

ALKYLATION OF TOLUENE WITH METHANOL OVER HETEROPOLY ACID/Y-ZEOLITE CATALYSTS

Chang Yeop HWANG, Jong Woon KWAK,
Wha Young LEE*, and Ho-In LEE**

Department of Chemical Technology, College of Engineering,
Seoul National University, Seoul 151, Korea

*Department of Chemical Engineering, College of Engineering
Seoul National University, Seoul 151, Korea

(Received 7 June 1985 • accepted 13 September 1985)

Abstract—Alkylation of toluene with methanol has been studied in a fixed bed reactor with a continuous flow system. As a promoter, heteropoly acids and their metal salts were impregnated on Y-zeolite. Catalyst impregnated with lower amount of heteropoly acid showed higher initial activity, and the catalytic activity was enhanced by more electronegative metal ion of heteropoly acid salt impregnated on Y-zeolite. Catalyst calcined at lower temperature showed higher initial activity, but its deactivation rate was faster than that calcined at higher temperature. Catalyst impregnated with $\text{BiPMo}_{12}\text{O}_{40}$ showed a good activity and a good regeneration ability of catalytic activity.

INTRODUCTION

p-xylene is an important compound for polyester fiber industry because of great demand for oxidation to terephthalic acid [1,2].

It is known that the benzene-ring alkylation of toluene with methanol to produce xylenes is catalyzed by solid acids [3]. Many workers have reported the use of zeolite catalysts for alkylation reactions with methanol [4-6]. Recently, Yashima reported that p-xylene could be obtained selectively by using highly active zeolite, and that this selectivity was due to the presence of Brønsted acidity [7]. Bhat also proposed that the formation of p-xylene was greatly influenced by Brønsted acidity and narrow pore structure [8].

It has been shown that Y-zeolite is more acidic than X-zeolite, H-mordenite or silica-alumina in the first part of this series work [9]. Therefore, Y-zeolite was chosen as a main catalyst, and modified by impregnation with heteropoly acids to enhance the selectivity of para isomer in the mixed xylene product. Heteropoly compounds have recently attracted for various industrial processes.

Because of only about 24% p-xylene in the total mixed xylene at thermodynamic equilibrium, separation-isomerization process must be repeated many times.

Direct alkylation of toluene with methanol is, therefore, prevailing progressively to produce high yield of p-xylene, which is a relatively simple and economical method [6].

Based on the reasons mentioned above, we had selected acidic Y-zeolite as a main catalyst and chosen direct alkylation method.

The purpose of this study is to obtain p-xylene selectively and to compare the catalytic activity of the various cation-exchanged heteropoly acids impregnated on Y-zeolite catalysts.

EXPERIMENTAL

1. Preparation of Catalysts

Many workers have reported that Y-zeolite has good activity in alkylation reaction. It has been shown that the activity of various zeolite catalysts for alkylation of toluene with methanol is high in the following order: $\text{HY} > \text{HX} > \text{HM}$ [9]. Y-zeolite is known to be more acidic than X-zeolite and as an effective catalyst in alkylation [10]. With the above reasons Y-zeolite was chosen as main catalyst employed in this study.

$\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ (H_3PMo) was prepared according to the literature [11]. One mole of MoO_3 (144 g) was placed in a flask equipped with a stirrer and a reflux condenser, and 1400 ml of water was added. To the above was then added 9.57 g of 85% H_3PO_4 , and the

** To whom all correspondence should be addressed.

Table 1. Thermal behavior of heteropoly compounds.

