Identification and influence of acidity on alkylation of phenol with propylene over ZSM-5

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The alkylation of phenol with propylene has been studied over several H-ZSM-5s with different Si/Al ratios and Cs^+-ion-exchanged H-ZSM-5s at temperature range 373–623 °C. Both O- and C-alkylation, which were closely dependent on the reaction temperature and acidity of the catalysts, were observed. O-alkylated compound is found to be formed preferably at temperature lower than 250 °C and over Cs^+-ion-exchanged H-ZSM-5s. However, at higher temperature, only C-alkylation is observed. The acidic properties of the zeolites were characterized by solid-state ^{31}P MAS-NMR of the probe molecule trimethylphosphine oxide and NH_3-TPD (temperature-programmed desorption) and it is suggested that in the case of C-alkylation, moderate acid sites are responsible for the formation of *para*-isopropylphenol, while *ortho*-isopropylphenol is favorable for weak acid sites.

KEY WORDS: phenol; isopropylation; H-ZSM-5; acidity; ^{31}P MAS-NMR; NH_3-TPD

1. Introduction

Isopropylphenols are useful materials in the synthesis of various products such as adhesives, agricultural chemicals and pharmaceuticals. Using solid acid catalysts may be a very promising way for their synthesis considering their activity, selectivity, re-usability and the increasing demand for eco and environmentally harmonized routes in the chemical industry. It has been reported that phenol isopropylation was carried out with propylene or 2-propanol over different solid acid catalysts [1–3], where *ortho*-isopropylphenol could be obtained over large pore zeolites such as H-Beta and H-ZSM-12, whereas medium pore opening H-ZSM-5 gave production of the *para* isomer. Swamy *et al.* reported alkylation of phenol with 1-propanol and 2-propanol over calcined magnesium aluminium hydrotalcites (MgAl-CHT) [4]. They reported that the reaction of phenol with 1-propanol proceeded without skeletal isomerization of the propyl moiety, suggesting an S_N2 type mechanism. Furthermore, phenol alkylation with 1-propanol gave rise to O- and C-alkylation, while with 2-propanol as alkylating agent, the alkylation took place exclusively at C-centers. Moreover, the preferential *ortho* position substitution was observed in C-alkylation of phenol with both 1- and 2-propanol.

But, so far, in comparison with methylation and *t*-butylation of phenols [5–9], less work has been done concerning the propylation of phenol derivatives. Especially, the literature concentrates mainly on the selective formation of propylated phenolic isomer over zeolites or modified clay according to reaction parameters such as reaction temperature, ratio of PhOH/alkylating agent and WHSV (weight hourly space velocity). The influences of acid type such as Brønsted or Lewis acid and degree of strength on catalytic properties such as the phenol conversion and product selectivity have not yet been studied.

Studies of small basic probe molecules by NMR to identify surface acidic sites on oxides of aluminum and silicon have yielded information on the types of surface acid sites, on the numbers of these sites, and about the molecular dynamics of the adsorbed probe molecules. Initial work in this area employed amines as probes via ^{13}C and ^{15}N magic-angle spinning (MAS) NMR [10,11]. More recent work has focused on the study of phosphines *via* ^{31}P NMR [12–14]. Probe molecules containing ^{31}P nuclei present substantial advantages over probes isotopically enriched with ^{13}C and ^{15}N nuclei. These advantages include increased sensitivity and chemical shift dispersion.

In this work, solid-state ^{31}P NMR of the probe molecule trimethylphosphine oxide (TMPO), combined with NH_3-TPD were used to characterize the acidic properties of ZSM-5s such as acid type and acidity. We have attempted to relate the acidity of H-ZSM-5s with different Si/Al ratios and Cs^+-exchanged H-ZSM-5s with their catalytic activity and selectivity in the phenol alkylation with propylene.

2. Experimental

2.1. Catalyst preparation

Zeolite H-ZSM-5s (Zeolyst) were used in this work. H-ZSM-5 with different silica to alumina ratio is denoted as HZ-X, where X represents silica to alumina ratio. Cesium-

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ion-loaded H-ZSM-5 samples were prepared by a solid-state ion-exchange method as follows: 3 g H-ZSM-5 was mixed with an estimated amount of cesium nitrate and ground homogeneously, then calcined at 500 °C for 5 h in air.

