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Selective Alkylation of *p*-Xylene with 2-Methylpropene by 12-Tungstophosphoric Acid

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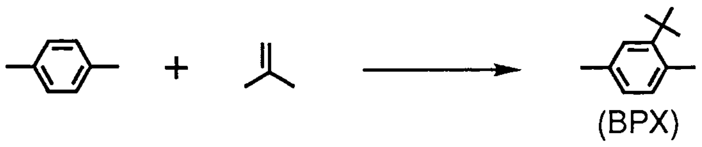
Solid $H_3PW_{12}O_{40}$ catalyzed the alkylation of *p*-xylene with 2-methylpropene to *t*-butyl-*p*-xylene with 75%-selectivity, while the selectivity with H_2SO_4 was only 7%. The selectivity of heteropolyacids tended to increase with the acid strength.

Alkylation of *p*-xylene with 2-methylpropene (Eq. (1)) has fascinated us, since the product *t*-butyl-*p*-xylene (abbreviated as BPX) is an important precursor for liquid crystalline polyesters and polyamides having low melting points and good solubilities.[1)] However, this reaction, i.e., the introduction of *t*-butyl group in the position *ortho* to the methyl group of *p*-xylene was very slow with H_2SO_4, $AlCl_3$, and acidic clays, while the alkylation at *meta*- or *para*-position of *o*- or *m*-xylene occurs rapidly.[2-5)] This is because the alkylation with the bulky *t*-butyl group at the *ortho*-position is sterically hindered.[2,3)] Friedman *et al.* reported that the yields of BPX were only 11 and 7% for $AlCl_3$-CH_3NO_2 and H_2SO_4, respectively, because of the formation of large amounts of by-products.[3)] Here we wish to report that solid $H_3PW_{12}O_{40}$ is a selective catalyst for the formation of BPX in this reaction.



(1)

$H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and $H_5BW_{12}O_{40}$ were prepared according to the methods in the literature.[6)] $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was obtained by the titration of an aqueous solution of $H_3PW_{12}O_{40}$ with an aqueous solution of Cs_2CO_3.[7,8)] For reference, SO_4^{2-}/ZrO_2,[9)] SiO_2-Al_2O_3 (Catalysts and

Chemicals Ind. Co., Ltd., Al_2O_3: 28.6wt%), Amberlyst-15 (Organo Corporation), H_2SO_4 (Nacalai Tesque) and CF_3COOH (Tokyo Kasei Co.) were used as catalysts.

The catalytic reaction was carried out in a three-neck flask (50 ml) at 30 °C under an N_2 atmosphere, where the solid catalysts were pretreated in a He flow at elevated temperatures (150 °C for the heteropoly compounds, 350 °C for SO_4^{2-}/ZrO_2 and SiO_2-Al_2O_3, and 95 °C for Amberlyst-15). After the catalyst (0.45 g) was added to liquid *p*-xylene (30 ml; 0.28 mol) which had been dried with molecular sieve 4A, 2-methylpropene (gas) was bubbled in the liquid with a rate of 0.37 $\mathrm{mmol \cdot min^{-1}}$. The products were analyzed with a gas chromatograph (Hitachi 163, FID) using an OV-1 column (capillary, 25 m) and GC-Mass spectrometer (Shimadzu GCMS-QP1100 EX).

Figure 1 shows the changes in the conversion of 2-methylpropene and the selectivity with time for $H_3PW_{12}O_{40}$ and H_2SO_4. As shown in Fig. 1, the conversions were above 80% for both catalysts, where conversion (%) was defined as [mol of 2-methylpropene reacted/mol of 2-methylpropene supplied]x100.

