

Direct preparation of dichloropropanol from glycerol and hydrochloric acid gas in a solvent-free batch reactor: Effect of experimental conditions

Sun Ho Song*, Sang Hee Lee*, Dong Ryul 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 4 September 2008 • accepted 24 September 2008)

Abstract—Solvent-free direct preparation of dichloropropanol (DCP) from glycerol and hydrochloric acid gas was carried out in a batch reactor with a variation of reaction conditions (agitation speed, reaction time, reaction temperature, and reaction pressure), amount of $H_3PW_{12}O_{40}$ catalyst, and amount of water absorbent (silica gel blue). The reaction was conducted at high agitation speed in order to avoid mass transfer limitation between glycerol and hydrochloric acid gas. In the direct preparation of DCP from glycerol and hydrochloric acid gas, DCP formation was increased with increasing reaction time, reaction temperature, and reaction pressure. Chlorination of glycerol occurred via the following consecutive reaction steps: glycerol \rightarrow monochloropropanediol (MCPD) \rightarrow dichloropropanol (DCP) \rightarrow trichloropropane (TCP). Reaction rate decreased in the order of first-step reaction > second-step reaction > third-step reaction. The presence of $H_3PW_{12}O_{40}$ catalyst and water absorbent (silica gel blue) enhanced the formation of DCP. DCP formation was increased with increasing the amount of $H_3PW_{12}O_{40}$ catalyst and water absorbent (silica gel blue). Strong Brønsted acid site of $H_3PW_{12}O_{40}$ catalyst and water removal from the reaction system favorably served in improving DCP formation.

Key words: Dichloropropanol, Glycerol, Hydrochloric Acid Gas, Heteropolyacid Catalyst, Water Absorbent

INTRODUCTION

Bio-diesel produced from vegetable oils has attracted much attention as a green fuel [1-7]. However, one of the major problems in the production of bio-diesel is that considerable amount of glycerol (ca. 10%) is formed as a by-product [8]. This leads to a surplus of glycerol in the industrial market and decreases the commercial value of glycerol [9]. Therefore, many attempts have been made on the direct conversion of glycerol to high-value chemicals [10]. One of the promising methods to convert glycerol to high-value chemicals is to produce dichloropropanol (DCP) from glycerol through single-step chlorination reaction [11-13].

Fig. 1 shows the conventional and proposed processes for producing dichloropropanol (DCP). The conventional preparation method of DCP consists of two consecutive processes: (i) preparation of allyl chloride through chlorination of propylene at high reaction temperature, and (ii) preparation of DCP through subsequent chlorination of allyl chloride under the condition of excess amount of industrial water [14]. However, a major problem of the conventional process is that a large amount of sludge is inevitably formed, which can cause severe technical and environmental problems [15]. Therefore, direct preparation of DCP from glycerol has been recognized as an economical and environmentally benign process [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 prob-

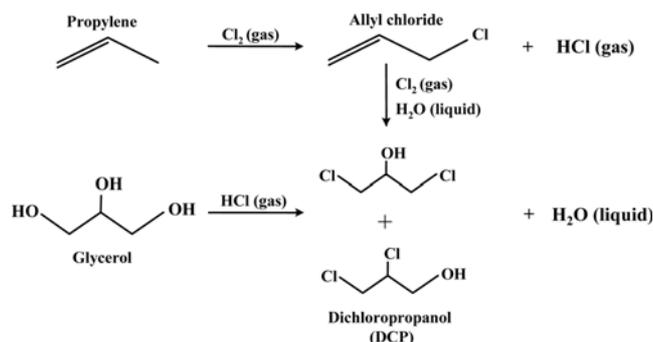


Fig. 1. Conventional and proposed processes for producing dichloropropanol (DCP).

lems in catalyst separation and product purification [16-18]. Thus, developing an efficient process 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]. It was also revealed that hydrochloric acid gas (in the solvent-free

[†]To whom correspondence should be addressed.

E-mail: inksong@snu.ac.kr

gas-liquid reaction) [13] was much more efficient than aqueous hydrochloric acid solution (in the water-solvent liquid-phase reaction) [11,12] as a chlorination agent for the direct preparation of DCP from glycerol. Among various HPA catalysts, $H_3PW_{12}O_{40}$ with the highest acid strength was found to show the best catalytic performance in the direct preparation of DCP from glycerol in both water-solvent and solvent-free chlorination reactions [11-13]. Moreover, addition of water absorbent (silica gel blue) to $H_3PW_{12}O_{40}$ catalyst system resulted in further enhancement of DCP formation in the solvent-free direct preparation of DCP from glycerol and hydrochloric acid gas [13].