2.2. Characterization

NH_3-TPD profiles were measured with a home-made apparatus and ammonia desorption was carried out from 100 to 600 °C at a heating rate of 10 °C/min.

Prior to characterization by solid-state NMR, according to the previous report [14], samples were prepared as follows. For each sample studied, approximately 0.4 g of solid was calcined at 500 °C for 4 h in a crucible. After lowering the oven temperature to 200 °C, the sample was put into a flask, capped with a rubber septum and transferred to a glovebox. A measured amount of dry TMPO/CH_2Cl_2 solution of known concentration was added to the flask, and the mixture was agitated overnight in the glovebox under Ar. The solvent was removed by connecting the flask to a high vacuum system (maximum vacuum of 10^{-6} atm) and the sample was transferred to the spinner while in the glovebox to avoid air contact. The ^{31}P MAS NMR spectra were measured on a Bruker DSX 300 MHz spectrometer operating at 121.49 MHz under the following conditions: magic-angle spinning at 6 kHz; single pulse. The repetition delay used in the present case is 6 s, which is about four times longer than the largest measured T_1. It is found that prolonging the repetition delays does not alter the spectra anymore. The number of scans collected for each spectrum was 612, and the spectra were referenced to ammonium orthophosphate as an external standard.

2.3. Phenol alkylation with propylene

Catalytic reactions were carried out in a fixed-bed flow reactor with phenol to propylene molar ratio of 1 : 1 and WHSV of 3.0 h^{-1}, for 2 h in the temperature range 373–623 °C and at atmospheric pressure. 0.5 g of catalyst was charged into the reactor of 6.0 mm inner diameter and preheated at 500 °C in an air flow for dehydration before use. Phenol was melted and transferred into a syringe, then fed with a syringe pump into the reactor. The reaction effluent was collected in an ice trap, quantified by GC (HP 5890) using FID furnished with a CP-SIL 5 CB 50 m capillary column and confirmed by GC-MS. Products obtained in this reaction are listed and abbreviated as follows: normal propylphenol (*n*-PP), isopropylphenol ether (IPPE), *para*-isopropylphenol (*p*-IPP), *meta*-isopropylphenol (*m*-IPP), *ortho*-isopropylphenol (*o*-IPP), di-isopropylphenol (DIPP), BP (butylphenol).

Conversion was defined as conversion (%) $= (100 - M_p) \times 100$, where M_p is the molar percentage of residual phenol in the final products.

3. Results and discussion

It is shown in table 1 that alkylation of phenol with propylene was carried out over HZ-30 and Cs^+-ion-exchanged HZ-30 as a function of reaction temperature. The conversion of phenol increases initially from 21.8 to 39.9% with increase of reaction temperature from 100 to 300 °C, and then decreases to 33.8% at 350 °C. So 300 °C is chosen as the optimum reaction temperature in the subsequent reactions. It can be interpreted that higher temperature is needed to overcome threshold energy and hasten the diffusion rate of reactants and products, but the conversion is lowered owing to deactivation when temperature is over 300 °C. As seen in table 1, IPPE is formed only at temperature lower than 250 °C over HZ-30, showing selectivities of 41.8, 38 and 5.0% at 100, 150 and 200 °C, respectively. This indicates that the O-alkylated compound is preferred to form at lower temperature. By using IPPE as the starting material over HZ-30 with WHSV of 3 h^{-1} at 300 °C, IPPE is not detected in the final products (see table 1). Large amounts of phenol and mono-alkylated phenol are obtained, together with minor quantities of di-alkylated phenol. In phenol alkylation with methanol, it is also reported that an O-alkylated compound, anisole, is formed and it can subsequently react with phenol to give rise to the C-alkylated compound, *o*-cresol [5]. As shown in ta-

Table 1
Activities and products distribution obtained in phenol alkylation with propylene over HZ-30 as a function of reaction temperature.[a]

Temperature (°C)	Conversion (%)	Selectivity (%)								
		Oligomer	IPPE	*o*-IPP	*p*-IPP	*m*-IPP	*n*-PP	BP	DIPP	Unknown
100	21.8	0	41.8	32.6	18.9	2.6	0	2	1.5	0.5
100[b]	3	0	100	0	0	0	0	0	0	0
150	29.8	0	38	35.4	19.6	3.0	0	2.3	2.3	0
200	32.0	0	5.0	49.0	29.5	7.5	0	1.6	6.0	1.4
250	30.5	0	0.9	50.8	32.0	7.2	0	0	7.5	1.5
300	39.9	0.5	0	39.0	37.8	11.6	2.1	0	6.5	2.5
350	33.8	0	0	32.9	32.5	22.0	7.4	0	2.5	3.0
300[c]	100	0	0	41.0	35.1	13.0	1.0	0	7.9	2.0

