

Regeneration of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst in direct preparation of dichloropropanol (DCP) from glycerol and hydrochloric acid gas

Sun Ho Song*, Sang Hee Lee*, Dong Ryl Park*, Heesoo Kim*, Sung Yul Woo**, Won Seob Song**, Myong Suk Kwon**, and In Kyu Song*,†

*School of Chemical and Biological Engineering, Institute of Chemical Processes, Seoul National University, Shinlim-dong, Kwanak-gu, Seoul 151-744, Korea

**Samsung Fine Chemicals Corporation, Nam-gu, Ulsan 680-090, Korea

(Received 1 February 2009 • accepted 30 March 2009)

Abstract—Methods for regenerating $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst in the solvent-free direct preparation of dichloropropanol (DCP) from glycerol and hydrochloric acid gas were investigated. Regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst was then applied to the solvent-free direct preparation of DCP. In the solvent-free direct preparation of DCP, selectivity for DCP over $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst regenerated by method I (recovery of solid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst by evaporating homogeneous liquid-phase product solution) significantly decreased with increasing recycling run, while that over $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst regenerated by method II (regeneration of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst by oxidative calcination of solid product recovered by method I) was slightly decreased with no significant catalyst deactivation with respect to recycling run. On the other hand, selectivity for DCP over $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst regenerated by method III (regeneration of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst by recrystallization and subsequent oxidative calcination of solid product recovered by method II) was the same as that over fresh catalyst without any catalyst deactivation with respect to recycling run. Thus, method III was found to be the most efficient method for the regeneration of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst.

Key words: Dichloropropanol, Glycerol, Hydrochloric Acid Gas, Heteropolyacid Catalyst, Regeneration Method

INTRODUCTION

The growing production of biodiesel from vegetable oils has led to a surplus of glycerol (by-product) in the industrial market [1-9]. Therefore, many attempts have been made on the direct conversion of glycerol to high-value chemicals [10]. One of promising methods to convert glycerol to high-value chemicals is to produce dichloropropanol (DCP) from glycerol through a single-step chlorination reaction [11-13].

Conventional and proposed processes for producing DCP are shown in Fig. 1. The conventional preparation process of DCP in-

cludes two consecutive processes of preparing allyl chloride through chlorination of propylene at high temperature and preparing DCP through subsequent chlorination of allyl chloride under the condition of excess amount of industrial water [14]. In the preparation of DCP from propylene, however, a large amount of sludge is formed, which eventually can cause severe technical and environmental problems [15]. Therefore, direct preparation of DCP from glycerol has attracted much attention as an economical and environmentally benign process (Fig. 1) [11-13]. Although several catalytic processes utilizing carboxylic acid-based catalysts have been developed for the direct preparation of DCP from glycerol, it is known that these processes have some problems in catalyst recovery and product purification [16-18]. Thus, developing an efficient and reusable catalyst for the direct preparation of DCP from glycerol would be of great interest.

Heteropolyacids (HPAs) are early transition metal-oxygen anion clusters that have been widely employed as homogeneous and heterogeneous catalysts for acid-base and oxidation reactions [19-26]. One of the great advantages of HPA catalysts is that their catalytic properties can be controlled by changing the identity of counter-cations, heteroatoms, and framework polyatoms [27-31]. Their excellent chemical and thermal stability also makes them well suited for catalytic applications that may require harsh environments [32-34].

It was reported by this research group that HPA catalysts were highly active in the direct preparation of DCP from glycerol [11-13]. Among various HPA catalysts, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ with the highest acid strength was found to show the best catalytic performance in the direct preparation DCP from glycerol and aqueous hydrochloric acid

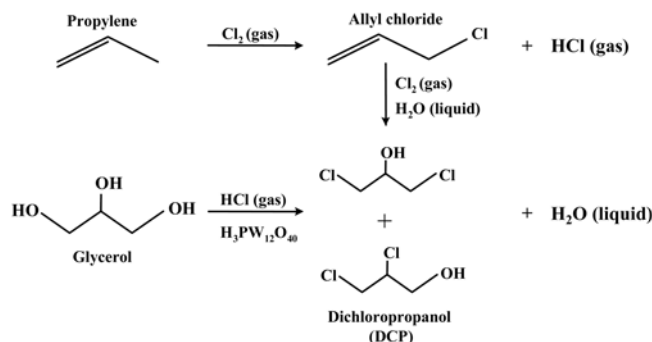


Fig. 1. Conventional and proposed processes for producing dichloropropanol (DCP).