In this work, solvent-free direct preparation of DCP from glycerol and hydrochloric acid gas was carried out in a batch reactor to see the effect of experimental conditions on DCP formation. The reaction was conducted in a systematic way with a variation of reaction conditions (agitation speed, reaction time, reaction temperature, and reaction pressure), amount of $H_3PW_{12}O_{40}$ catalyst, and amount of water absorbent (silica gel blue), with an aim of increasing DCP formation. The reaction pathway for the chlorination of glycerol was proposed.

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 $H_3PW_{12}O_{40}$ HPA 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. Silica gel blue (water absorbent) was purchased from Samchun Chemicals.

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

DCP was directly prepared from glycerol and hydrochloric acid gas in a solvent-free batch reactor (200 ml). Fig. 2 shows the schematic diagram of the reaction apparatus. Interior parts of the batch reactor were made of Hastelloy C and Teflon which were highly resistant to the chlorination agent. Non-catalytic direct preparation of DCP from glycerol was carried out with a variation of agitation speed (150-1050 RPM), reaction time (2-30 h), reaction temperature (110-170 °C), and reaction pressure (1-18 bar). 100 g of glycerol

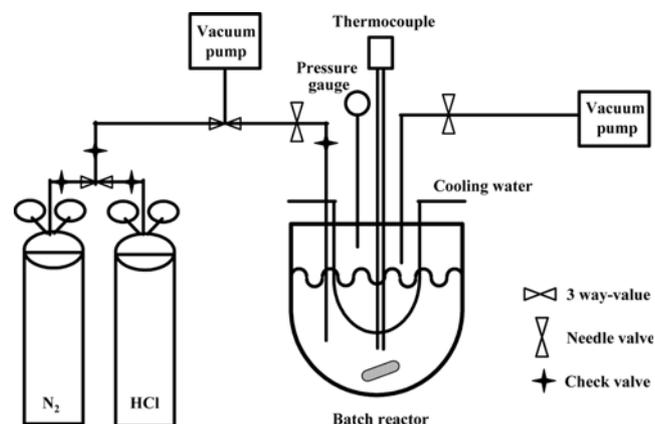


Fig. 2. Schematic diagram of reaction apparatus.

(reactant) was charged into the reactor at room temperature. After being purged with nitrogen (Daesung Industrial Gas), the reactor was heated to the reaction temperature under a given agitation speed. Hydrochloric acid gas was then continuously fed into the reactor at constant pressure to conduct the chlorination of glycerol for a given reaction time.

DCP was also directly prepared from glycerol and hydrochloric acid gas in the presence of $H_3PW_{12}O_{40}$ catalyst (1-9 g). Furthermore, the reaction was carried out in the presence of silica gel blue (1-5 g) with the aim of removing water formed during the reaction. Other experimental procedures were identical to those of non-catalytic reaction.

Reaction products were analyzed with a gas chromatograph (HP 5890 II) equipped with a DB-WAX capillary column and a flame ionization detector (FID). Conversion of glycerol and selectivity for product were calculated according to the following equations.

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

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

RESULTS AND DISCUSSION

1. Effect of Agitation Speed on DCP Formation

In the non-catalytic direct preparation of DCP from glycerol and hydrochloric acid gas performed with a variation of agitation speed, selectivity for DCP increased with increasing RPM at low agitation speed (≤ 600 RPM). This result indicates that agitation speed is very important for the efficient formation of DCP in the solvent-free gas (hydrochloric acid gas)-liquid (glycerol) reaction. However, selectivity for DCP was almost constant at high agitation speed (≥ 600 RPM), suggesting that mass transfer between glycerol and hydrochloric acid gas is one of the important factors to be considered in our reaction system. Therefore, all the reaction experiments conducted

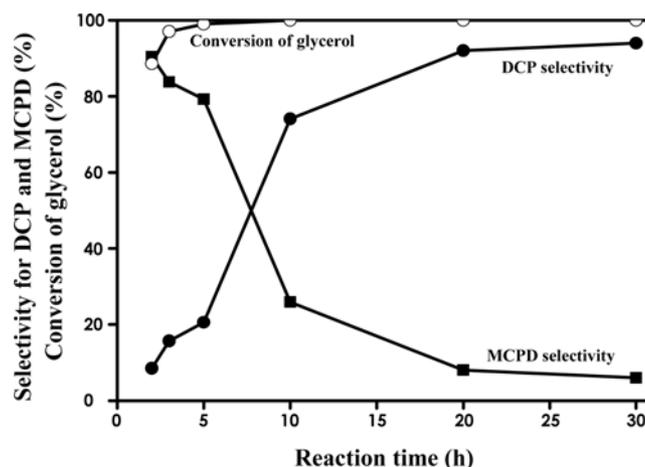


Fig. 3. Effect of reaction time on DCP formation in the solvent-free direct preparation of DCP from glycerol and hydrochloric acid gas: glycerol=100 g, reaction temperature=110 °C, reaction pressure=3 bar, RPM=900.