[a] Reaction conditions: 3.0 h^{-1}, 2 h, phenol/propylene = 1.
[b] Catalyst: Cs-HZ-30 (1 wt% Cs).
[c] IPPE as unique reagent.

ble 1, phenol alkylation with propylene over Cs-HZ-30 at 100 °C exhibits 100% selectivity for O-alkylated compound with 3% phenol conversion. Obviously, formation of IPPE is favored over weak acid sites at low temperature. In the case of phenol alkylation with methanol, Kim *et al.* reported that anisole was exclusively formed over Cs^+-exchanged-zeolite X [15]. Swamy *et al.* carried out phenol alkylation with 1-propanol over a catalyst derived from hydrotalcite-like anionic clays. It was found that acid–base properties of catalysts had great influence on product distribution. Comparison of product selectivity at a constant phenol conversion (40–45%) level revealed that MgAl 3.0-CHT was more selective to O-alkylation giving n-propyl phenyl ether as the major product. The higher selectivity for O-alkylation in the case of MgAl 3.0-CHT was due to the high basicity of the catalyst. In contrast, the higher surface acidity of CuAl 3.0-CHT and NiAl 3.0-CHT, obtained by isomorphous substitution of Mg^{2+} in MgAl 3.0 CHT by Cu^{2+} or Ni^{2+}, favored predominantly C-alkylation to give 2-n-propylphenol [4]. In our experiment, it is also found that weakening acidity, *i.e.*, strengthening basicity by Cs^+ ion exchange, improves selectivity for O-alkylation.

Furthermore, selectivity for DIPP increases from 1.5 to 7.5% at temperature from 100 to 300 °C, then, decreases at temperature higher than 300 °C. At high reaction temperature, once formed mono-alkylated phenol is easy to continue secondary reaction with propylene, and high reaction temperature of 350 °C leads to dealkylation and cracking of formed products, which was also reported in t-butylation of phenol [8,9]. It is known that thermodynamically favored isomers follow the order of *meta* > *para* > *ortho* [16,17]. With the increase of reaction temperature o-IPP and p-IPP can isomerize to m-IPP which leads to its enhanced selectivity apparently from 2.6 to 22%.

Table 2 shows phenol alkylation with propylene over H-ZSM-5s with different Si/Al ratios and Cs^+-ion-exchanged H-ZSM-5s. Over H-ZSM-5s, moderate selectivity for p-IPP is observed, in the order of HZ-30 < HZ-80 < HZ-150 with $1.0 < p\text{-IPP}/o\text{-IPP} < 5.7$. It seems that high silica to alumina ratio of H-ZSM-5 benefits the formation of *para* isomer. However, the conversion of phenol presents the different order of HZ-30 > HZ-80 ≈ HZ-150 with 39.9, 34.6 and 34.3%, respectively. Because of the medium pore openings of ZSM-5s, shape selectivity is expected in this reaction over H-ZSM-5. However, since the pore sizes of H-ZSM-5 zeolites with different Si/Al ratios are almost identical, the difference in selectivity over H-ZSM-5s could only be explained by their different acidic properties, such as strength and concentration of acid sites.

In order to understand the acidity dependence of catalyst on conversion and selectivity, H-ZSM-5 was modified by Cs^+ ion exchange. Compared with their parent H-ZSM-5s, the conversions decrease in the order of Cs-HZ-30 > Cs-HZ-80 > Cs-HZ-150 with 38.9, 23.1 and 13.1%, respectively. In comparison with HZ-30, Cs^+ ion exchange induces the increase of the *para* to *ortho* ratio in mono-alkylated phenol from 1.0 to 3.3. At almost the same conversion as the parent zeolite, Cs-HZ-80 also shows the same effect with *para* to *ortho* ratio from 3.6 to 4.0. However, Cs^+-exchanged HZ-150 leads to decrease of *para* to *ortho* ratio from HZ-150 of 5.7 to Cs-HZ-150 of 1.1. (The possible explanation is suggested based on NH_3-TPD and ^{31}P NMR, see below.) It can be suggested to make a comparison of the selectivity for DIPP, which is regarded as preferably formed over strong acidic site rather than weak one [9]. The selectivities for DIPP over HZ-30, HZ-80 and HZ-150 are, respectively, 6.5, 3.6 and 2.5%. Cesium exchange leads to the corresponding decrease of selectivity for DIPP to 4.1, 1.9 and 2.3%.