Compound	Hydration Number (x/mole)	Dehydration Temperature (°C)				Decomposition Temperature (°C)
H ₃ PMo ₁₂ O ₄₀	16.5	88	120	432		432
BiPMo ₁₂ O ₄₀	12.5	76	107	128	418	418
FePMo ₁₂ O ₄₀	16.4	118	145	224	443	443
CoHPMo ₁₂ O ₄₀	13.5	86	156	233	414	414
NiHPMo ₁₂ O ₄₀	17.3	86	116	187	246 447	447
H ₄ SiMo ₁₂ O ₄₀	9.0	80	128	373		373
H ₃ PW ₁₂ O ₄₀	5.4	78	110	218	445	445
H ₄ SiW ₁₂ O ₄₀	7.7	82	95	205	452	452

solution was brought to boiling and kept for 3 hrs with vigorous stirring. The green color developed during this period was removed by addition of a few drops of bromine water. The mother liquor was then concentrated to a volume of 100 ml by evaporative boiling for 3 to 4 hrs. Upon cooling, the concentrate developed yellow crystals, which were then filtered and air-dried for approximately 130g of final product. H₄SiMo₁₂O₄₀·xH₂O (H₄SiMo), H₃PW₁₂O₄₀·xH₂O (H₃PW), and H₄SiW₁₂O₄₀·xH₂O (H₄SiW) were prepared following up Tsigidinos' [11], Rosenheim and Jaenicke's [12], and North's method [12], respectively.

HY-zeolite was prepared by conventional ion exchange of NaY-zeolite using NH₄Cl solution. Solution of heteropoly acid was kept over 10⁻³ M of concentration to prevent it from hydrolysis [13]. The considered heteropoly acids and their metal salts were impregnated on HY-zeolite by conventional impregnation method. Thermal behaviors of various heteropoly compounds prepared in this work are presented in Table 1.

2. Structural Analysis of Heteropoly Acids

The results of DTA and TGA for H₃PMo prepared in this work are shown in Fig. 1 which is similar to previous works [14]. The other heteropoly acids and their salts showed similar results. As shown in TGA curve of Fig. 1, H₃PMo begins evolving water at about 80°C suggesting desorption of species adsorbed on the substrate. Two other weight changes are observed at about 130 and 420°C. These changes are supposed to be due to removal of coordinated water and due to destruction of Keggin structure resulting in formation and removal of water, respectively.

Infrared spectra of heteropoly compounds used KBr pellet method were examined to understand their bonding states. They were consistent with Rocchiccioli-Deltcheff et al. [15] suggesting our heteropoly compounds employed in this work to have the typical Keggin structure. Characteristic bands of all compounds appeared in the range of 1100-700 cm⁻¹.

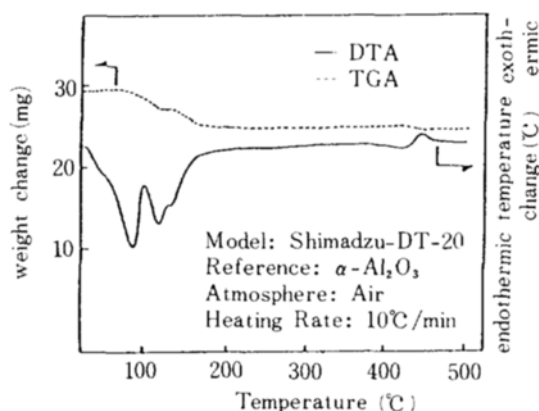


Fig. 1. DTA and TGA of heteropoly 12-molybdophosphoric acid.

X-ray diffraction analyses of various heteropoly compounds prepared in this work were carried out to confirm them to have Keggin structure, and all the spectra showed their most strong peak at $2\theta = 8^\circ$ and several peaks at 7 to 10° of 2θ which are characteristic peaks of Keggin structure [16].

From the above analytic results, all the heteropoly compounds prepared in the present study are supposed to have Keggin structure and to be enough for research in viewpoint of their purity and crystallinity.

