) is proposed, in which MA is a more economic feed

material that can be produced from *n*-butane [13,14].

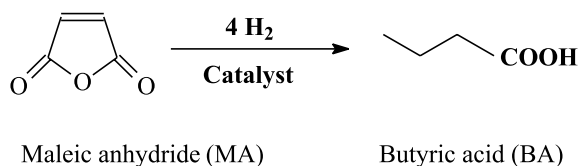
In the catalytic hydrogenation of MA, many products can be obtained, such as succinic anhydride (SA) [15], γ-butyrolactone (GBL) [16,17], 1,4-butanediol (BDO) and tetrahydrofuran (THF) [18,19]. But the study of hydrogenation of MA to BA, that is BA as the main product, has not been reported.

For the gas-phase hydrogenation of MA, the copper-substrate catalysts modified with Zn, Zr and Cr [16,20–22] and palladium catalyst [23,24] were reported. Cu/TiO₂/γ-Al₂O₃ can catalyze effectively the hydrogenation of MA to GBL [25]. Here, as a promoter of the Cu/TiO₂/γ-Al₂O₃ catalyst, the effect of Pd on the hydrogenation of MA to BA is investigated. By hydrogenation of

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C=C bond and hydrogenolysis of one carboxyl group in MA, BA may be prepared as follows:



2. Experimental

The preparation of catalyst: γ - Al_2O_3 powder was put into de-ionized water at room temperature. The mixture solution of tetrabutyl titanate and alcohol was dropped into it and stirred continually for 10 h, filtered, dried at 120 °C for 24 h. The solid powder obtained was added into the aqueous solution of copper nitrate and palladium chloride dissolved in ammonia. After stirring and scattering by ultrasonic equipment at room temperature for 2 h, the resulting product was dried at 120 °C for 24 h and calcined in air at 500 °C for 4 h. Then it was crushed to granule with diameter of 0.45–0.90 mm and reduced in H_2/N_2 . In the Pd–CuO/TiO₂/ γ -Al₂O₃ (Pd–Cu–Ti–Al–O) catalyst, CuO:TiO₂:Al₂O₃ = 14:28:58 (wt) and Pd/Cu (atom ratio) was 8/10⁴, 12/10⁴ and 3/100, respectively.

The activity testing of catalyst for the hydrogenation of MA was carried out in a fixed-bed reactor system at atmospheric pressure and 200–280 °C. An 8.0 ml catalyst was packed in the silica glass reactor (i.d. 12 mm) and some quartz sands were placed on both sides of the catalyst. Before being used, the catalyst was reduced in the reactor with 5–10% H_2/N_2 at 120–180 °C for 5–10 h and finally with 30% H_2/N_2 at 300–400 °C for 5 h. The exact reduction temperature of catalyst was decided by temperature programmed reduction (TPR), and was generally the top temperature of peaks in the TPR curves. The reduced catalyst was kept in nitrogen. 20% (wt) maleic anhydride in propanol was pumped into the reactor, while it was gasified on the layer of quartz sands and mixed with H_2 , and then passed through the catalyst bed. LHSV of MA was 0.20 h⁻¹, and GHSV

of H_2 was 255 h⁻¹. After the reaction temperature was kept on stable for 1 h, the reaction products in the outlet of reactor was collected for 1 h at 0 °C, then it was analyzed by gas chromatograph (Perkin–Elmer, Autosystem XL, USA), in which 25 m × 0.32 mm (Ø) capillary column with 5% methyl phenyl silicone and the flame ionization detector were used.

The experiments of TPR were similar to [26]. X-ray diffraction (XRD) was used to examine the bulk structure of catalyst and analysis the dispersion of Cu in the catalyst. The XRD data were recorded at 25 °C by Rigaku D/Max-III B diffractometer (Japan) with Ni filter and Cu-K α radiation. BaF₂ annealed at 500 °C for 2 h in air was used as a non-intrinsic broadening sample to extract the micro-structure value of the reduced catalysts.