†To whom correspondence should be addressed.
E-mail: inksong@snu.ac.kr

[11,12]. It was also revealed that formation of DCP over $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst was much enhanced by reacting glycerol with hydrochloric acid gas under solvent-free condition (Fig. 1) [13]. Therefore, an investigation of the regeneration method for $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst in the solvent-free direct preparation of DCP from glycerol and hydrochloric acid gas would be worthwhile.

In this work, methods for regenerating $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst in the solvent-free direct preparation of DCP from glycerol and hydrochloric acid gas were investigated. Regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst was characterized by FT-IR, TGA, NH_3 -TPD, and CHNS elemental analyses. Regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst was then applied to the solvent-free direct preparation of DCP from glycerol and hydrochloric acid gas to check the effectiveness of regeneration method. This is the first example reporting the method of catalyst recovery in the direct preparation of DCP from glycerol and hydrochloric acid gas.

EXPERIMENTAL

1. Catalyst and Material

Glycerol ($\geq 99.5\%$) and hydrochloric acid gas (99.7%) were purchased from Sigma-Aldrich Chemicals and Tsurumi Soda, respectively. Commercially available $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst was purchased from Sigma-Aldrich Chemicals. The catalyst was thermally treated at 300°C for 2 h for precise quantification, prior to use in the reaction.

2. Direct Preparation of DCP from Glycerol and Hydrochloric Acid Gas

DCP was directly prepared from glycerol and hydrochloric acid gas in a gas-liquid phase batch reactor (200 ml). Fig. 2 shows a schematic diagram of the reaction apparatus. Interior parts of the batch reactor were made of Hastelloy C and Teflon, which are highly re-

sistant to the chlorination agent. Solvent-free direct preparation of DCP from glycerol was carried out with identical agitation speed (900 rpm), reaction time (3 h), reaction temperature (130°C), reaction pressure (3 bar), and fresh/regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalysts (3 g). 100 g of glycerol (reactant) and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst (3 g) were charged into the reactor at room temperature. After being purged with nitrogen, the reactor was heated to the reaction temperature (130°C) under a given agitation speed (900 rpm). Hydrochloric acid gas was then continuously fed into the reactor at constant pressure (3 bar) to conduct the chlorination of glycerol for a given reaction time (3 h). After the reaction, the autoclave was purged with nitrogen and cooled to room temperature for analysis. Reaction products were analyzed with a gas chromatograph (HP 5890 II) equipped with a DB-WAX capillary column and a flame ionization detector (FID). The conversion of glycerol and selectivity for DCP were calculated according to the following equations.

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

$$\text{Selectivity for DCP (\%)} = \frac{\text{Moles of DCP formed}}{\text{Moles of glycerol reacted}} \times 100 \quad (2)$$

3. Regeneration Method for $\text{H}_3\text{PW}_{12}\text{O}_{40}$ Catalyst

Fig. 3 shows a schematic diagram of the regeneration method for $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst. A series of three different regeneration methods for $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst were employed as follows. A homogeneous liquid-phase product solution containing $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst was evaporated at 300°C for 2 h in an evaporator with condenser under nitrogen atmosphere to recover solid-state catalyst from liquid product. The solid was then ground to obtain fine powders of