3. Apparatus and Procedure

The experiment was carried out in a fixed bed type reactor with a continuous flow system at atmospheric pressure. Before reaction, each catalyst was calcined at 250°C in N₂ stream for 3 hrs and brought to a reaction temperature in situ. 5 g of pellet-typed catalyst was positioned in the fixed bed pyrex reactor ($\phi 2.5$ cm \times 57 cm) which was electrically heated. Temperature was measured with a alumel-chromel thermocouple buried at the center of catalyst bed. The mixture of toluene and methanol having a desired mole ratio was then fed into

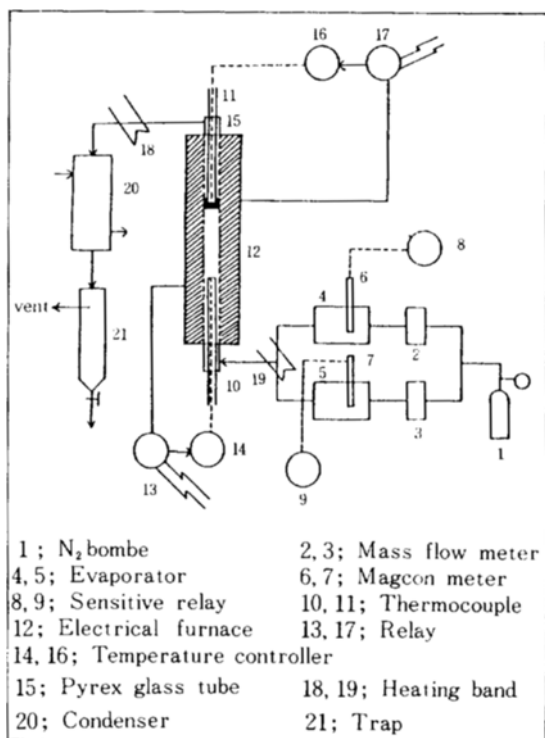


Fig. 2. Flow diagram for alkylation of toluene.

the catalyst bed by a mass flow meter. Products were analyzed periodically by 30 min interval using a gas chromatograph (Packard, Model 438) equipped with a stainless steel column of $\phi 4 \text{ mm} \times 4 \text{ m}$. Packing material was Bentone-34 (5 wt%) and DNP (5 wt%) on Chromosorb W. Carrier gas was N_2 and oven temperature was 80°C . The flow diagram of apparatus used in this work is shown in Fig. 2.

RESULTS AND DISCUSSION

1. Reaction Condition

The effect of temperature on the yields of total xylene and p-xylene over HY-zeolite has been studied from 200 to 350°C . The results appear in Fig. 3. The yield of total xylene increases with increasing temperature, and that of p-xylene maximizes at about 300°C . Above 400°C , the experiment was not carried out to prevent catalyst employed from being decomposed. At high temperature, the formation of m-xylene is enhanced suggesting that isomerization among isomeric xylenes, which occurs via movement of methyl group step by step is accelerated with temperature [4]. Selectivity of p-xylene shows maximum at 300°C in the temperature region employed in this study, but the amount of cracking also increases correspondingly. Therefore, reaction temperature was chosen of 275°C which is the center value bet-

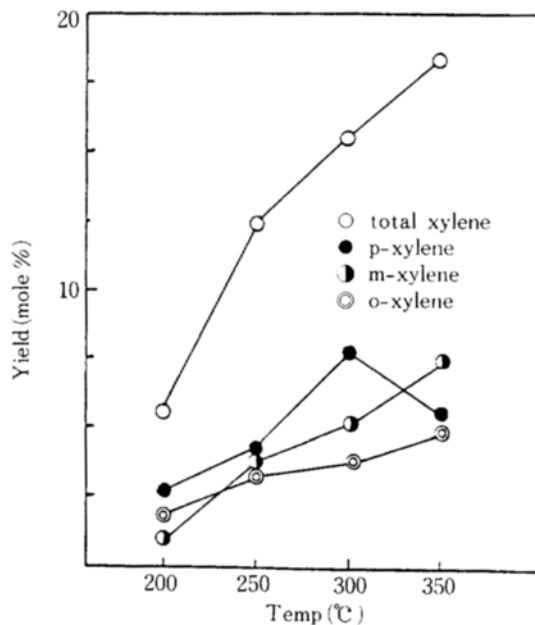


Fig. 3. Effect of temperature on the yields of total and p-xylene(space velocity: $0.72 \text{ l/g} \cdot \text{cat} \cdot \text{hr}$, toluene/methanol = 1).