hereafter were performed at 900 RPM in order to avoid mass transfer limitation in the solvent-free batch reaction.

2. Effect of Reaction Time on DCP Formation

Fig. 3 shows the effect of reaction time on DCP formation in the solvent-free direct preparation of DCP from glycerol and hydrochloric acid gas. Conversion of glycerol increased with increasing reaction time and reached 100% after a 10 h-reaction. Conversion of glycerol in the solvent-free gas-liquid reaction utilizing hydrochloric acid gas was much higher than that in the water-solvent liquid-phase reaction utilizing aqueous hydrochloric acid solution under the same reaction conditions [11-13]. This means that hydrochloric acid gas was much more efficient than aqueous hydrochloric acid solution as a chlorination agent in the direct preparation of DCP. Selectivity for DCP was continuously increased with increasing reaction time, while selectivity for monochloropropanediol (MCPD) was continuously decreased with increasing reaction time. The above results indicate that DCP was formed via the following consecutive chlorination reaction steps: glycerol → MCPD → DCP.

3. Effect of Reaction Temperature on DCP Formation

Fig. 4 shows the effect of reaction temperature on DCP formation in the solvent-free direct preparation of DCP from glycerol and hydrochloric acid gas. In all experimental runs, conversion of glycerol was 100%. Selectivity for DCP was gradually increased with increasing reaction temperature and became almost constant (ca. 98%) at above 150 °C, while selectivity for MCPD was gradually decreased with increasing reaction temperature. It is interesting to note that trichloropropane (TCP), a chlorination product of DCP, was formed at high reaction temperature, although the amount of TCP was very small. These results indicate that chlorination of glycerol occurred via the following consecutive reaction steps: glycerol → MCPD → DCP → TCP. It can be inferred from Fig. 3 and Fig. 4 that reaction rate decreased in the order of first-step reaction > second-step reaction > third-step reaction. This means that DCP formation can be maximized by controlling the reaction conditions.

4. Effect of Reaction Pressure on DCP Formation

Fig. 5 shows the effect of reaction pressure on DCP formation in the solvent-free direct preparation of DCP from glycerol and hy-

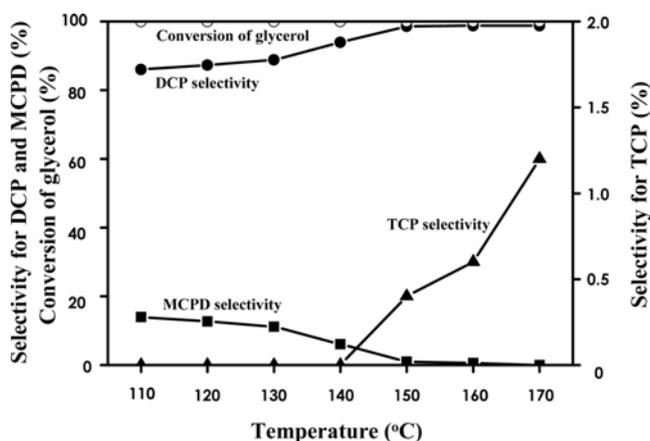


Fig. 4. Effect of reaction temperature on DCP formation in the solvent-free direct preparation of DCP from glycerol and hydrochloric acid gas: glycerol=100 g, reaction time=3 h, reaction pressure=9 bar, RPM=900.