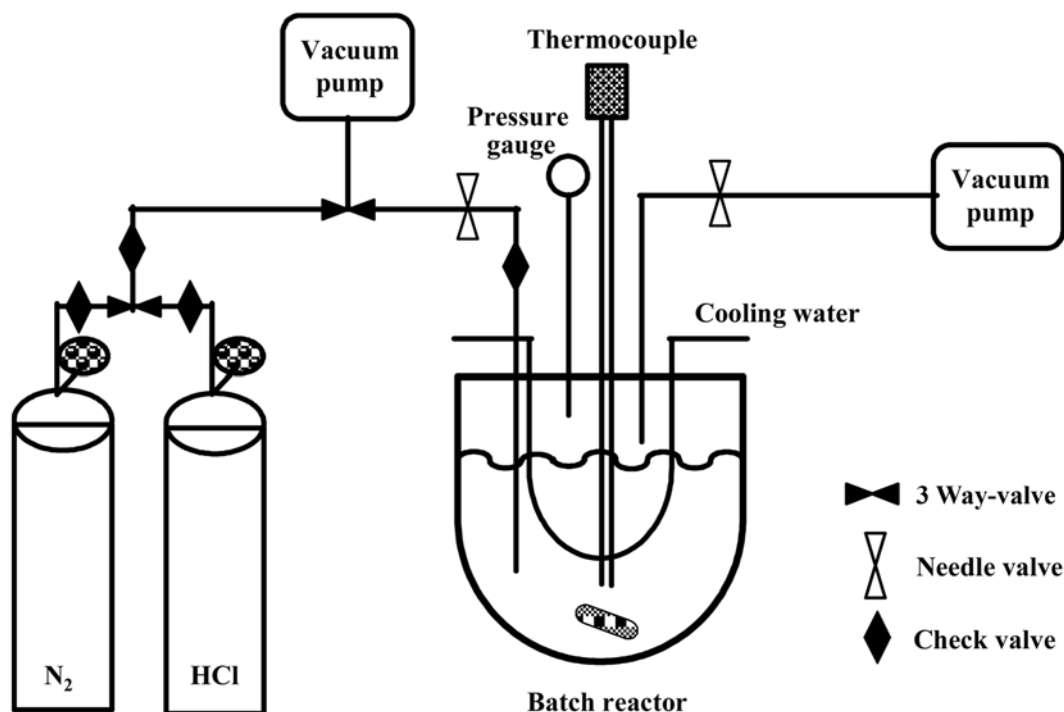


Fig. 2. Schematic diagram of reaction apparatus.

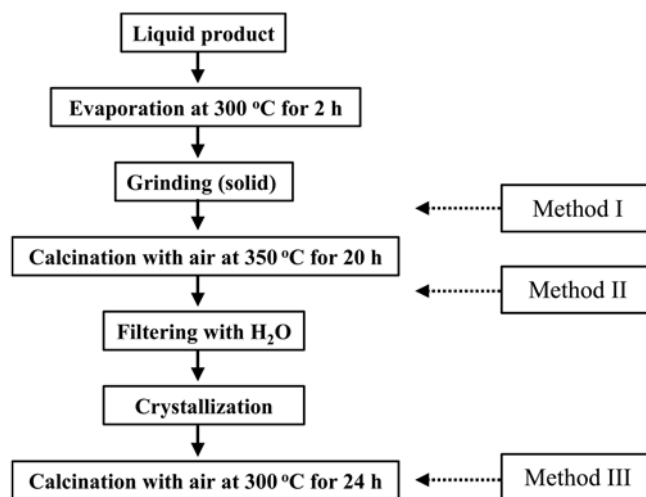


Fig. 3. Schematic diagram of regeneration method for $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst.

$\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst (the regeneration method was denoted as method I). The solid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst regenerated by method I was additionally calcined at $350\text{ }^\circ\text{C}$ for 20 h in an electric furnace with an air stream (15 ml/min) to remove any residual carbon species in the catalyst (the regeneration method was denoted as method II). After the solid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst regenerated by Method II was dissolved in distilled water, the solution was filtered to remove any insoluble species. The solid catalyst recrystallized from distilled water at $80\text{ }^\circ\text{C}$ was further calcined at $300\text{ }^\circ\text{C}$ for 24 h with an air stream (15 ml/min) (the regeneration method was denoted as method III).

4. Characterization

IR spectra of fresh and regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalysts were obtained with an FT-IR spectrometer (Nicolet, Impact 410). Thermal behavior of fresh and regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalysts was examined by TGA analysis (Pheometric Scientific, TGA-100). Carbon content in the regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalysts was determined by CHNS elemental analysis (Leco, CHNS 932). Acid properties of fresh and regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalysts were measured by NH_3 -TPD experiments. Each catalyst (0.1 g) was charged into a tubular quartz reactor of the conventional TPD apparatus. The catalyst was pretreated at $200\text{ }^\circ\text{C}$ for 1 h under a flow of helium (20 ml/min) to remove any physisorbed organic molecules. 20 ml of NH_3 was then pulsed into the reactor every minute at room temperature under a flow of helium (5 ml/min), until the acid sites were saturated with NH_3 . Physisorbed NH_3 was removed by evacuating the catalyst sample at $100\text{ }^\circ\text{C}$ for 1 h. Furnace temperature was increased from room temperature to $800\text{ }^\circ\text{C}$ at a heating rate of $5\text{ }^\circ\text{C}/\text{min}$ under the flow of helium (10 ml/min). The desorbed NH_3 was detected by a GC-MSD (Agilent, MSD-6890N GC).