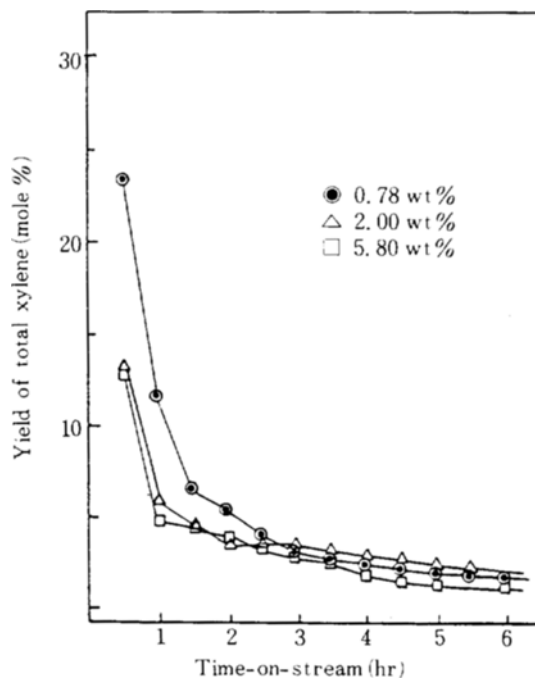


Fig. 4. Yield of total xylene vs. time-on-stream on various $H_3 \text{ PMo/HY}$ -zeolite catalysts at 275°C (space velocity: $0.72 \text{ l/g} \cdot \text{cat} \cdot \text{hr}$, toluene/methanol = 1).

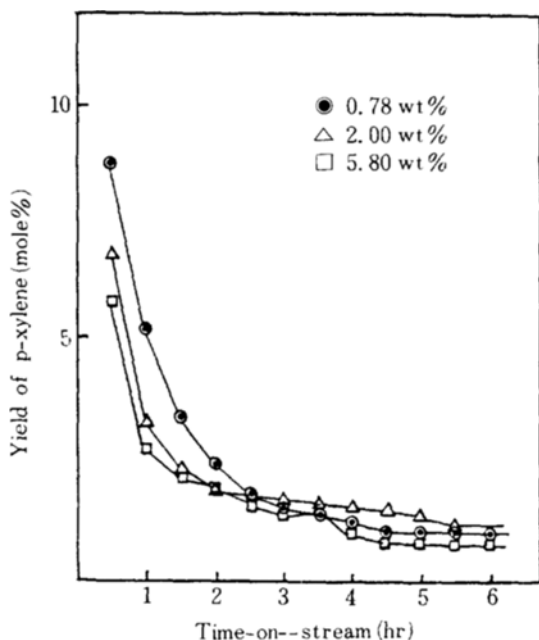


Fig. 5. Yield of p-xylene vs. time-on-stream on various H_3PMo/HY -zeolite catalysts at $275^\circ C$ (space velocity: $0.72 \text{ l/g-cat}\cdot\text{hr}$, toluene/methanol = 1).

ween $250^\circ C$ showing difficulty of cracking and $300^\circ C$ showing maximum selectivity of p-xylene. The mole ratio of reactants was 1:1 (toluene:methanol) and space velocity was fixed at $0.72 \text{ l/g-cat}\cdot\text{hr}$, as selected as an optimum condition in earlier work [9].

2. Effect of the Amount of H_3PMo Impregnated

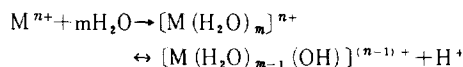
The catalytic activity of HY -zeolite impregnated with heteropoly acid, H_3PMo , is presented in Figs. 4 and 5. At the initial reaction stage, yields of total xylene and p-xylene decrease with increasing the amount of H_3PMo impregnated, but after 3 hrs the highest activity is shown on 2.00 wt%-impregnated catalyst even if the activity gap is very small. This suggests that 0.78 wt%-impregnated catalyst gives a nice dispersion state of H_3PMo on the zeolite while the two higher impregnations do worse ones with rather a pore blocking as reported by Izumi [17] that the lower amount supported gives the better dispersion state from the results of X-ray diffraction and by Breck [18] that in the case of zeolite support a nice impregnation is difficult due to its own pore size distribution. As reaction proceeds activity decreases sharply mainly due to well-known coke formation whose rate is bigger on the catalyst with a better dispersion which gives higher exposure to react easily. After a certain reaction period (about 3 hrs) the 2.00 wt%-impregnated catalyst which has medium disper-