3. Results and discussion

The hydrogenation of MA was carried out over the Cu–Pd–Ti–Al–O (Pd/Cu = 8/10⁴) and Cu–Ti–Al–O catalysts, and the results are presented in Fig. 1. The Cu–Pd–Ti–Al–O catalyst has better catalytic activities of MA hydrogenation to BA

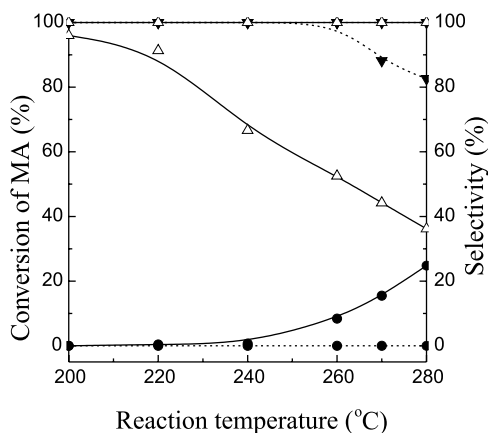


Fig. 1. Catalytic performance of the Cu–Pd–Ti–Al–O (Pd/Cu = 8/10⁴) (—) and Cu–Ti–Al–O (---) catalysts. (▼) Conversion of MA; (●) selectivity to BA and (Δ) selectivity to GBL. (The plot of MA conversion over Cu–Pd–Ti–Al–O is overlapped with the plot of selectivity to GBL over Cu–Ti–Al–O.)

than the Cu–Ti–Al–O catalyst. Over the Cu–Pd–Ti–Al–O catalyst, 24.8% selectivity to BA was obtained at 100% conversion of MA at 280 °C, and over the Cu–Ti–Al–O catalyst, BA was not detected in the outlet of the reactor and GBL was only product. These results indicate that Pd is an effective promoter of the Cu–Ti–Al–O catalyst for the selective hydrogenation of MA to BA. Using the Pd–Ti–Al–O catalyst (the loading of Pd is the same as the Cu–Pd–Ti–Al–O catalyst), only 0.02% selectivity to BA was obtained at 9.6% conversion of MA at 280 °C.

The effect of palladium loading on the performance of the Cu–Pd–Ti–Al–O catalyst for the hydrogenation of MA to BA is shown in Fig. 2. The MA conversion is affected by the change of palladium loading in the catalysts, and kept on ~100% at 200–280 °C. The selectivity to BA increases rapidly with an increase of the reaction temperature and loading of palladium. At 280 °C, 56.2% selectivity to BA can be obtained when the ratio of Pd/Cu is 3/100 in the Cu–Pd–Ti–Al–O catalyst. The other products are BDO, THF, GBL, butanol and so on.

The XRD patterns of three Cu–Pd–Ti–Al–O catalysts show that there are the phases of Cu, TiO₂ (anatase) and γ -Al₂O₃ and the diffraction

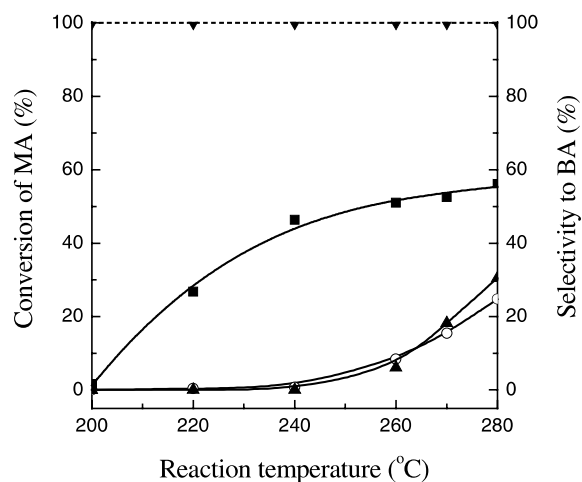


Fig. 2. Catalytic performance of the Cu–Pd–Ti–Al–O catalyst. Pd/Cu (atom ratio): (▲) 8/10⁴; (○) 12/10⁴ and (■) 3/100. (---) Conversion of MA and (—) selectivity to BA. (The plots of MA conversion are overlapped over three catalysts.)

peaks of Pd are not observed. It attributes to very low loading and high dispersion of palladium in the catalysts. Fig. 3 shows the XRD patterns of the Cu–Pd–Ti–Al–O (Pd/Cu = 8/10⁴) catalyst.