RESULTS AND DISCUSSION

1. Characterization of Regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ Catalyst

Carbon content in the regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalysts determined by CHNS elemental analysis is listed in Table 1. Carbon content in the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst regenerated by method I was ca. 60 wt%, while that in the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst regenerated by method II and

Table 1. Carbon content in the regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalysts determined by CHNS elemental analysis

Regeneration method	Carbon content (wt%)
Method I	59.1
Method II	2.1
Method III	1.7

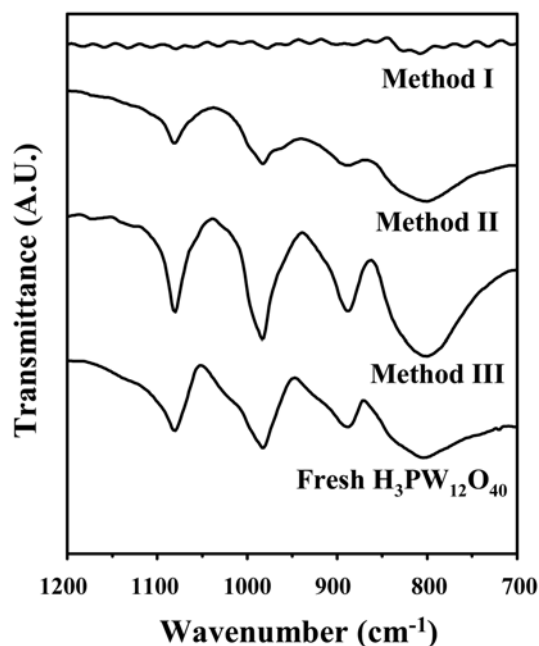


Fig. 4. FT-IR spectra of fresh and regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$.

method II was negligible. This means that a large amount of carbon species was deposited on the catalyst regenerated by method I, indicating that method I was not efficient for the regeneration $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst. The above result also implies that the catalyst regenerated by method I needs further treatments for the successful regeneration of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst, as evidenced by the following FT-IR analysis.

Fig. 4 shows the FT-IR spectra of fresh and regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$. The Keggin structure (the primary structure) of HPA catalyst could be identified by four characteristic IR bands appearing in the range of $700\text{--}1,200\text{ cm}^{-1}$, as observed for fresh $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst. It was found that $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst regenerated by method II and method III showed the characteristic IR bands of fresh catalyst at the same positions, while no characteristic IR bands were observed in the catalyst regenerated by method I due to the strong absorbance of carbon species by infrared beam. Table 1 and Fig. 4 clearly show that most of the carbon species were removed by the oxidative calcination at $350\text{ }^\circ\text{C}$ (method II). This result indicates that calcination at high temperature to remove carbon species from the catalyst was essential for successful regeneration of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst. It should be noted that IR bands of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst regenerated by method III were almost identical to those of fresh $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst.

Fig. 5 shows the TGA profiles of fresh and regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$. Weight loss below $200\text{ }^\circ\text{C}$ observed for fresh $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was attributed to the removal of physisorbed water molecules. $\text{H}_3\text{PW}_{12}\text{O}_{40}$

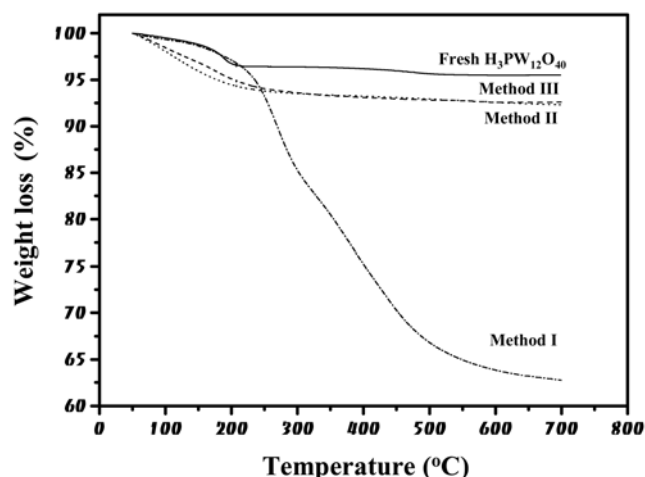


Fig. 5. TGA profiles of fresh and regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$.