In order to understand the acidic property of ZSM-5, solid-state ^{31}P NMR of a TMPO probe was attempted, from which Brønsted and Lewis acid sites are characterized. Quantification of spectral intensities of resonances is employed to calculate the relative concentrations of Brønsted

Table 2
Phenol alkylation with propylene over various acidic zeolites.[a]

Catalyst	Conversion (%)	Selectivity (%)									p-IPP/
		Oligomer	IPPE	o-IPP	p-IPP	m-IPP	n-PP	BP	DIPP	Unknown	o-IPP
HZ-30	39.9	0.5	0	39.0	37.8	11.6	2.1	0	6.5	2.5	1.0
HZ-80	34.6	13.5	0	9.2	32.7	22.6	6.2	9.8	3.6	2.4	3.6
HZ-150	34.3	5.9	0	10.0	57.2	15.5	3.6	3.4	2.5	1.6	5.7
Cs-HZ-30 (1 wt% Cs)	38.9	0.5	0	18.0	59.5	15.4	1.0	0	4.1	1.4	3.3
Cs-HZ-80 (1 wt% Cs)	23.1	0	0	17.0	73.6	7.9	0	0	1.9	0	4.3
Cs-HZ-80[b] (1 wt% Cs)	34.1	0	0	17.7	70.6	9.6	0	0	2.1	0	4.0
Cs-HZ-150 (1 wt% Cs)	13.1	0	0	36.0	51.7	9.8	0	0	2.3	0	1.4
Cs-HZ-150[c] (1 wt% Cs)	34.0	0	0	40.8	44.8	11.0	0	0	3.4	0	1.1

[a] Reaction conditions: 300 °C, 3.0 h^{-1}, 2 h, phenol/propylene = 1.
[b] Catalyst 0.7 g, 2.0 h^{-1}.
[c] Catalyst 1.2 g, 1.2 h^{-1}.

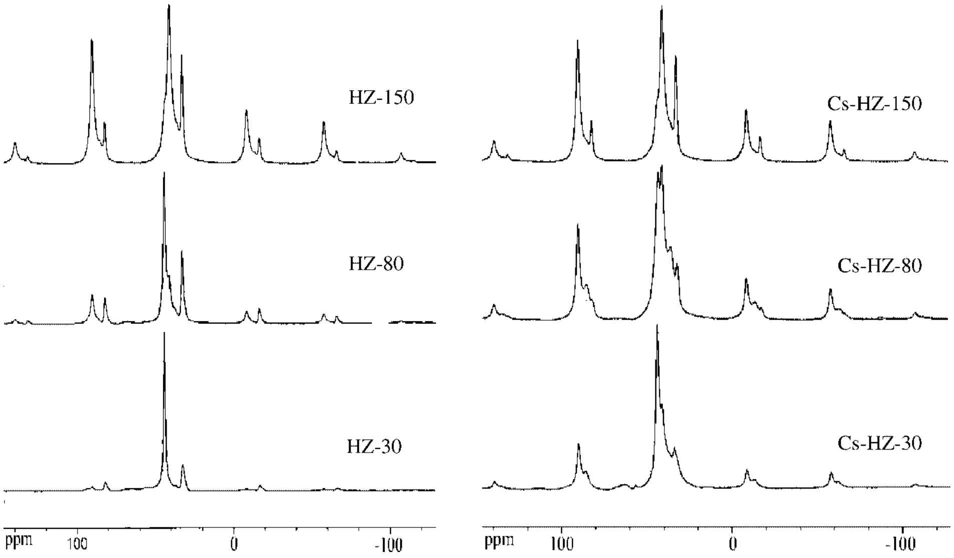

Figure 1. ^{31}P MAS NMR spectra of $(CH_3)_3PO$ on H-ZSM-5s and Cs^+-ion-exchanged H-ZSM-5s. The sample spinning rate is 6.0 kHz.