It was found that the selectivity to BPX observed for $H_3PW_{12}O_{40}$ was 75% until 30 min of the reaction, and then decreased to 66% at 50 min,

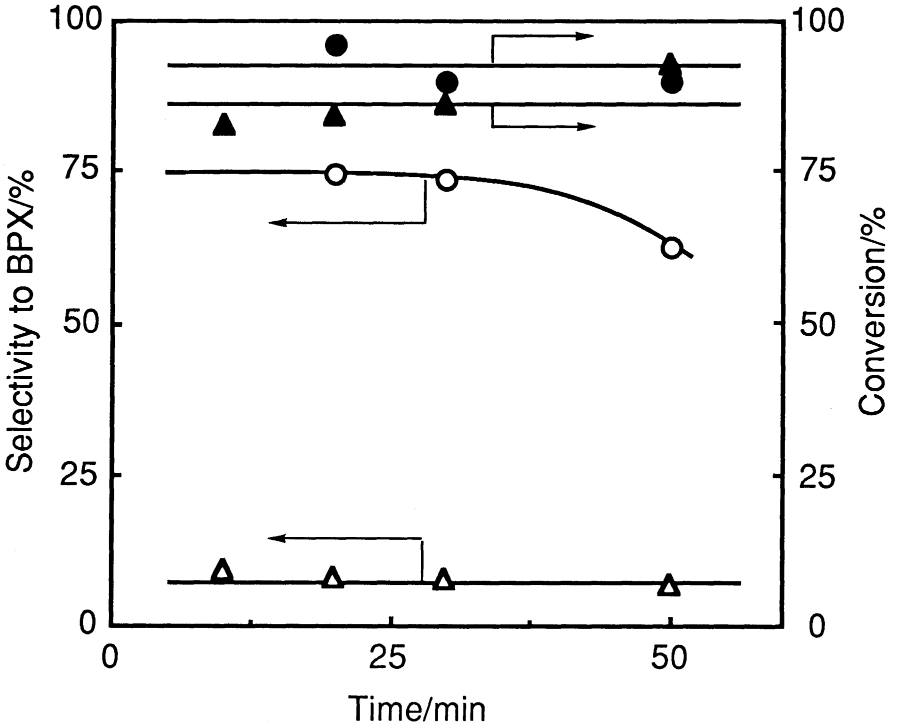


Fig. 1. Time course of alkylation of *p*-xylene with 2-methylpropene by $H_3PW_{12}O_{40}$ and H_2SO_4 at 30 °C. Catalyst; 0.45 g, *p*-xylene; 0.28 mol, rate of 2-methylpropene feed; 0.37 $\mathrm{mmol \cdot min^{-1}}$. Conversion: ●; $H_3PW_{12}O_{40}$, ▲; H_2SO_4. Selectivity: ○; $H_3PW_{12}O_{40}$, △; H_2SO_4.

while H_2SO_4 gave only 7%-selectivity to BPX. By-products were oligomers (dimer, trimer and tetramer) of reactant 2-methylpropene, octyl-*p*-xylene (OPX), and di-*p*-xylylmethane (PXM).[2,3]

In Table 1, the results for various acid catalysts are summarized, where the data were collected after 30 min of reaction. The conversions were in the range of 75-97%, except for the case of CF_3COOH (10%). The selectivity to BPX was in the order; $H_3PW_{12}O_{40}$ (75%) > $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (51%), SO_4^{2-}/ZrO_2 (51%)> H_2SO_4 (7%) > Amberlyst-15 (4%) > SiO_2-Al_2O_3 (1%) > CF_3COOH (0%), where the figures in the parentheses are the selectivities (mol%) to BPX.

We already reported that $H_3PW_{12}O_{40}$ possessed superacidity (H_0 = -13.16),[8,10] while the acid strength was lower than that of SO_4^{2-}/ZrO_2 (H_0 = -16.04).[9] H_2SO_4, Amberlyst-15, and SiO_2-Al_2O_3 are acids weaker than the above heteropoly compounds and SO_4^{2-}/ZrO_2.[7,8,10] Thus, the difference in the selectivity may be attributable to the different acid strength.