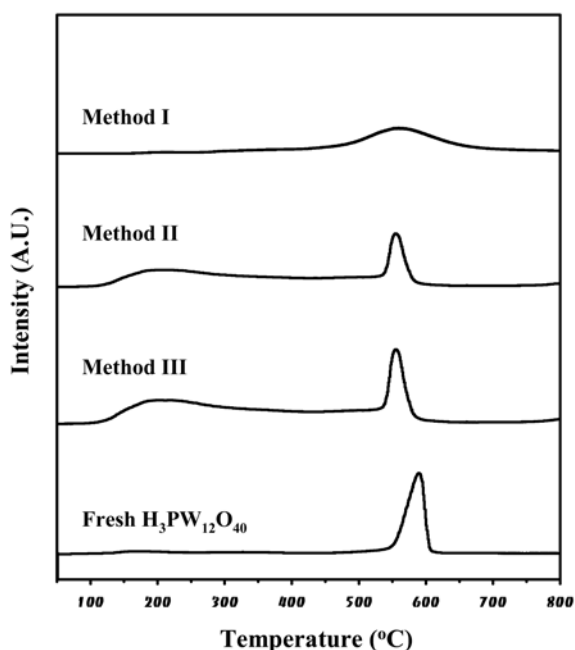


Fig. 6. NH_3 -TPD profiles of fresh and regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$.

regenerated by method I showed sharp weight loss due to the removal of carbon species. On the other hand, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ regenerated by method II and method III experienced slight weight loss

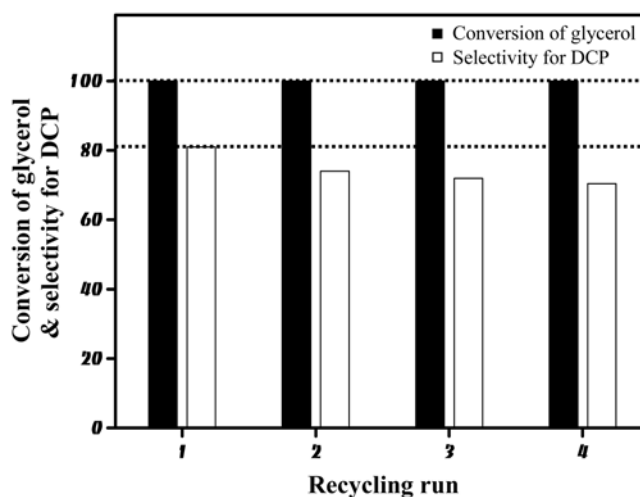


Fig. 8. Conversion of glycerol and selectivity for DCP in the direct preparation of DCP from glycerol and hydrochloric acid gas over fresh $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst (Run 1) and regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst by Method I (Run 2-Run 4) with respect to recycling run: glycerol=100 g, reaction temperature=130 °C, reaction pressure=3 bar, reaction time=3 h, RPM=900, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ =3 g.

due to the presence of small amount of carbon species. These results were in good agreement with CHNS elemental analyses (Table 1).

Fig. 6 shows the NH_3 -TPD profiles of fresh and regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$. All the regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalysts retained comparable acid strength to the fresh $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst. However, the acid amount of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ regenerated by method I was significantly smaller than that of the other catalysts. This was due to the presence of a large amount of carbon species in the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ regenerated by method I.

