

Effect of reaction conditions on the catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ heteropolyacid catalyst in the direct preparation of dichloropropanol from glycerol in a liquid-phase batch reactor

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Abstract—Direct chlorination of glycerol to dichloropropanol (DCP) was conducted in a liquid-phase batch reactor using homogeneous $\text{H}_3\text{PW}_{12}\text{O}_{40}$ heteropolyacid (HPA) catalyst. The effect of reaction conditions (reaction time, reaction pressure, reaction temperature, and catalyst amount) on the catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the direct preparation of DCP from glycerol was examined. The optimum reaction pressure and reaction temperature were found to be 10 bar and 130 °C, respectively. The reaction temperature was more crucial than the reaction pressure in improving the selectivity to DCP. Selectivity to DCP increased with increasing reaction time and with increasing catalyst amount. Acid sites of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst favorably devoted to the chlorination of glycerol. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ served as an efficient catalyst in the direct preparation of DCP from glycerol under the mild reaction conditions.

Key words: Heteropolyacid Catalyst, Dichloropropanol, Glycerol, Chlorination, Bio-diesel

INTRODUCTION

Bio-diesel has attracted worldwide attention as a green fuel [1-7]. However, a major problem in the production of bio-diesel is that considerable amount of glycerol (ca. 10%) is formed as a by-product [8]. This results in an over-supply of glycerol and decreases its commercial value. Therefore, much attention has been paid to the direct conversion of glycerol to high-value chemicals [9]. One of the promising methods to convert glycerol to high-value chemical is to produce dichloropropanol (DCP) from glycerol in a single step. DCP is mainly used as a feedstock for the production of epichlorohydrin (ECH).

Fig. 1 shows the commercial process for producing DCP from propylene. The conventional preparation method of DCP is composed of two consecutive processes, which include the preparation of allyl chloride through chlorination of propylene at a high temperature and the preparation of DCP through subsequent chlorination of allyl chloride under the condition of excess amount of industrial water [10]. Therefore, the direct preparation of DCP from glycerol has many environmental and economical advantages over the conventional preparation method. Several processes utilizing carboxylic acids as catalysts have been developed for the direct preparation of DCP from glycerol [11-13]. However, it is known that these processes have some problems in separation of DCP from organic catalyst and in reuse of the catalyst. Therefore, the development of an efficient and reusable catalyst for the direct preparation of DCP from glycerol would be worthwhile.

Heteropolyacids (HPAs) are early transition-metal oxygen anion clusters that have been widely employed as homogeneous and het-

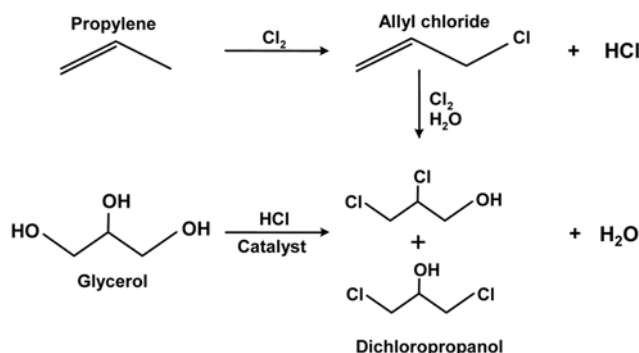


Fig. 1. A commercial process for producing dichloropropanol (DCP) from propylene.

erogeneous catalysts for acid-base and oxidation reactions [14-22]. One of the great advantages of HPA catalysts is that their catalytic properties can be controlled in a systematic way by changing the identity of heteroatom and framework polyatom [23-30]. Their excellent thermal and chemical stability also makes HPAs good candidates in catalytic applications that may require extreme environments [16-18].

A series of preliminary experiments investigating the catalytic performance of heteroatom- and/or polyatom-substituted HPA catalysts ($\text{H}_3\text{PMo}_{12-X}\text{W}_X\text{O}_{40}$ ($X=0-12$), $\text{H}_4\text{SiMo}_{12-X}\text{W}_X\text{O}_{40}$ ($X=0-12$), $\text{H}_{3+X}\text{PW}_{12-X}\text{V}_X\text{O}_{40}$ ($X=0-3$), and $\text{H}_{3+X}\text{PMo}_{12-X}\text{V}_X\text{O}_{40}$ ($X=0-3$)) in the direct preparation of DCP from glycerol in a liquid-phase batch reactor revealed that the catalytic performance increased with increasing acid strength of the HPA catalyst [31]. It was found that $\text{H}_3\text{PW}_{12}\text{O}_{40}$ with the highest acid strength showed the best catalytic performance among the HPA catalysts examined. In this work, therefore, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was chosen as a model catalyst for the direct preparation of DCP

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from glycerol. The effect of reaction conditions (reaction time, reaction pressure, reaction temperature, and catalyst amount) on the catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the direct preparation of DCP from glycerol in a liquid-phase batch reactor was investigated. We are the first to report the catalytic activity of HPA catalyst in the direct preparation of DCP from glycerol.