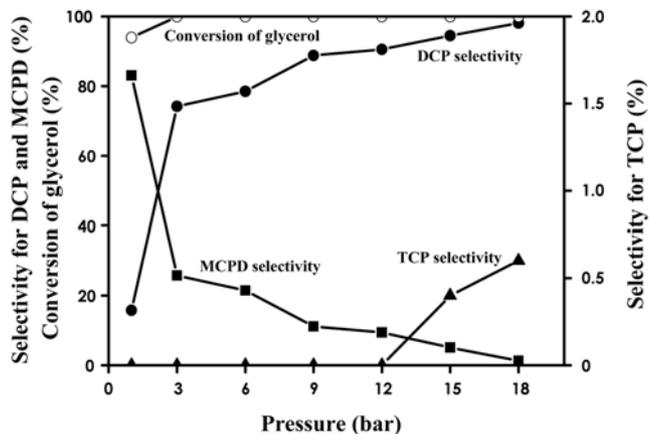


Fig. 5. Effect of reaction pressure on DCP formation in the solvent-free direct preparation of DCP from glycerol and hydrochloric acid gas: glycerol=100 g, reaction time=3 h, reaction temperature=130 °C, RPM=900.

drochloric acid gas. Conversion of glycerol reached 100% at 3 bar. Selectivity for DCP was continuously increased, whereas selectivity for MCPD was continuously decreased with increasing reaction pressure. On the other hand, a small amount of TCP was formed at high reaction pressure. The dependencies of product selectivity with respect to reaction pressure (Fig. 5) showed the same trend as those with respect to reaction temperature (Fig. 4). In other words, selectivity for DCP increased with increasing reaction pressure and reaction temperature.

5. Effect of $H_3PW_{12}O_{40}$ Catalyst Amount on DCP Formation

It was previously reported [11-13] that $H_3PW_{12}O_{40}$ showed the best catalytic performance in the direct preparation of DCP from glycerol in both water-solvent and solvent-free chlorination reactions among various HPA catalysts. In this work, therefore, $H_3PW_{12}O_{40}$

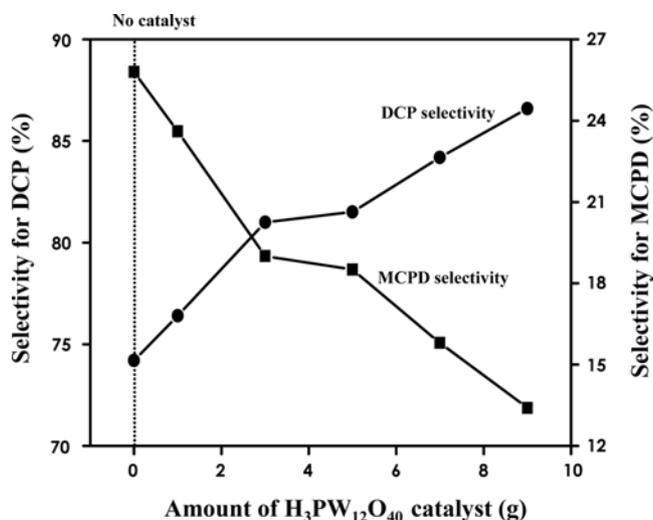


Fig. 6. Effect of $H_3PW_{12}O_{40}$ catalyst amount on DCP formation in the solvent-free direct preparation of DCP from glycerol and hydrochloric acid gas: glycerol=100 g, reaction time=3 h, reaction temperature=130 °C, reaction pressure=3 bar, RPM=900.

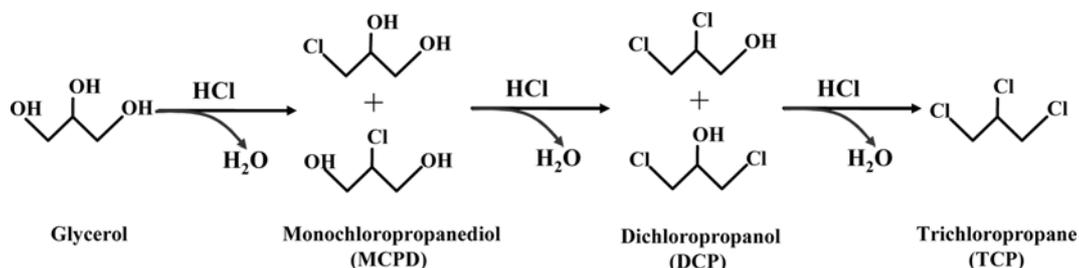


Fig. 7. Reaction pathway for the chlorination of glycerol utilizing hydrochloric acid gas.

was chosen as a model catalyst to see the effect of catalyst amount on DCP formation. Fig. 6 shows the effect of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst amount on DCP formation in the solvent-free direct preparation of DCP from glycerol and hydrochloric acid gas. Under the given reaction conditions, conversion of glycerol was 100% in all experimental runs. Selectivity for MCPD decreased with increasing catalyst amount. On the other hand, TCP formation was not observed in all experimental runs. It should be noted that DCP formation in the presence of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst was much higher than that in the absence of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst. Furthermore, DCP formation was continuously increased with increasing catalyst amount. These results indicate that strong Brønsted acid site of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst favorably contributed to the chlorination of glycerol to DCP.

