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A Study of Catalysis by Metal Phosphates. V.[1] The Alkylation of Toluene with Methanol over Metal Phosphate Catalysts

Toshiaki SODESAWA,* Isao KIMURA, and Fumio NOZAKI

Department of Industrial Chemistry, Faculty of Engineering, Chiba University, Yayoi-cho, Chiba 260

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Synopsis. The side chain alkylation of toluene with methanol over the catalyst of $Ca_3(PO_4)_2$ or K_3PO_4 supported on active carbon gave more ethylbenzene than that over MgO. It was found that there are correlations between the catalytic activities and acid-base properties.

In a previous paper a report was given on the alkylation of phenol with methanol over metal phosphate catalysts.[1] It is well-known that metal phosphates have acid properties. However, it was found that $Ca_3(PO_4)_2$ and K_3PO_4 have not only acidic but also basic sites.[2,3] In this paper, the correlation between the catalytic activity of metal phosphates and their acid-base properties are discussed. The activity sequence and catalytic behavior of metal phosphates are compared with those of other solid acid-base catalysts.

Experimental

The metal phosphates, MgO, and CaO catalysts were prepared according to the method reported.[1] Commercial chemicals of guaranteed grade were used: H-Zeolon, SiO_2–Al_2O_3, $Al_2(SO_4)_3$, Al_2O_3, Na_2WO_4. The catalysts of Na_3PO_4 and K_3PO_4 supported on active carbon (Tsurumicoal Kogyo Co.) were prepared by the impregnating method, the concentration being made about 15 wt %. All the catalysts were activated by calcination in a stream of nitrogen gas at 500 °C for 1 h prior to each test.

The acidity of catalysts was measured by Benesi's method,[4] using the following Hammett indicators: Neutral Red (pK_a= +6.8), Methyl Red (+4.8), Dimethyl Yellow (+3.3), 4-phenylazodiphenylamine (+1.5), dicinnamylideneacetone (−3.0), benzylideneacetophenone (−5.6), anthraquinone (−8.2). As a titration reagent *n*-buthylamine of 0.1 mol/l in benzene solution was added to a known amount of catalysts calcined at 500 °C for 4 h. Hammett indicators were then added and the resulting with coloration was compared visually. Titration with benzoic acid of 0.1 mol/l using Bromothymol Blue (pK_a=7.1), phenolphthalein (9.3), 2,4-dinitroaniline (15.0), and 4-chloro-2-nitroaniline (17.2) as indicators was carried out in order to measure the basicity of catalysts. The procedure was almost the same as in the acidity measurements.

The apparatus and procedure were almost the same as described previously. The reaction products were trapped with ice and analyzed by gas chromatography on a 3 m column of Benton 34(5%)+DNP(5%), hydrogen being passed through as a carrier gas.

Results and Discussion

In the case of alkylation of phenol with methanol over $Ca_3(PO_4)_2$ catalyst, the main products are *o*-cresol and 2,4-xylenol which are produced by the ortho-position alkylation of benzene ring. Results of alkylation of toluene with methanol over various catalysts are given in Table 1. We see that the alkylation of toluene does not occur readily as compared with that of phenol. The methylation of benzene ring over BPO_4 and $Zr_3(PO_4)_2$ gave selectively as much xylenes as that over SiO_2–Al_2O_3 and H-Zeolon catalysts. The BPO_4 catalyst showed the highest activity of all the metal phosphates and produced much *o*-xylene in all xylenes, while $Ca_3(PO_4)_2$ and K_3PO_4 gave only ethylbenzene by the alkylation of side chain. The results differ from those in the case of the base catalyst such as MgO which produced both ethylbenzene and styrene. The Na_3PO_4 catalyst supported on active carbon gave both xylenes and ethylbenzene. The active carbon gave only benzene and no alkylated products. This seems to be in line with other reported results.[5,6] The activity of K_3PO_4 catalyst for the side chain alkylation was not higher than that of MgO–TiO_2[7,8] and Zeolite catalysts exchanged K cation.[9] Improvement in the preparation

Table 1. Activities of catalysts for alkylation of toluene

Conditions: reaction temperature t=500 °C (except for SiO_2–Al_2O_3 and H-Zeolon catalysts, in which t was 400 °C), W/F=14.8 g h/mol, feed molar ratio of methanol/toluene/N_2=1/2/5.3.

Catalyst	Conversion of toluene (%)	Yield (%)					
		Ethylbenzene	Styrene	*o*-Xylene	*m*-Xylene	*p*-Xylene	Benzene
BPO_4	9.6	0	0	4.6	3.2	1.8	0
$Zr_3(PO_4)_4$	0.7	0	0	0.3	0.2	0.2	0
$Ca_3(PO_4)_2$	0.3	0.3	0	0	0	0	0
Na_3PO_4–AC[a]	2.3	0.7	0	0.3	0.2	0.1	1.0
K_3PO_4–AC[a]	1.8	1.8	0	0	0	0	0
SiO_2–Al_2O_3	21.7	0	0	9.0	7.0	5.7	0
H-Zeolon	32.6	0	0	9.0	16.0	7.6	7.6
MgO	1.0	0.3	0.7	0	0	0	0

a) AC denotes activated carbon used as a carrier. Na_3PO_4 or K_3PO_4 was supported to make the concentration about 15 wt %.