EXPERIMENTAL

Commercially available $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst was purchased from Sigma-Aldrich Chemical Co. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst was thermally treated at 300 °C for 2 h for precise quantification, prior to use in the reaction.

Direct preparation of DCP from glycerol was carried out in a liquid-phase batch reactor (200 ml) using homogeneous $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst, with a variation of reaction time, reaction pressure, reaction temperature, and catalyst amount. Interior parts of the batch reactor were made of Hastelloy C and Teflon which were highly resistant to the chlorination agent. 12.6 g of glycerol (reactant), 78.9 g of aqueous HCl solution (37 wt%, chlorination agent), 20 g of H_2O (solvent), and a known amount of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst (15–48 g) were charged into the batch reactor. After the homogeneous solution was heated to the reaction temperature (100–150 °C) with vigorous stirring (450 rpm), nitrogen was fed into the reactor to keep the reaction pressure at a constant level (1–25 bar). The catalytic reaction was carried out for a given time (5–30 h) with vigorous stirring. The reaction products were analyzed with a gas chromatograph (HP 5890 II) equipped with an FID. Conversion of glycerol and selectivity to DCP were calculated according to the following equations.

Conversion of glycerol (%)

$$= \frac{\text{Moles of glycerol reacted}}{\text{Moles of glycerol supplied}} \times 100 \quad (1)$$

Selectivity to DCP (%)

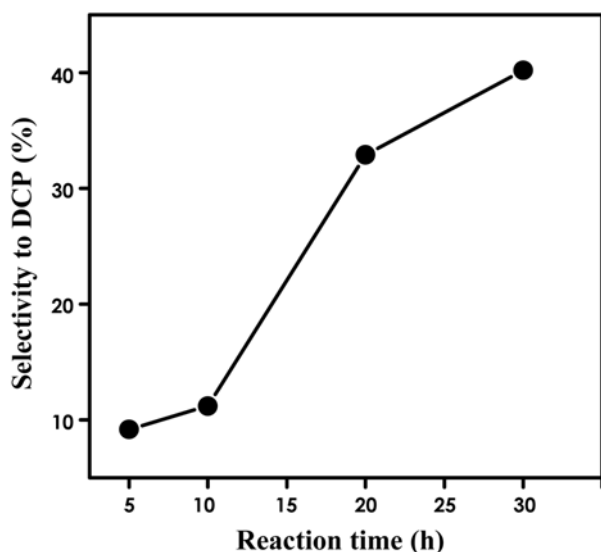


Fig. 2. Effect of reaction time on the catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the direct preparation of DCP from glycerol: reaction temperature=110 °C, reaction pressure=10 bar, catalyst amount=15 g.

$$= \frac{\text{Moles of dichloropropanol produced}}{\text{Moles of glycerol reacted}} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Fig. 2 shows the effect of reaction time on the catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the direct preparation of DCP from glycerol. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst showed 100% conversion of glycerol in all the experimental runs. In the catalytic reaction, small amounts of acrolein, dichloropropane, propanediol, and dichloroethane were formed as by-products. Importantly, monochloropropanediol (MCPD) was produced as a major intermediate. As shown in Fig. 2, selectivity to DCP increased with increasing reaction time. Selectivity to by-products was ca. 8% with no great difference. The balance selectivity in Fig. 2 corresponds to the MCPD selectivity. This result indicates that glycerol is converted to MCPD, and in turn, MCPD is further chlorinated to DCP via the reaction route of glycerol → MCPD → DCP.

Fig. 3 shows the effect of reaction pressure on the catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the direct preparation of DCP from glycerol. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst showed 100% conversion of glycerol in each run. Selectivity to DCP increased with increasing reaction pressure at low pressure region and showed the maximum value (32.9%) at 10 bar. However, selectivity to DCP was slightly decreased at reaction pressures above 10 bar. Thus, the optimum reaction pressure was found to be 10 bar.

Fig. 4 shows the effect of reaction temperature on the catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the direct preparation of DCP from glycerol. The HPA catalyst showed 100% conversion of glycerol in all the experimental runs. Selectivity to DCP increased with increasing reaction temperature at low temperature region and showed the maximum value (78.0%) at 130 °C. However, selectivity to DCP was slightly decreased at temperatures above 130 °C. This result indicates that the optimum reaction temperature was 130 °C. As

