

# Articles

## Acidity Effect on the Catalytic Properties for Phenol Isopropylation

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Isopropylation of phenol with 2-propanol has been carried out over Na-exchanged ZSM-5 zeolites to determine the effect of catalyst acidity on phenol conversion and product selectivity. The acid type and strength of the catalyst such as Lewis, weak and strong Brønsted acid sites are measured by pyridine adsorbed XPS and the catalytic properties are interpreted in terms of the acid properties. The active site and mechanism for the reaction are suggested based on evidence of study from the reactant adsorbed FT-IR.

**Keywords :** Solid acid, Isopropylation, XPS, ZSM-5, FT-IR.

### Introduction

Propylated phenolic compounds are useful materials in the synthesis of a range of products such as adhesives, agricultural chemicals and pharmaceuticals.<sup>1</sup> Many studies on the alkylation of phenol with methanol over zeolite as environmentally-benign catalysts have been reported, but only a few papers<sup>2,3</sup> and patents<sup>4,5,6</sup> apply to the isopropylation of phenol with alcohol and olefin. 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, PhOH/alkylating agent ratio and WHSV. The influences of acid type (Brønsted or Lewis) and strength (strong or weak) on catalytic properties such as the phenol conversion and product selectivity have not yet been established. Furthermore, no paper dealing with active site and mechanistic study supported by spectroscopic evidence has been reported.

To contribute to the understanding of the relationship between catalytic conversion/selectivity and the type, number and strength of acid sites such as Brønsted or Lewis acid site, for the catalyst on the isopropylation of phenol with 2-propanol, we modified the acidity of HZSM-5 by Na ion-exchange and characterized the acid property by pyridine adsorbed XPS. Finally, we suggest the active site and reaction mechanism based on the reactant adsorbed FT-IR experiment.

### Experimental Section

HZSM-5 zeolite with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 30 was provided by Zeolyst Company. 27NaHZSM-5 and 61NaHZSM-5 were prepared by Na-exchange of HZSM-5 with 0.01 M NaNO<sub>3</sub> solution. Na-exchanged amounts were determined by ICP-AES (ICP-1000 III, Shimadzu I). 27 and 61 in 27NaHZSM-

5 and 61NaHZSM-5 mean degree (percentage) of Na ion-exchange, respectively.

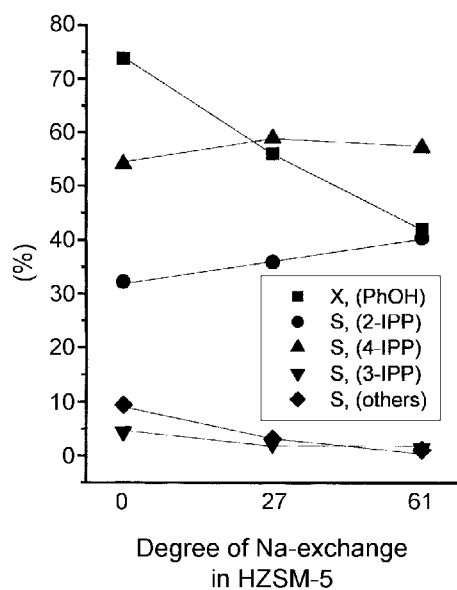
The catalytic isopropylation of phenol (Aldrich 99 + %) with 2-propanol (Aldrich 99 + %) at 250 °C was carried out at atmospheric pressure using a fixed-bed flow reactor. A mixture of phenol and 2-propanol with a molar ratio of 1 : 1 was introduced into the reactor by means of a syringe pump with WHSV = 3.0 h<sup>-1</sup>. The products were determined by GC using FID furnished with CP-SIL 5 CB 50 m capillary column.

For the XPS study, 1 Torr of pyridine vapor was adsorbed on the samples and evacuated to remove physically adsorbed pyridine. The X-ray photoelectron spectra were obtained using a ESCA LAB MK II spectrometer provided with a hemispherical electron analyzer and a Mg anode X-ray exciting source (MgK $\alpha$  = 1253.6 eV). A binding energy of 284.6 eV for C (1s) was chosen as an internal reference. For the FT-IR study, a 12 mg sample was pressed into a self-supported wafer. This wafer was mounted in an infrared vacuum cell with calcium fluoride windows and degassed at 450 °C for 2 h. 2-propanol and phenol were added to the degassed sample successively to investigate active site and reaction mechanism. The IR peak intensities were normalized with the 1882 cm<sup>-1</sup> band assigned to the Si-O overtone of the zeolite framework.<sup>7</sup> The FT-IR spectra were recorded at room temperature, using a Nicolet Magna-IR 560 spectrometer over the range of 1000-4000 cm<sup>-1</sup> with 2 cm<sup>-1</sup> resolution.

### Results and Discussion

The isopropylation of phenol with 2-propanol over HZSM-5 yielded a mixture of monoisopropylphenol isomers, 2-isopropylphenol (2-IPP), 3-isopropylphenol (3-IPP), 4-isopropylphenol (4-IPP) as major products. Other mixtures containing diisopropylphenols, *n*-propylphenols, methyl and ethyl phenols made up less than 10%. The striking feature in this reaction is that the isopropylation takes place exclusively at C-centers (only C-alkylation). The effect of catalyst acidity by