sion and medium pore blocking shows the highest equilibrium activity supporting the above discussion of dispersion and blocking concept.

3. Effect of Metal Cation Exchanged in H_3PMo

Metal cation-exchanged heteropoly acids were impregnated on the zeolite, and their activities are presented in Figs. 6 and 7. Each metal salt was impregnated by 1.18, 1.09, 1.19 and 1.44 wt% for Bi^{3+} , Fe^{3+} , Co^{2+} and Ni^{2+} salts, respectively depending on their different impregnating abilities. The acid not cation-exchanged was impregnated by 0.78 wt% as used for Figs. 4 and 5. In Fig. 6, the initial yield of total xylene increases with the order of electronegativity of substituted metal cation backing up Ai who reported in his work [19] that the acidity of heteropoly acid salt was deeply related to the electronegativity of the substituted metal cation.

Niiyama et al. reported that catalytic active site might be metal cation in an acid-catalyzed reaction because the metal cation was supposed to form a proton by residual water from the following process[20]:



In alkylation of toluene with methanol, one mole of

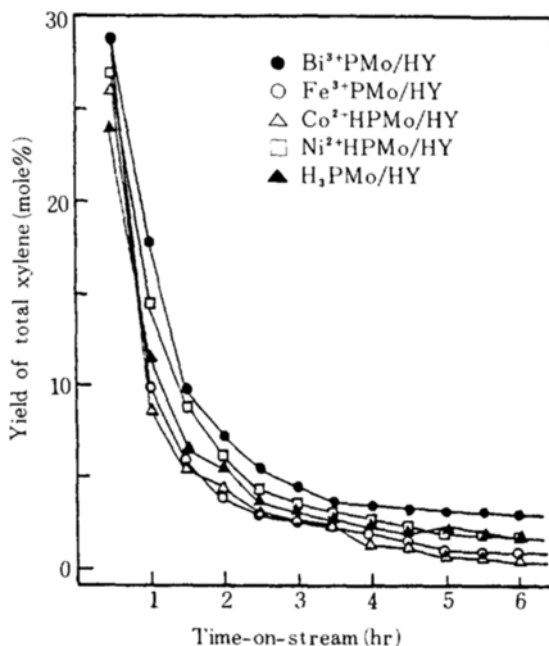


Fig. 6. Yield of total xylene vs. time-on-stream on heteropoly 12-molybdophosphoric acid and its various salts/ HY -zeolite at $275^\circ C$ (space velocity: $0.72 \text{ l/g-cat}\cdot\text{hr}$, toluene/methanol = 1).

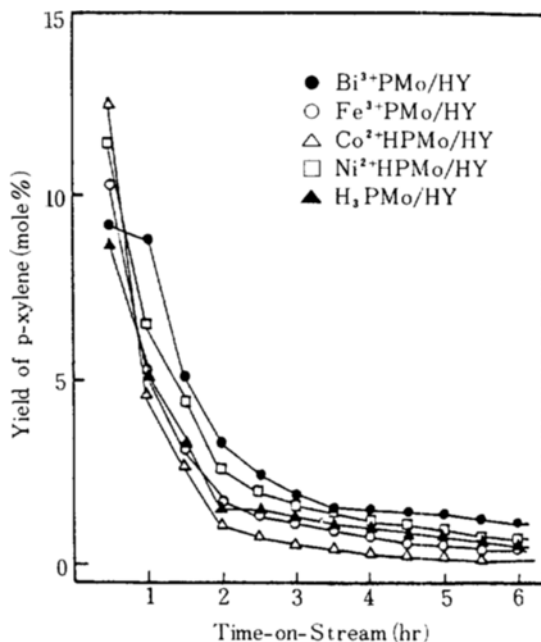


Fig. 7. Yield of p-xylene vs. time-on-stream on heteropoly 12-molybdophosphoric acid and its various salts/HY-zeolite at 275 °C (space velocity: 0.72 l/g-cat·hr, toluene/methanol = 1).