6. Effect of Water Absorbent Amount on DCP Formation

It was reported that addition of water absorbent (silica gel blue) to the solvent-free reaction system in the direct preparation of DCP from glycerol and hydrochloric acid gas resulted in enhancement of DCP formation [13]. It was also revealed that DCP formation in the solvent-free gas-liquid reaction utilizing hydrochloric acid gas was much higher than that in the water-solvent liquid-phase reaction utilizing aqueous hydrochloric acid solution [11-13]. This means that water gives a negative effect on DCP formation in the chlorination of glycerol. Fig. 7 shows the reaction pathway for the chlorination of glycerol utilizing hydrochloric acid gas, proposed on the

basis of experimental findings in this work. As shown in Fig. 7, water is inevitably formed as a by-product in each reaction step. Judging from the reaction pathway and reaction rate, one may expect that DCP formation would be much enhanced by removing water from the solvent-free reaction system.

Fig. 8 shows the effect of water absorbent (silica gel blue) amount on DCP formation in the solvent-free direct preparation of DCP from glycerol and hydrochloric acid gas. In all experimental runs, conversion of glycerol was 100% under the given reaction conditions. Selectivity for DCP was continuously increased with increasing water absorbent amount, while selectivity for MCPD was continuously decreased with increasing water absorbent amount. TCP was not formed in all experimental runs. It is noteworthy that DCP formation in the presence of water absorbent was much higher than that in the absence of water absorbent. Thus, removal of water from the reaction system favorably served in improving DCP formation in the solvent-free chlorination of glycerol.

CONCLUSIONS

Direct preparation of DCP from glycerol and hydrochloric acid gas was carried out in a solvent-free batch reactor to see the effect of experimental conditions on DCP formation. For this purpose, the reaction was conducted in a systematic way with a variation of reaction conditions (agitation speed, reaction time, reaction temperature, and reaction pressure), amount of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst, and amount of water absorbent (silica gel blue). In the direct preparation of DCP from glycerol and hydrochloric acid gas, mass transfer between glycerol and hydrochloric acid gas was very important for the efficient formation of DCP. It was observed that DCP formation was increased with increasing reaction time, reaction temperature, and reaction pressure. Chlorination of glycerol occurred via the following consecutive reaction steps: glycerol \rightarrow MCPD \rightarrow DCP \rightarrow TCP, and the reaction rate decreased in the order of first-step reaction $>$ second-step reaction $>$ third-step reaction. The presence of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst and water absorbent (silica gel blue) resulted in enhancement of DCP formation. DCP formation was increased with increasing $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst amount, indicating that strong Brønsted acid site of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst favorably contributed to the chlorination of glycerol to DCP. Water formed during the reaction gave a negative effect on DCP formation. DCP formation was much enhanced with increasing water absorbent (silica gel blue) amount. Removal of water from the reaction system was favorable for improving DCP formation in the solvent-free chlorination of glycerol.

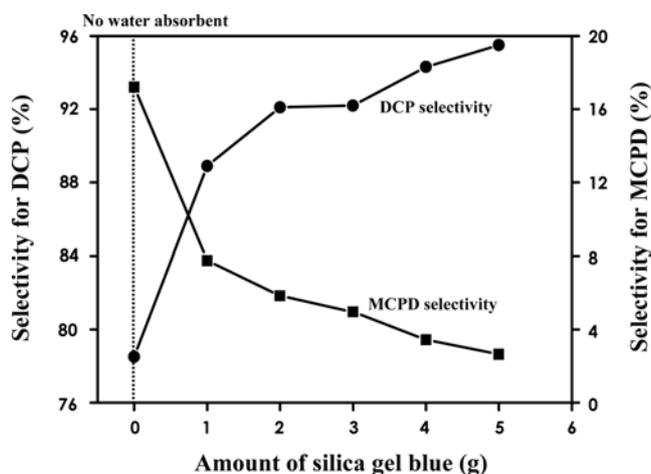


Fig. 8. Effect of water absorbent (silica gel blue) amount on DCP formation in the solvent-free direct preparation of DCP from glycerol and hydrochloric acid gas: glycerol=100 g, reaction time=3 h, reaction temperature=130 °C, reaction pressure=6 bar, RPM=900.

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 4,634,784/160 (2008)(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).