2. Catalytic Performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ Regenerated by Method I

According to our previous works [11-13], chlorination of glycerol occurs via the following consecutive reaction steps as shown in Fig. 7; glycerol \rightarrow MCPD \rightarrow DCP \rightarrow TCP. Reaction rate decreases in the order of first-step reaction > second-step reaction > third-step reaction. Among various HPA catalysts, it was also reported [11-13] that $\text{H}_3\text{PW}_{12}\text{O}_{40}$ showed the best catalytic performance in the direct preparation of DCP from glycerol in both water-solvent and solvent-free chlorination reactions. In this work, therefore, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was chosen as a model catalyst to see the effect of regeneration method on the catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst for DCP for-

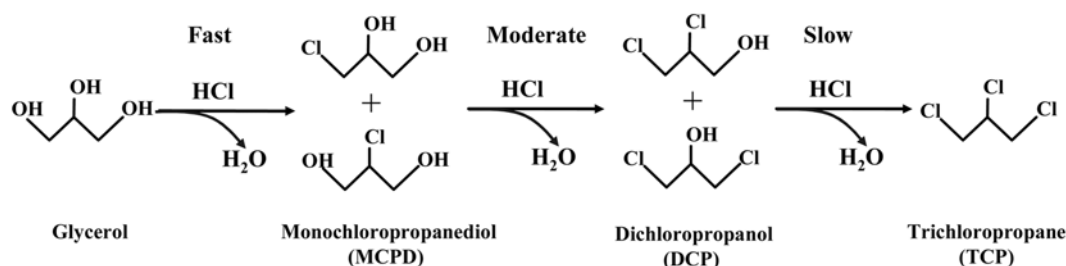


Fig. 7. Reaction pathway for the chlorination of glycerol.

mation.

Fig. 8 shows the conversion of glycerol and selectivity for DCP in the direct preparation of DCP from glycerol and hydrochloric acid gas over fresh $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst (run 1) and regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst by method I (run 2-run 4) with respect to recycling run. In all the catalytic reactions utilizing fresh/regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst under the reaction conditions employed in this work, the conversion of glycerol was 100% while selectivity for DCP was different depending on the regeneration method and recycling run. Selectivity for DCP over fresh $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst was found to be ca. 80%. However, selectivity for DCP over $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst regenerated by method I significantly decreased with increasing recycling run (selectivity for TCP was less than 2% and balance selectivity corresponds to selectivity for MCPD, although they were not shown here). This indicates that method I was not efficient for the regeneration of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst in the direct preparation of DCP from glycerol and hydrochloric acid gas. The drastic decrease of DCP selectivity over $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst regenerated by method I was due to the large amount of carbon species deposited on the catalyst as revealed by CHNS (Table 1), FT-IR (Fig. 4), and TGA (Fig. 5) analyses.

3. Catalytic Performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ Regenerated by Method II

Fig. 9 shows the conversion of glycerol and selectivity for DCP in the direct preparation of DCP from glycerol and hydrochloric acid gas over fresh $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst (run 1) and regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst by method II (run 2-run 4) with respect to recycling run. All the catalysts exhibited 100% conversion of glycerol. Unlike the catalyst regenerated by method I (Fig. 8), $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst regenerated by method II showed a slightly decreased selectivity for DCP with no great catalyst deactivation with respect to recycling run. This means that method II was relatively efficient for the regeneration of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst. In other words, oxidative calcination of

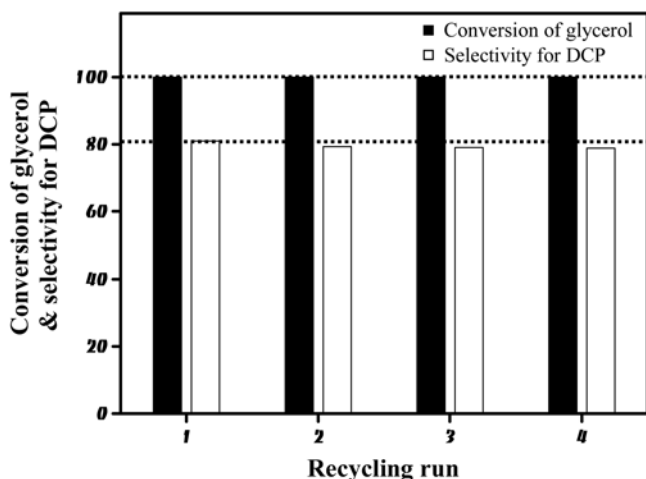


Fig. 9. Conversion of glycerol and selectivity for DCP in the direct preparation of DCP from glycerol and hydrochloric acid gas over fresh $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst (Run 1) and regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst by Method II (Run 2-Run 4) with respect to recycling run: glycerol=100 g, reaction temperature=130 °C, reaction pressure=3 bar, reaction time=3 h, RPM=900, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ =3 g.