toluene and one mole of methanol produce one mole of water which may influence to the acidity of catalyst as mentioned above. That is, the results of Fig. 6 are consistent with the relative strength of polarizing power which is stronger with the higher charge density of the substituted metal cation. It is known that the stronger polarizing power produces the more protons [21, 22]. From that results of Fig. 6, as expected, Bi- and Fe-salts having larger cationic charge than the other metal cations showed higher activities in the early stage of reaction, and this result agrees well with Kwak and Lee [9]. The fast deactivation rate of Fe-exchanged salt might be due to water produced during reaction, which influences to the secondary structure between metal cation and heteropoly anion in the case of relatively highly soluble salt like Fe-exchanged salt. In Fig. 7, the initial yield of p-xylene for Bi-exchanged salt is relatively low suggesting that its isomerization activity is high as confirmed from the experimental result of 50% of m-xylene in the product.

4. Effect of Central and Coordinated Atoms in Heteropoly Acid

The activities of various heteropoly acids as a promoter are shown in Figs. 8 and 9. All the catalysts used in this experiment were impregnated with the consid-

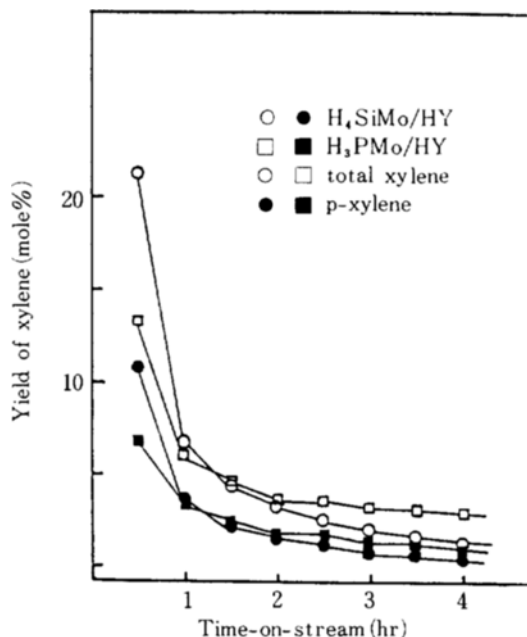


Fig. 8. Yields of total and p-xylenes on H₃PMo/HY-zeolite and H₄SiMo/HY-zeolite at 275°C (space velocity: 0.72 l/g-cat·hr, toluene/methanol = 1).

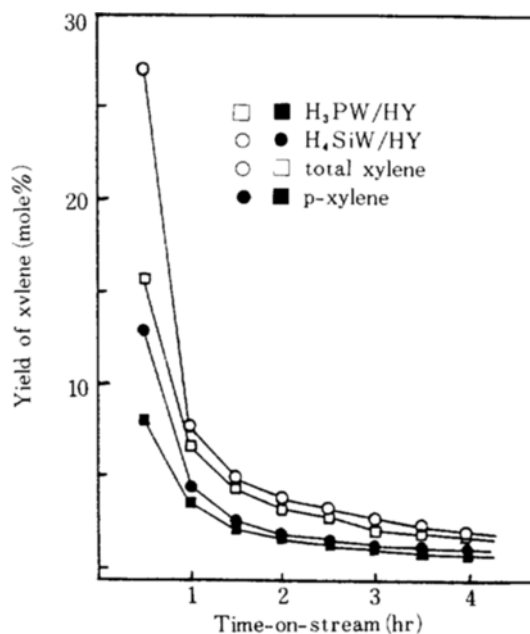


Fig. 9. Yields of total and p-xylenes on H₃PW/HY-zeolite and H₄SiW/HY-zeolite at 275°C (space velocity: 0.72 l/g-cat·hr, toluene / methanol = 1).