The micro-structure parameters of the catalyst were calculated based on the XRD data. The crystallite size and the crystallite micro-strain value of Cu (in Cu(1 1 1) a peak direction) are 2.4 nm and 5.8×10^{-3} , which means that copper disperses highly in the catalyst, too. But it is difficult to form the multi-hydrogen-group on the surface of Cu catalyst [27], and the multi-hydrogen-group can form on the surface of Pd catalyst [28,29]. The results above (Fig. 1) show that in the process of MA hydrogenation, BA was not obtained over the Cu–Ti–Al–O catalyst, and BA was produced abundantly over the catalyst including Pd. It indicates that the production of BA in the hydrogenation of MA has relation to the multi-hydrogen-group formed on the surface of catalyst. The presence of palladium in the Cu–Ti–Al–O catalyst helps to the formation of a multi-hydrogen-group on the catalyst. The multi-hydrogen-group can be provided by the cluster or small crystallite of palladium near Cu sites and results in MA hydrogenation to form BA, which is shown in Fig. 4(a). Moreover, the active H* formed on Pd can transfer from Pd to Cu, or to TiO₂, then from TiO₂ to Cu by spillover [30–32], which is also described as the Fig. 4(b). If the rate of transferring H* is quicker

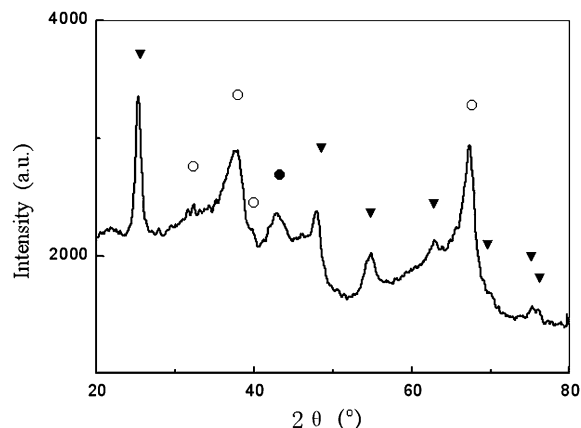


Fig. 3. XRD pattern of the Cu–Pd–Ti–Al–O (Pd/Cu = 8/10⁴) reduced catalyst. (●) Cu; (▼) TiO₂ and (○) γ -Al₂O₃.

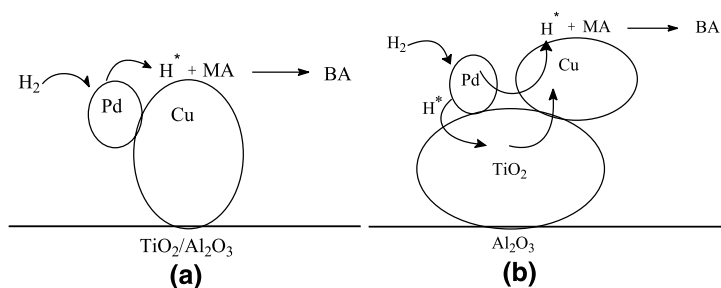


Fig. 4. Multi-hydrogen-group of $\text{Pd}^{\text{H}}\text{PD}^{\text{H}}\text{PD}^{\text{H}}$ and hydrogenation of MA to BA over the Cu–Ti–Al–O catalyst promoted by Pd.

than the rate of the surface reaction, MA adsorbed on the catalyst would be hydrogenated to BA by H^* .

4. Conclusion

Nanoparticle copper was obtained and palladium is dispersed highly on the Cu–Ti–Al–O catalyst promoted by Pd. The presence of Pd leads to the hydrogenation of MA to BA, the reason is that Pd helps to the formation of the multi-hydrogen-group on the catalyst. At 280 °C, 56.2% selectivity to BA and 100% conversion of MA were obtained over the Cu–Pd–Ti–Al–O (Pd/Cu = 3/100) catalyst. If Pd or Cu absents in the Cu–Pd–Ti–Al–O catalyst, the selectivity to BA is nearly zero. So, a novel method of producing butyric acid is proposed by the selective hydrogenation of maleic anhydride.

Acknowledgements

This study has been supported by Research Funds by Shanghai Nanotechnology Promotion Center of Shanghai Municipality (No. 0212 nm 007).