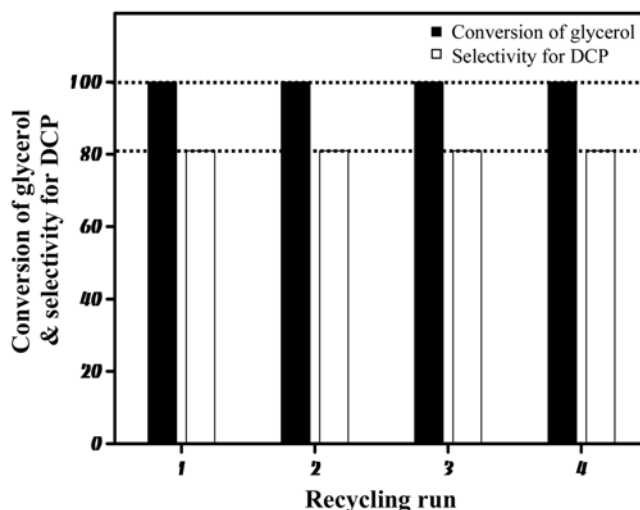


Fig. 10. Conversion of glycerol and selectivity for DCP in the direct preparation of DCP from glycerol and hydrochloric acid gas over fresh $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst (Run 1) and regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst by Method III (Run 2-Run 4) with respect to recycling run: glycerol=100 g, reaction temperature=130 °C, reaction pressure=3 bar, reaction time=3 h, RPM=900, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ =3 g.

$\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst at high temperature was efficient for the removal of carbon species from the catalyst, leading to the successful regeneration of the catalyst.

4. Catalytic Performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ Regenerated by Method III

Fig. 10 shows the conversion of glycerol and selectivity for DCP in the direct preparation of DCP from glycerol and hydrochloric acid gas over fresh $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst (run 1) and regenerated $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst by method III (run 2-run 4) with respect to recycling run. All the catalysts exhibited 100% conversion of glycerol. Unlike the catalyst regenerated by method I (Fig. 8) and method II (Fig. 9), $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst regenerated by method III showed the same selectivity for DCP as fresh catalyst without any catalyst deactivation with respect to recycling run. This means that method III was the most efficient method for the regeneration of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst. The constant catalytic activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ regenerated by method III was due to very small amount of carbon species (Table 1) and perfect recovery of primary structure of $[\text{PW}_{12}\text{O}_{40}]^{3-}$. Thus, we have successfully demonstrated that $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst efficient for solvent-free direct preparation of DCP could be easily recovered by a series of simple physical treatments (evaporation, oxidative calcination, recrystallization, and subsequent oxidative calcination).

CONCLUSIONS

Regeneration methods for $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst in the solvent-free direct preparation of DCP from glycerol and hydrochloric acid gas were investigated. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst regenerated by method I retained ca. 60 wt% carbon species, while that regenerated by method II and method III contained negligible amount of carbon species. FT-IR analysis revealed that $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst regenerated by method I showed no characteristic IR bands, while that regenerated by method II and method III showed the characteristic IR bands of fresh

catalyst at the same positions. TGA analysis showed that $\text{H}_3\text{PW}_{12}\text{O}_{40}$ regenerated by method I exhibited sharp weight loss due to the removal of carbon species, while that regenerated by method II and method III experienced slight weight loss due to the presence of small amount of carbon species. NH_3 -TPD analysis also revealed that the acid amount of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ regenerated by method I was significantly smaller than that of the other catalysts, due to the presence of a large amount of carbon species. In the solvent-free direct preparation of DCP from glycerol and hydrochloric acid gas, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst regenerated by method I showed a drastically decreased selectivity for DCP with increasing recycling run due to large amount of carbon deposited on the catalyst. However, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst regenerated by method II showed a slightly decreased selectivity for DCP with no great catalyst deactivation with respect to recycling run. Furthermore, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst regenerated by method III showed the same selectivity for DCP as fresh catalyst without any catalyst deactivation with respect to recycling run. Among the regeneration methods examined in this work, method III was the most efficient method for the regeneration of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst.

ACKNOWLEDGMENTS

The authors wish to acknowledge support from the Korean Institute of Industrial Technology (2007-A027-00).