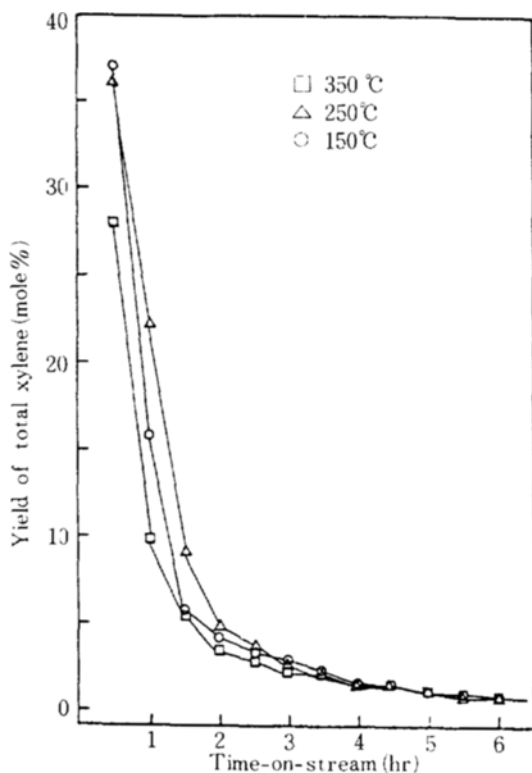


Fig. 10. Yield of total xylene vs. time-on-stream for various calcination temperatures on Fe^{3+} PMo/HY-zeolite at 275°C (space velocity: 0.72 l/g-cat·hr, toluene/methanol = 1).

ered heteropoly acids by 2.0 wt%. The initial activity was ordered as follows; $\text{H}_4\text{SiW} > \text{H}_4\text{SiMo} > \text{H}_3\text{PW} > \text{H}_3\text{PMo}$. Even though the acid strength of H_3PMo is much stronger than that of H_4SiW [17], the initial activity was higher on H_4SiW which was reported to have the same structure parameters as of aluminosilicate [13].

Methanol which is one of reactants is smaller in size and more polar compared to the other reactant, toluene, so it is supposed to have higher affinity to the heteropoly anion. Therefore, as reported by Okuhara et al. [23], methanol molecules presumably react more easily in the bulk of heteropoly acid contacting directly with the central atom of the acid. This suggests that methanol molecules adsorb too strongly to react more easily on a catalyst having P as a central atom than on one having Si because P is more electronegative than Si, resulting in a lower activity in the case of P.

5. Effect of Calcination Temperature

The catalyst impregnated with Fe-salt which has relatively high activity in the early stage of reaction was chosen in order to know the dependence of calcination

temperature on the activity of xylene formation. As shown in Fig. 10, the activity was higher on a catalyst calcined at lower temperature. This suggests that hydrated water of the catalyst still remains at low calcination temperature till 250°C and it increases acidity of the catalyst as discussed in section (3). The result agrees well with Ai's [18]. Ai reported that the acidity of heteropoly acid decreased drastically above 350°C of calcination temperature in an acidic catalytic reaction resulting in a decrease of activity only with a constant surface area. In the case of catalyst calcined at 150°C, deactivation is most rapid suggesting rapid coke formation due to relatively severe reaction in virtue of the strongest catalytic activity.

6. Regeneration of Deactivated Catalyst

Coke formation is a well-known phenomenon in alkylation reaction. After running for 6 hrs, each deactivated catalyst was generated by calcination at 350°C for 8 hrs under air stream of 1000 cc/min. In the case of two catalysts impregnated with BiPMo and FePMo which were relatively high in activity, Bi-catalyst was deactivated relatively slowly and Fe-catalyst was done fast as shown in Figs. 6 and 7. After running for 1 hr, the regenerated Bi-catalyst showed 15.0% of total xylene yield (17.8% for the fresh Bi-catalyst), whereas the regenerated Fe-catalyst showed activity below detection limit (14.5% for the fresh Fe-catalyst). This suggests that the structure of Fe-catalyst was changed irreversibly due to complete dehydration during rapid deactivation.