References

- [1] S.E. Lower, Seifen, Oele, Fette, Wachse 117 (1991) 403.
- [2] R.W. Johnson, R.W. Daniels, in: J.I. Kroschwitz, M. Howe-Grand, C.A. Treacy (Eds.), *Kirk-Othmer Encyclopedia of Chemical Technology*, vol. 3, fourth ed., Wiley, Canada, 1992, p. 188.
- [3] J.M. Allen, A.K. Wilson, P.L. Lucas, L.G. Curtis, US 5668273, 1997.
- [4] P.J. Villa, Pierre, F. Pieri, G.L. Ronco, E.P.R. Segard, Appl. WO 8902895, 1989.
- [5] P.P. Singh, P.S. Bedi, D. Singh, J. Stored Prod. Res. 23 (1987) 169.
- [6] J. Zigova, E. Sturdik, D. Vandak, S. Schlosser, Process Biochem. 34 (1999) 835.
- [7] Y.L. Chen, T.C. Chou, J. Appl. Electrochem. 26 (1996) 543.
- [8] S.B. Li, S.M. Zhang, K. Wu, Y.L. Li, Huaxue Shiji 14 (1992) 60.
- [9] H. Springer, P. Lappe, Appl. WO 066504, 2001.
- [10] J. Zigova, J. Svitel, E. Sturdik, Chem. Biochem. Eng. Q. 14 (2000) 95.
- [11] Y.C. Meng, T. Luo, CN 1229785, 1999.
- [12] J. Zigova, E. Sturdik, J. Ind. Microbiol. Biotechnol. 24 (2000) 153.
- [13] G. Stefani, F. Budi, C. Fumagalli, G.D. Suci, Chim. Ind. (Milan) 72 (1990) 604.
- [14] D. M. Sutton, G. Ahiles, A.F. Bacbes, Appl. WO 027058, 2001.
- [15] P. Liu, Y. Liu, Y.Q. Yin, J. Mol. Catal. A: Chem. 138 (1999) 129.
- [16] G.L. Castiglioni, C. Fumagalli, Appl. WO 9935139, 1999.
- [17] S.H. Cho, T.H. Kim, K.I. Kim, S.C. Cho, J.K. Park, H.D. Jeong, H.C. Bajaj, US 029302, 2001.
- [18] H.J. Wang, L.H. Tong, X.J. Zhang, Y.A. Zhou, CN 1154 872, 1999.
- [19] J. Raymond, T.G. Attig, R.A. Dubbert, EP 848991, 1998.
- [20] G.L. Castiglioni, C. Fumagalli, E. Armbruster, M. Messori, A. Vaccari, Chem. Ind. (Dekker) 75 (1998) 391.
- [21] A. Vaccari, G.L. Castiglioni, G. Fierro, M. Inversi, M. Lo Jacono, G. Minelli, L. Pettiti, P. Porta, M. Gazzano, Appl. Catal. A: Chem 123 (1995) 123.
- [22] A. Kuksal, E. Klemm, G. Emig, Stud. Surf. Sci. Catal. 130C (2000) 2111.
- [23] M. Neurock, P.S. Venkataraman, G.W. Coulston, Prepr. Am. Chem. Soc. Div. Pet. Chem. 42 (1997) 43.
- [24] V. Pallassana, M. Neurock, J. Phys. Chem. B 104 (2000) 9449.
- [25] W.J. Lu, Ph.D. Thesis, East China University of Science and Technology, Shanghai, 2003.

- [26] G.Z. Lu, X.Y. Wang, J.S. Wang, R. Wang, *J. Rare Earths* 18 (2000) 190.
- [27] S.S. Jing, in: Z.Y. Zhou (Ed.), *Organic Catalysis*, Shanghai Science and Technology Press, Shanghai, 1986, p. 65.
- [28] E.W. Plummer, A.E. Bell, *J. Vac. Sci. Tech.* 9 (1972) 583.
- [29] B.D. Barford, R.R. Rye, *J. Chem. Phys.* 60 (1974) 1046.
- [30] F. Roessner, T. Braunschweig, U. Roland, *J. Mol. Catal. A: Chem.* 127 (1997) 61.
- [31] R. Prins, *Stud. Surf. Sci. Catal.* 138 (2001) 1.
- [32] A.K. Hodnett, B. Delmon, *Stud. Surf. Sci. Catal.* 27 (1986) 53.