Table 3
The ratio of Brønsted acid sites to Lewis acid sites calculated on the basis of relative intensity of resonance at 43 and 32 ppm in ^{31}P MAS NMR spectra of $(CH_3)_3PO$ adsorbed on H-ZSM-5s and Cs^+-ion-exchanged H-ZSM-5s.

Sample	HZ-30	HZ-80	HZ-150
B/L[a]	5.3	3.3	0.9
Sample	Cs-HZ-30	Cs-HZ-80	Cs-HZ-150
B/L[a]	3.2	2.4	0.8

[a] B: concentration of Brønsted acid site, L: concentration of Lewis acid site.

and Lewis acid sites in ZSM-5. Figure 1 shows ^{31}P MAS NMR spectra of H-ZSM-5s with different Si/Al ratios and Cs^+-ion-exchanged H-ZSM-5s impregnated with a moderate loading of $(CH_3)_3PO$ (2.70 mmol of TMPO/g of solid). Isotropic peaks at 43, 41 and 32 ppm and wide spinning sidebands appear in all the spectra except the absence of resonance at 41 ppm in HZ-30. The spectra are interpreted based on the previous report [14]. The resonance at 41 ppm can be assigned to physisorbed $(CH_3)_3PO$, 43 ppm to $(CH_3)_3POH^+$ bound to Brønsted acid site and the lower resonance at 32 ppm to $(CH_3)_3PO$ bound to Lewis acid site. With the increase of Si/Al ratio and Cs^+ ion exchange, the peak at 43 ppm decreases in intensity, while the peaks at 41 and 32 ppm increase in relative intensity. Based on the relative intensity of the resonance at 43 and 32 ppm, the ratio of number of Brønsted acid to Lewis acid sites is calculated in table 3. The increment of Si/Al ratio results in decrease of ratio of number of Brønsted acid to Lewis acid sites in H-ZSM-5s from HZ-30's 5.3 to HZ-80's 3.3 and HZ-150's 0.9, respectively. Cs^+ ion exchange also leads to the decrease of ratio of Brønsted acid (B) to Lewis acid (L) sites in parent H-ZSM-5s, showing the order of Cs-HZ-30 > Cs-HZ-80 > Cs-HZ-150 with 3.2, 2.4 and 0.8, respectively. This indicates that HZ-30 and HZ-80 have much more Brønsted acid sites than Lewis acid sites and the Cs^+ ion exchange neutralizes Brønsted acid sites. Misono *et al.* estimated the concentrations of Brønsted acid and Lewis acid sites of ZSM-5 (SiO_2/Al_2O_3 = 23.3) by FT-IR study, and they found that the ratio of B/L is about 6 and Pd^{2+} ion exchange induces the reduction of B/L [18]. In our previous work, *t*-butylation of catechol with t-butyl alcohol and isopropylation of phenol with 2-propanol have been carried out over H-ZSM-5s with different Na^+ ion exchange levels. The acid type and strength are determined by pyridine adsorbed XPS, and Brønsted acid sites are the main active sites [19,20]. In the case of ZSM-5s, Brønsted acid sites seem to be the active sites. The Brønsted acid sites strongly interact with the aromatic ring of the adsorbed phenol, thus bring it closer to the surface and permit isopropylation in the *ortho*, *meta* and *para* positions, respectively.

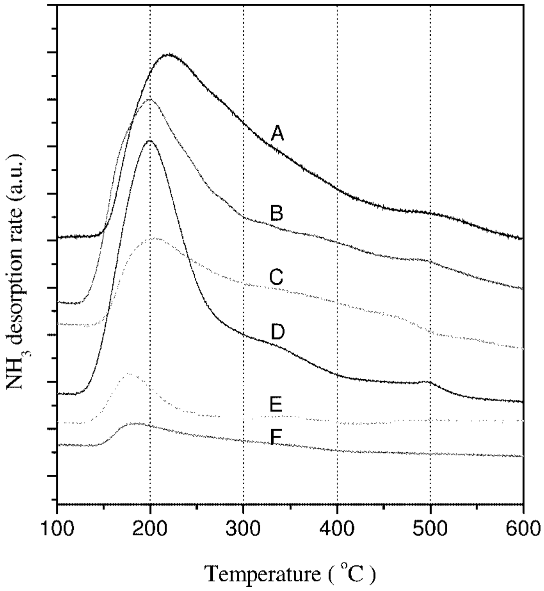

Figure 2. NH_3-TPD profiles of (A) HZ-30, (B) HZ-80, (C) HZ-150, (D) Cs-HZ-30, (E) Cs-HZ-80 and (F) Cs-HZ-150.