In order to confirm this, the reaction was performed by using heteropolyacids having different acid strength. It has been confirmed that the acid strength increases as the valency of the central atom increases

Table 1. Selectivity for Alkylation of *p*-Xylene with 2-Methylpropene by Various Acid Catalysts

Catalyst	Selectivity[a]/%				Conv./%	Mass balance/%
	BPX[b]	Oligomers[c]	OPX[d]	PXM[e]		
$H_3PW_{12}O_{40}$	74.6	11.5	6.3	7.6	90	96
$H_4SiW_{12}O_{40}$	26.6	70.2	0.4	2.8	91	108
$H_5BW_{12}O_{40}$	6.1	93.9	0	0	97	119
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	50.5	48.0	0.8	0.7	89	110
SO_4^{2-}/ZrO_2	50.9	26.0	3.4	19.7	86	86
Amberlyst-15	4.2	95.8	0	0	92	109
SiO_2-Al_2O_3	1.3	98.7	0	0	75	101
H_2SO_4	7.2	92.8	0	0	86	68
CF_3COOH	0	100	0	0	10	81

a) Mol%. b) *t*-Butyl-*p*-xylene. c) Sum of dimer, trimer, and tetramer of 2-methylpropene. d) Octyl-*p*-xylene. e) Di-*p*-xylylmethane. The reaction was performed at 30 °C for 30 min. *p*-Xylene; 0.28 mol, 2-methylpropene; 0.37 $mmol \cdot min^{-1}$, catalyst; 0.45 g.

(B^{3+} to P^{5+}).11) In acetonitrile solution, H_0 values were -2.14, -1.98, and -1.55 for $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and $H_5BW_{12}O_{40}$, respectively.11) As shown in Table 1, the selectivity to BPX significantly increased (from 6% to 75%) as the valency of the central atom increased, where the conversions of 2-methylpropene were at similar levels. This result clearly indicates that the acid strength is essential for the selectivity; strong acid sites are effective for the alkylation to BPX, but the weak acid sites catalyze preferentially the oligomerization of 2-methylpropene.

Although the acid strength of SO_4^{2-}/ZrO_2 is higher than that of $H_3PW_{12}O_{40}$,8) SO_4^{2-}/ZrO_2 was less selective than $H_3PW_{12}O_{40}$ for the formation of BPX. Temperature programmed desorption of NH_3 showed that SO_4^{2-}/ZrO_2 had a large amount of weak acid sites together with a small amount of superacid sites, while the acid strength of $H_3PW_{12}O_{40}$ was nearly uniform.8) Probably the weak acid sites on SO_4^{2-}/ZrO_2 catalyzed the oligomerization, resulting in the low selectivity to BPX. It was reported that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was highly active for the alkylation of 1,3,5-trimethylbenzene with cyclohexene.7,8) As shown in Table 1, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ gave BPX with the selectivity of 51%.

References

1) H. R. Kricheldorf and J. Engelhardt, J. Polym. Sci., 28, 2335 (1990).
2) G. A. Olah, "Friedel-Crafts and Related Reactions," John Wiley and Sons Inc., New York (1964), Vol. II, p. 40.
3) B. S. Friedman, F. L. Morritz, C. T. Morrissey, and R. Koncos, J. Am. Chem. Soc., 80, 5867 (1958).
4) B. B. Corson, W. J. Heintzelman, R. C. Odioso, H. E. Tiefenthal, and F. J. Pavlik, Ind. Eng. Chem., 48, 1180 (1956).
5) S. K. Ghosh and M. M. Sharma, Ind. Eng. Chem. Res., 31, 445 (1992).
6) C. Hu, M. Hashimoto, T. Okuhara, and M. Misono, J. Catal., 143, 437 (1993).
7) T. Nishimura, T. Okuhara, and M. Misono, Appl. Catal., 73, L7 (1991).
8) T. Okuhara, T. Nishimura, H. Watanabe, and M. Misono, J. Mol. Catal., 74, 247 (1992).
9) M. Hino, S. Kobayashi, and K. Arata, J. Am. Chem. Soc., 101, 6439 (1979).
10) M. Misono and T. Okuhara, CHEMTECH, 1993, 23.
11) C. Hu, M. Hashimoto, T. Okuhara, and M. Misono, Bull. Chem. Soc. Jpn., in press.

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