CONCLUSION

1. The optimum amount of H_3PMo impregnated is between 0.78 and 5.80 wt% suggesting a competition between dispersion and pore blocking for the catalytic activity.
2. Catalysts impregnated with BiPMo and FePMo show relatively high activities due to high polarizing power, and the latter is deactivated fast due to high solubility of Fe-salt.
3. The initial activity is higher on a catalyst calcined at lower temperature but its deactivation rate is faster, and the initial activity as a function of central atom of heteropoly acid is ordered as follows: $\text{H}_4\text{SiW} > \text{H}_4\text{SiMo} > \text{H}_3\text{PW} > \text{H}_3\text{PMo}$.
4. Catalyst impregnated with BiPMo is deactivated more slowly than that with FePMo, and the former is regenerated easily to 80% plus of the fresh catalyst whereas the latter is scarcely regenerated below detection limit.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support by Yukong Limited for this study.

REFERENCES

1. Kirk, R. E. and Othmer, D. F.: "Kirk-Othmer Encyclopedia of Chemical Technology," 3rd ed., Vol. 22, John Wiley & Sons, Inc., New York, NY (1979).
2. 한국화학공학회: "한국의 화학공업", 한국화학공학회, 서울(1982).
3. Itoh, H., Miyamoto, A. and Murakami, Y.: *J. Catal.*, **64**, 284 (1980).
4. Yashima, T.: *J. Catal.*, **16**, 273 (1970).
5. Yashima, T., Yamazaki, K. and Ahmad, H.: *J. Catal.*, **17**, 151 (1970).
6. Kaeding, W. W., Chu, C. and Butter, S. A.: *J. Catal.*, **67**, 159 (1981).
7. Yashima, T., Sato, K., Hayasaka, T. and Hara, N.: *J. Catal.*, **26**, 303 (1972).
8. Bhat, S. G. T.: *J. Catal.*, **75**, 196 (1982).
9. Kwak, J. W. and Lee, H. -I.: *J. KICChE*, **22**, 173 (1984).
10. Ward, J. W.: *J. Catal.*, **22**, 237 (1971).
11. Tsigdinos, G. A.: *Ind. Eng. Chem. Prod. Res. Dev.*, **13**, 267 (1974).
12. Bailar, J. C., Jr.: "Inorganic synthesis," Vol. 1, McGraw-Hill, New York, NY (1953).
13. Kozhevnikov, I. V. and Matveev, K. I.: *Russian Chemical Reviews*, **51**, 1075 (1982).
14. Kim, J. J.: Ph. D. Dissertation, S. N. U., Seoul, Korea (1981).
15. Rocchiccioli-Deltcheff, C., Thouvenut, R. and Frank, R.: *Spectrochimica Acta*, **32A**, 587 (1976).
16. Lee, W. Y.: *J. KICChE*, **17**, 317 (1979).
17. Izumi, Y., Hasebe, R. and Urabe, K.: *J. Catal.*, **84**, 402 (1983).
18. Breck, D. W.: "Zeolite Molecular Sieves," John Wiley & Sons, Inc., New York, NY (1973).
19. Ai, M.: *J. Catal.*, **71**, 88 (1981).
20. Niiyama, H., Saito, Y. and Echigoya, E.: Proc. 7th Int. Congr. Catalysis, Tokyo, 1980, reprint C13.
21. Barrer, R. M. and Riley, D. W.: *Trans. Faraday Soc.*, **46**, 853 (1950).
22. Aiello, R., Barrer, R. M. and Arthur, J.: *Trans. Faraday Soc.*, **66**, 1610 (1970).
23. Okuhara, T., Kasai, A. and Misono, M.: *J. Catal.*, **83**, 121 (1983).