NH_3-TPD in figure 2 shows strength and concentration of acid sites. It is observed that the profiles of H-ZSM-5s are much broader that those of Cs^+-ion-exchanged samples, which represents acid sites with a wide range of acid strength in H-ZSM-5s. Especially the strong acid sites concentration ($T > 400\,^{\circ}\mathrm{C}$) in HZ-30 is much higher than those in HZ-80 and HZ-150. However, a relatively higher portion of weak and medium acid sites ($T < 400\,^{\circ}\mathrm{C}$) is observed in HZ-80 and HZ-150, respectively. The conversions of phenol over H-ZSM-5s are 39.9, 34.6 and 34.3%, respectively, in the order of HZ-30 > HZ-80 > HZ-150. However, the ratios of *para* to *ortho* isomer in mono-alkylated phenol are 1.0, 3.6 and 5.7, respectively, exhibiting reverse order of HZ-30 < HZ-80 < HZ-150. It seems that acid concentration is responsible for conversion, whereas acid strength for the distribution of products.

Furthermore, conversions over Cs-HZ-80 and Cs-HZ-150, with only moderate and weak Brønsted acid sites, are 23.1 and 13.1%, respectively. Hence, it can be proposed that this reaction is associated with the weak and moderate Brønsted acid sites.

It is observed that Cs^+ ion exchange leads to increase of the *para* to *ortho* ratio over HZ-30 and HZ-80, but to a reverse result over HZ-150. This may be explained by their acidic properties. $\mathrm{NH_3}$-TPD shows that, compared with parent H-ZSM-5s, Cs^+ on exchange results in a large decrease of acid concentration, especially strong acid sites. In the case of Cs-HZ-80 and Cs-HZ-30, only some weak and medium acid sites exist ($T < 400\,^{\circ}\mathrm{C}$). So it can be interpreted that moderate acid sites benefit the formation of *para* isomer, and weak acid sites are attributed to the formation of *ortho* isomer. It is shown in table 2 that in the case of HZ-150, Cs^+ ion exchange leads to drastic increase of o-IPP from 10.0 to 40.8% and also much decrease of p-IPP from 57.2 to 44.8%. In fact, HZ-150 contains suitable medium acid sites and shows high *para* to *ortho* ratio of 5.7. Cs^+ ion exchange results in a considerable decrease of original medium acid sites, and only weak acid sites remain, which can only catalyze the formation of o-IPP and results in the decrease of selectivity for *para* isomer.

It is shown in figure 3 that after 5 h reaction time, phenol conversions over HZ-30 and HZ-50 change from 50 to 26.5% and 34.6 to 28%, respectively, however, HZ-80 and HZ-150 are not the serious cases. It is observed that compared to HZ-80 and HZ-150, HZ-30 and HZ-50 change color markedly from white to dark brown after 5 h reaction time, which might be due to coke formation. HZ-30 is deactivated much faster due to its strong acidity. Coke formation is preferred over strong acidic sites and clogs the pore opening, and these effects can decrease the secondary reaction of formed mono-alkylated phenol. It is reported that *ortho* isomer was preferred to form over weak acid sites [9]. In this work, the same trend was also observed. Accompanying deactivation of the catalyst, strong acidic sites were covered by coke and o-IPP increased.

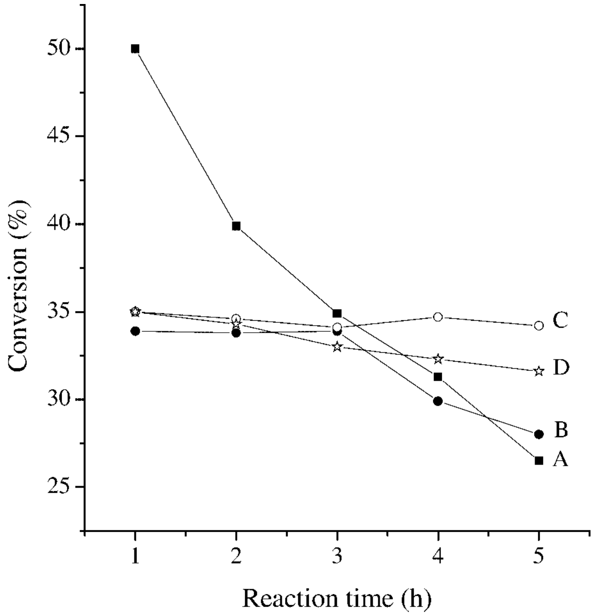

Figure 3. Phenol alkylation with propylene over HZSM-5s as a function of reaction time: (A) HZ-30, (B) HZ-50, (C) HZ-80 and (D) HZ-150.