Table 2. Acid-base properties of catalysts

Catalyst[a]	pK_a							
	−8.2	−5.6	−3.0	+3.3	+4.8	+6.8	+7.1	+9.3
BPO_4	−	+	0.160[b]	+	+	+	−	
$Zr_3(PO_4)_4$	−	+	0.063[b]	+	+	+	−	
$Ca_3(PO_4)_2$				−	+	+	+	0.001[c]
Na_3PO_4					−	+	+	0.006[c]
K_3PO_4						−	+	0.010[c]
SiO_2–Al_2O_3	+	+	0.471[b]	+	+	+	−	
H-Zeolon	+	+	0.513[b]	+	+	+	−	
MgO					−	+	+	0.007[c]
CaO					−	+	+	0.011[c]

a) Calcined at 500 °C. + and − denote positive and negative, respectively. b) Acidity (mmol/g) measured at $H_0 \leqq -3.0$. c) Basicity (mmol/g) measured at $H_0 \geqq 9.3$.

of these catalysts might afford higher activity. The alkylation of ethylbenzene with methanol over K_3PO_4 and Na_3PO_4 supported on active carbon gave a greater amount of cumene than over MgO or CaO. The alkylation over the metal phosphates is essentially different in the reaction route from that of solid base catalysts such as MgO.

The acidity and basicity of various catalyst surfaces were measured (Table 2). It is obvious that the BPO_4 and $Zr_3(PO_4)_4$ catalysts, being as active as SiO_2–Al_2O_3 and H-Zeolon for xylene production in toluene alkylation, have acid sites at $H_0 \leqq -3.0$, while the $Ca_3(PO_4)_2$ and K_3PO_4 being as effective as MgO for ethylbenzene formation have basic sites at $H_0 \geqq 9.3$. The catalytic activities in each case seem to be strongly related to acid or base amounts of each catalyst. However, the route of side chain alkylation over $Ca_3(PO_4)_2$ or K_3PO_4 seems to differ from that over MgO which gives both ethylbenzene and styrene.

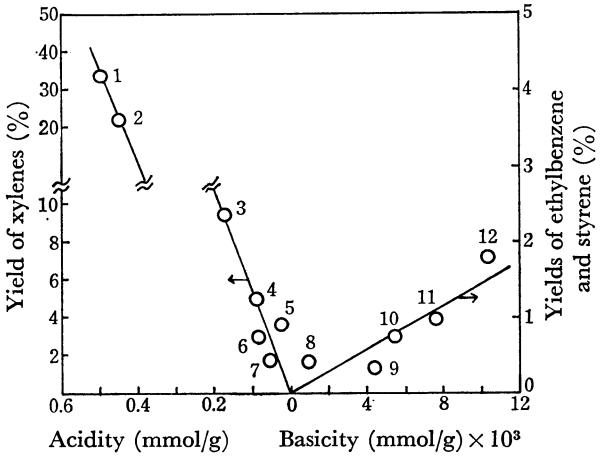

Fig. 1. Correlation between the catalytic activity and the acidity or basicity of various catalysts in the alkylation of toluene with methanol (acidity; $H_0 \leqq -3.0$, basicity; $H_0 \geqq 9.3$)
1: H-Zeolon, 2: SiO_2–Al_2O_3, 3: BPO_4, 4: $Al_2(SO_4)_3$, 5: Al_2O_3, 6: $CrPO_4$, 7: $Ti_3(PO_4)_4$, 8: $Ca_3(PO_4)_2$, 9: Na_2WO_4, 10: Na_3PO_4–AC, 11: MgO, 12: K_3PO_4–AC.

The correlations between the acid-base properties and the activities of various solid catalysts in the alkylation of toluene are shown in Fig. 1. There are correlations between the yields of xylenes and the acidity at $H_0 \leqq -3.0$ or the yields of ethylbenzene and styrene and the basicity at $H_0 \geqq 9.3$. The correlation between the acid-base property and the catalytic activity of $Ca_3(PO_4)_2$ calcined at various temperatures in the alkylation of phenol was reported.[1] It was found that the catalytic activities can be classified into three types of linear relationships, (a) highly dependent on acidity, (b) strongly dependent on basicity, (c) dependent on both acidity and basicity as indicated over $Ca_3(PO_4)_2$ catalyst. In the case of toluene (Fig. 1), it seems that the alkylation is highly related to acidity or basicity of catalysts. The alkylation of toluene over $Ca_3(PO_4)_2$ or K_3PO_4 supported on the active carbon is strongly related to base amounts of the catalyst.

References

1) Part IV of this series: F. Nozaki and I. Kimura, *Bull. Chem. Soc. Jpn.*, **50**, 614 (1977).
2) T. Imanaka, Y. Okamoto, and S. Teranishi, *Bull. Chem. Soc. Jpn.*, **45**, 1353 (1972).
3) A. Tada, *Bull. Chem. Soc. Jpn.*, **48**, 1391 (1975).
4) H. A. Benesi, *J. Phys. Chem.*, **61**, 970 (1975).
5) H. Pines and L. Shaap, *Adv. Catal.*, **12**, 117 (1960).
6) T. Yashima, H. Ahmad, K. Yamazaki, M. Katsuta, and N. Hara, *J. Catal.*, **16**, 273 (1972).
7) O. Takahashi, H. Hattori, and K. Tanabe, Abstr. No. 3E07, 39th Meeting of the Catalysis Society of Japan, Sapporo, August 1976.
8) K. Tanabe, O. Takahashi, and H. Hattori, *React. Kinet. Catal. Lett.*, **7**, 347 (1977).
9) Y. Murakami and H. Ito, 41st Meeting of the Catalysis Society of Japan, Toyama, October 1977, Abstr. No. C-3.