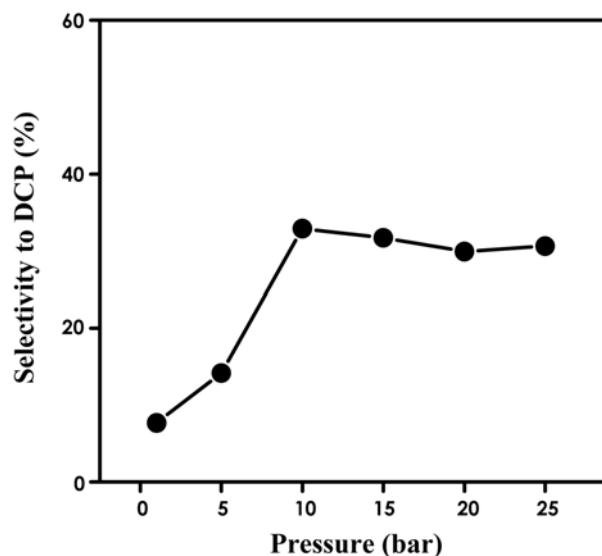


Fig. 3. Effect of reaction pressure on the catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the direct preparation of DCP from glycerol: reaction time=20 h, reaction temperature=110 °C, catalyst amount=15 g.

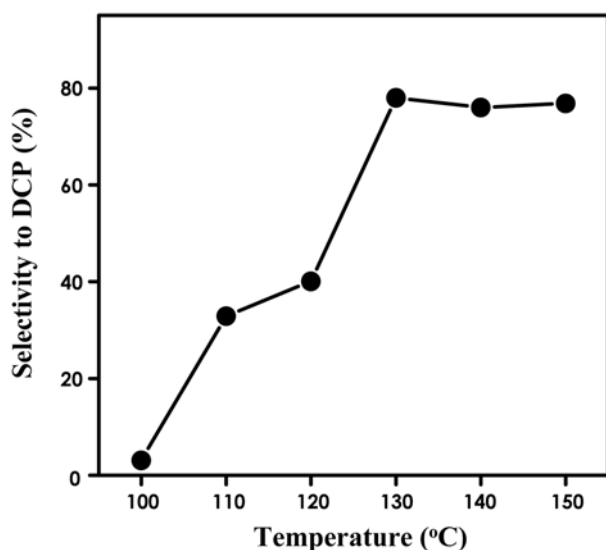


Fig. 4. Effect of reaction temperature on the catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the direct preparation of DCP from glycerol: reaction time=20 h, reaction pressure=10 bar, catalyst amount=15 g.

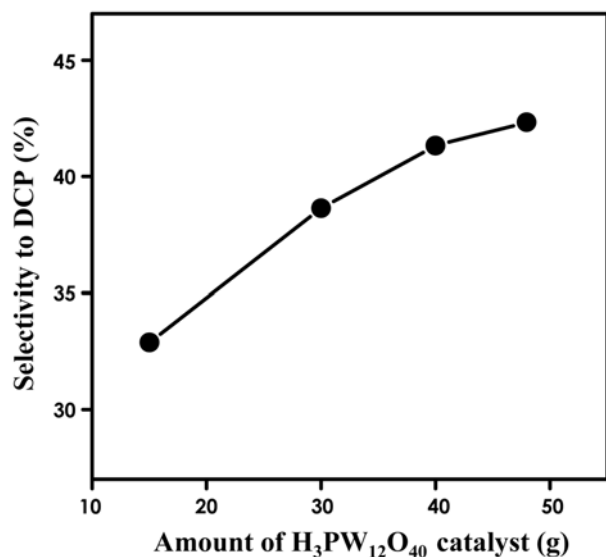


Fig. 5. Effect of catalyst amount on the catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the direct preparation of DCP from glycerol: reaction time=20 h, reaction temperature=110 °C, reaction pressure=10 bar.

shown in Fig. 3 and Fig. 4, it is noticeable that the reaction temperature was more crucial than the reaction pressure in improving the selectivity to DCP.

Fig. 5 shows the effect of catalyst amount on the catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the direct preparation of DCP from glycerol. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst showed 100% conversion of glycerol in all the catalytic reactions. It was observed that selectivity to DCP increased with increasing catalyst amount. This indicates that Brønsted acid sites of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst were favorably devoted to the chlorination of glycerol. It also means that large acid amount of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst was favorable for the direct preparation of DCP

from glycerol. It is concluded that $\text{H}_3\text{PW}_{12}\text{O}_{40}$, which retained the highest acid strength among the HPA catalysts, served as an efficient catalyst in the direct preparation of DCP from glycerol under the mild reaction conditions.

CONCLUSIONS

Direct preparation of DCP from glycerol was carried out in a liquid-phase batch reactor using homogeneous $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst. The effect of reaction conditions (reaction time, reaction pressure, reaction temperature, and catalyst amount) on the catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the direct preparation of DCP from glycerol was investigated. It was revealed that selectivity to DCP increased with increasing reaction time. Selectivity to DCP showed the maximum value at a reaction pressure of 10 bar and a reaction temperature of 130 °C. The reaction temperature played a more important role in improving the selectivity to DCP than the reaction pressure. It was also found that selectivity to DCP increased with increasing catalyst amount. Brønsted acid sites of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst were favorably devoted to the chlorination of glycerol. It is concluded that $\text{H}_3\text{PW}_{12}\text{O}_{40}$ efficiently catalyzed the direct conversion of glycerol to DCP under the mild reaction conditions.