REFERENCES

1. Y. C. Bak, J. H. Choi, S. B. Kim and D. W. Kang, *Korean J. Chem. Eng.*, **13**, 242 (1996).
2. Z. M. Wang, J. S. Lee, J. Y. Park, C. Z. Wu and Z. H. Yuan, *Korean J. Chem. Eng.*, **24**, 1027 (2007).
3. 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).
4. Y. K. Hong and W. H. Hong, *Korean Chem. Eng. Res.*, **45**, 424 (2007).
5. Z. M. Wang, J. S. Lee, J. Y. Park, C. Z. Wu and Z. H. Yuan, *Korean J. Chem. Eng.*, **25**, 670 (2008).
6. K. B. Vu, T. D. N. Phan, S. Kim and E. W. Shin, *Korean Chem. Eng. Res.*, **46**, 189 (2008).
7. J.-D. Choi, D.-K. Kim, J.-Y. Park, Y.-W. Lee and J.-S. Lee, *Korean Chem. Eng. Res.*, **46**, 194 (2008).
8. Y.-M. Park, D.-W. Lee, D.-K. Kim, J.-S. Lee and K.-Y. Lee, *Catal. Today*, **131**, 238 (2008).
9. V. L. C. Gonçalves, B. P. Pinto, J. C. Silva and C. J. A. Mota, *Catal. Today*, **133**, 673 (2008).
10. H. Atia, U. Armbruster and A. Martin, *J. Catal.*, **258**, 71 (2008).
11. 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).
12. S. H. Lee, D. R. Park, H. Kim, J. Lee, J. C. Jung, S. Park, K. M. Cho and I. K. Song, *React. Kinet. Catal. Lett.*, **94**, 71 (2008).
13. S. H. Lee, S. H. Song, D. R. Park, J. C. Jung, J. H. Song, S. Y. Woo, W. S. Song, M. S. Kwon and I. K. Song, *Catal. Commun.*, **10**, 160 (2008).
14. N. Nagato, H. Mori, K. Maki and R. Ishioka, US Patent 4,634,784 (1987).
15. R. K. Pandey and R. Kumar, *Catal. Commun.*, **8**, 379 (2007).
16. P. Krafft, P. Gilbeau, B. Gosselin and S. Claessens, PCT Patent WO2005/054167 A1 (2005).
17. P. Kubicek, P. Sladek and I. Buricova, PCT Patent WO2005/021476 A1 (2005).
18. 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).
19. I. K. Song, S. H. Moon and W. Y. Lee, *Korean J. Chem. Eng.*, **8**, 33 (1991).
20. M. Misono, *Korean J. Chem. Eng.*, **14**, 427 (1997).
21. W. Y. Lee, I. K. Song, J. K. Lee, G. I. Park and S. S. Lim, *Korean J. Chem. Eng.*, **14**, 432 (1997).
22. J. S. Choi, I. K. Song and W. Y. Lee, *Korean J. Chem. Eng.*, **17**, 280 (2000).
23. R. Wang, *Korean J. Chem. Eng.*, **20**, 659 (2003).
24. 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).
25. K. W. La, H. Kim, J. C. Jung, J. Lee, D. R. Park, S. H. Lee and I. K. Song, *Korean J. Chem. Eng.*, **25**, 710 (2008).
26. H. Kim, J. C. Jung, D. R. Park, J. Lee, K. M. Cho, S. Park, S. H. Lee and I. K. Song, *Korean J. Chem. Eng.*, **25**, 231 (2008).
27. I. K. Song and M. A. Barteau, *Korean J. Chem. Eng.*, **19**, 567 (2002).
28. I. K. Song and M. A. Barteau, *J. Mol. Catal. A*, **182**, 175 (2002).
29. M. A. Barteau, J. E. Lyons and I. K. Song, *J. Catal.*, **216**, 236 (2003).
30. I. K. Song, H. S. Kim and M.-S. Chun, *Korean J. Chem. Eng.*, **20**, 844 (2003).
31. I. K. Song and M. A. Barteau, *J. Mol. Catal. A*, **212**, 229 (2004).
32. I. V. Kozhevnikov, *Catal. Rev. -Sci. Eng.*, **37**, 311 (1995).
33. C. L. Hill and C. M. Prosser-McCartha, *Coord. Chem. Rev.*, **143**, 407 (1995).
34. T. Okuhara, N. Mizuno and M. Misono, *Adv. Catal.*, **41**, 113 (1996).