4. Conclusions

(1) The alkylation of phenol over H-ZSM-5 occurs at both the carbon atom of the aromatic ring and the oxygen atom of the hydroxy group. IPPE is found to be formed preferably at lower than 250 °C and over Cs^+-ion-exchanged H-ZSM-5. In the case of C-alkylation, H-ZSM-5 presents moderate selectivity for *para* isomer among three mono-alkylated products. While acid concentration is responsible for conversion, acid strength for the product distribution.

(2) Apart from shape selectivity taking effect in phenol alkylation with propylene, acidic properties, *i.e.*, acid strength and acid denstiy of H-ZSM-5 zeolites also have influence on product distribution. It is observed that selectivity for *para* isomer is improved with increase of silica to alumina ratio in the range from 30 to 150. Meanwhile, Cs^+ ion exchange of HZ-30 and HZ-80 leads apparently to the increase of selectivity for p-IPP. It is characterized by $^{31}\mathrm{P}$ NMR of the probe molecule trimethylphosphine oxide and $\mathrm{NH_3}$-TPD that p-IPP is favorable for moderate acid sites.

(3) Furthermore, HZ-30 is easy to be deactivated owing to its strong acidity and the deactivation rate of phenol alkylation with propylene over H-ZSM-5s is in the order of HZ-30 > HZ-50 > HZ-80 ≈ HZ-150.

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References

[1] M.M. Wu, US Patent 4 391 998 (1983).
[2] G.E. Stead and L.B. Young, US Patent 4 405 818 (1983).

[3] C.D. Chang and S.D. Hellring, US Patent 5 175 375 (1992).

[4] S. Velu and C.S. Swamy, Catal. Lett. 40 (1996) 265.

[5] S. Sato, K. Koizumi and F. Nozaki, Appl. Catal. A 133 (1995) L7.

[6] E. Santacesaria and D. Grasso, Appl. Catal. 64 (1990) 83.

[7] E. Santacesaria, M. Diserio, P. Ciambelli, D. Gelosa and S. Carra, Appl. Catal. 64 (1990) 101.

[8] K. Zhang, C.H. Huang, H.B. Zhang, S.H. Xiang, S.Y. Liu, D. Xu and H.X. Li, Appl. Catal. A 166 (1998) 89.

[9] S. Subramanian, A. Mitra, C.V.V. Satyanarayana and D.K. Chakrabarty, Appl. Catal. A 159 (1997) 229.

[10] D. Michel, A. Germanus and H.J. Pfeifer, J. Chem. Soc. Faraday Trans. 79 (1982) 237.

[11] J.A. Ripmeester, J. Am. Chem. Soc. 105 (1983) 2925.

[12] L. Baltusis, J.S. Frye and G.E. Maciel, J. Am. Chem. Soc. 108 (1986) 7119.

[13] W.P. Rothwell, W.X. Shen and J.H. Lunsford, J. Am. Chem. Soc. 106 (1984) 2452.

[14] E.F. Rakiewicz, A.W. Peters, R.F. Wormsbecher, K.J. Sutovich and K.T. Mueller, J. Phys. Chem. B 102 (1998) 2890.

[15] S.C. Lee, S.W. Lee, K.S. Kim, T.J. Lee, D.H. Kim and J.C. Kim, Catal. Today 44 (1998) 253.

[16] R.H. Allen and L.D. Yats, J. Am. Chem. Soc. 83 (1961) 2799.

[17] J. Wei, J. Catal. 76 (1982) 433.

[18] M. Misono, Y. Nishizaka, M. Kawamoto and H. Kato, Stud. Surf. Sci. Catal. 105 (1997) 1501.

[19] J.W. Yoo, C.W. Lee, B. Wang and S.E. Park, Bull. Korean Chem. Soc. 22 (2001) 263.

[20] J.W. Yoo, C.W. Lee, B Wang and S.E. Park, Res. Chem. Intermed, accepted for publication.