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REFERENCES

1. Y. C. Bak, J. H. Choi, S. B. Kim and D. W. Kang, *Korean J. Chem. Eng.*, **13**, 242 (1996).
2. A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, *Science*, **311**, 484 (2006).
3. Z. M. Wang, J. S. Lee, J. Y. Park, C. Z. Wu and Z. H. Yuan, *Korean J. Chem. Eng.*, **24**, 1027 (2007).
4. K. W. Lee, J. X. Yu, J. H. Mei, L. Yan, Y. W. Kim and K. W. Chung, *J. Ind. Eng. Chem.*, **24**, 1027 (2007).
5. Y.-M. Park, D.-W. Lee, D.-K. Kim, J.-S. Lee and K.-Y. Lee, *Catal. Today*, **131**, 238 (2008).
6. C. S. MacLeod, A. P. Harvey, A. F. Lee and K. Wilson, *Chem. Eng. J.*, **135**, 63 (2008).
7. U. Rashid and F. Anwar, *Fuel*, **87**, 265 (2008).
8. A. Strivastava and R. Prasad, *Renew. Sust. Energ. Rev.*, **4**, 111 (2000).
9. V. L. C. Gonçalves, B. P. Pinto, J. C. Silva and C. J. A. Mota, *Catal. Today*, **133**, 673 (2008).
10. N. Nagato, H. Mori, K. Maki and R. Ishioka, US Patent 4,634,784 (1987).
11. P. Kraft, P. Gilbeau, B. Gosselin and S. Claessens, PCT Patent WO2005/054167 A1 (2005).
12. P. Kubicek, P. Sladek and I. Buricova, PCT Patent WO2005/021476 A1 (2005).
13. D. J. Schreck, W. J. Kruper Jr., R. D. Varjian, M. E. Jones, R. M. Campbell, K. Kearns, B. D. Hook, J. R. Briggs and J. G. Hippler, PCT Patent WO2006/020234 A1 (2006).

14. C. Y. Hwang, J. W. Kwak, W. Y. Lee and H.-I. Lee, *Korean J. Chem. Eng.*, **3**, 31 (1986).
15. I. K. Song, S. H. Moon and W. Y. Lee, *Korean J. Chem. Eng.*, **8**, 33 (1991).
16. I. V. Kozhevnikov, *Catal. Rev. -Sci. Eng.*, **37**, 311 (1995).
17. C. L. Hill and C. M. Prosser-McCartha, *Coord. Chem. Rev.*, **143**, 407 (1995).
18. T. Okuhara, N. Mizuno and M. Misono, *Adv. Catal.*, **41**, 113 (1996).
19. M. Misono, *Korean J. Chem. Eng.*, **14**, 427 (1997).
20. W. Y. Lee, I. K. Song, J. K. Lee, G. I. Park and S. S. Lim, *Korean J. Chem. Eng.*, **14**, 432 (1997).
21. J. S. Choi, I. K. Song and W. Y. Lee, *Korean J. Chem. Eng.*, **17**, 280 (2000).
22. R. Wang, *Korean J. Chem. Eng.*, **20**, 659 (2003).
23. J. S. Lee, J. W. Woo, C. W. Lee, K. S. Hong and J. K. Yeo, *Korean J. Chem. Eng.*, **7**, 145 (1990).
24. H. C. Kim, S. H. Moon and W. Y. Lee, *Chem. Lett.*, **20**, 447 (1991).
25. I. K. Song and M. A. Barteau, *Korean J. Chem. Eng.*, **19**, 567 (2002).
26. I. K. Song and M. A. Barteau, *J. Mol. Catal. A*, **182**, 175 (2002).
27. M. A. Barteau, J. E. Lyons and I. K. Song, *J. Catal.*, **216**, 236 (2003).
28. I. K. Song, H. S. Kim and M.-S. Chun, *Korean J. Chem. Eng.*, **20**, 844 (2003).
29. I. K. Song and M. A. Barteau, *J. Mol. Catal. A*, **212**, 229 (2004).
30. M. H. Youn, D. R. Park, J. C. Jung, H. Kim, M. A. Barteau and I. K. Song, *Korean J. Chem. Eng.*, **24**, 51 (2007).
31. S. H. Lee, D. R. Park, H. Kim, J. Lee, J. C. Jung, S. Y. Woo, W. S. Song, M. S. Kwon and I. K. Song, *Catal. Commun.*, **9**, 1920 (2008).