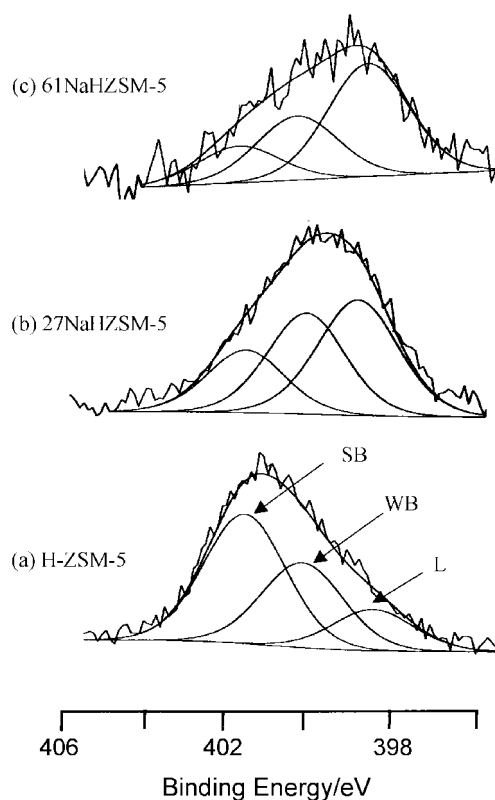
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**Figure 1.** Effect of catalyst acidity on the phenol conversion (X) and product selectivity (S).

altering the Na ion-exchange degrees of HZSM-5 on catalytic properties is shown in Figure 1. The phenol conversion and product selectivity, interestingly with the exception of 4-IPP, exhibit a constant relationship with the amount of Na ion-exchange. The conversion is quickly reduced as increment of Na ion-exchange level in HZSM-5, indicating the conversion is closely related to the reduction of the concentration of acid sites by Na ions. Hence phenol isopropylation depends upon the acidity of the catalysts. These data are in good agreement with Su *et al.*'s results. They said that basic cations-exchanged faujasites in aniline alkylation indicate a decrease in catalytic activity due to a reduction of number of acid sites.<sup>8</sup> Furthermore, the conversion for phenol is increased with the increment of loading of zeolite. In contrast to the conversion, 2-IPP formation is dominant in 61NaHZ-3, which has weak acid sites. This is consistent with the results by Zhang *et al.*, explaining that the substitution of an alkylating agent on the ortho position of phenol is favorable for weak acid sites.<sup>9</sup> The 4-IPP selectivity does not change significantly with Na content, indicating that 4-IPP formation is controlled mainly by zeolite pores. HZSM-5 exhibits a higher selectivity for 3-IPP and other products compared with those of 61NaHZSM-5, suggesting that strong acid sites prefer the formation of 3-IPP and other products.

Catalysts acid properties such as strong, weak Brønsted, and Lewis acid sites are evaluated by pyridine adsorbed XPS, which provides detailed evidence for the correlation between catalytic properties and acid sites. As shown in Figure 2, the  $N_{1s}$  XPS lines of chemisorbed pyridine on catalysts were deconvoluted to distinguish the acid type and strength distribution. It was reported by S. Kaliaguine *et al.* that  $N_{1s}$  XPS spectra of pyridine chemisorbed on HZSM-5 zeolites showed three  $N_{1s}$  components at  $398.7 \pm 0.3$ ,  $400.3 \pm 0.3$  and  $401.8 \pm 0.3$  eV, corresponding to Lewis, weak and strong Brønsted acid sites, respectively.<sup>10</sup> However, in the



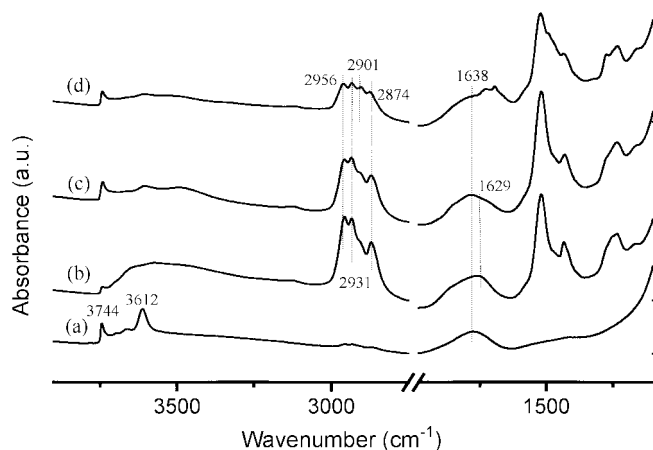
**Figure 2.** Deconvolution of XPS  $N_{1s}$  spectra of chemisorbed pyridine onto (a) HZSM-5, (b) 27NaHZSM-5, and (c) 61NaHZSM-5. SB indicates strong Brønsted acid site centered at 401.8 eV. WB indicates weak Brønsted acid site centered at 400.3 eV. L indicates Lewis acid site centered at 398.7 eV.

case of HY zeolite, three components at  $398.7 \pm 0.3$ ,  $400.3 \pm 0.3$  and  $401.8 \pm 0.3$  eV were assigned in a different way to weak Lewis, strong Lewis and Brønsted acid sites, respectively.<sup>11</sup> And the difference was explained in detail on the basis of changes in the relative intensity of this medium binding energy  $N_{1s}$  component upon dehydroxylation of both zeolites. In our experiment, The  $N_{1s}$  XPS lines of chemisorbed pyridine on catalysts were deconvoluted according to reference 11, as shown in Figure 2, to distinguish the acid type and strength distribution. The total acid site concentrations of samples determined by XPS are calculated based on the relative concentration of HZSM-5, which is adopted as the standard and normalized to 100%. Each relative acid site concentration is shown in Table 1. For example, the concentration of total acid sites for 61NaHZSM-5 is shown as 57% when the concentration of HZSM-5 is 100%, *i.e.*, the acid

**Table 1.** Concentration of acid sites on ZSM-5 zeolites

Sample	Surface			
	Total	L	WB	SB
H-ZSM-5	100	15.9	33.3	50.8
27NaH-ZSM-5	67	27.9	24.3	14.8
61NaH-ZSM-5	57	30.5	17.4	9.1

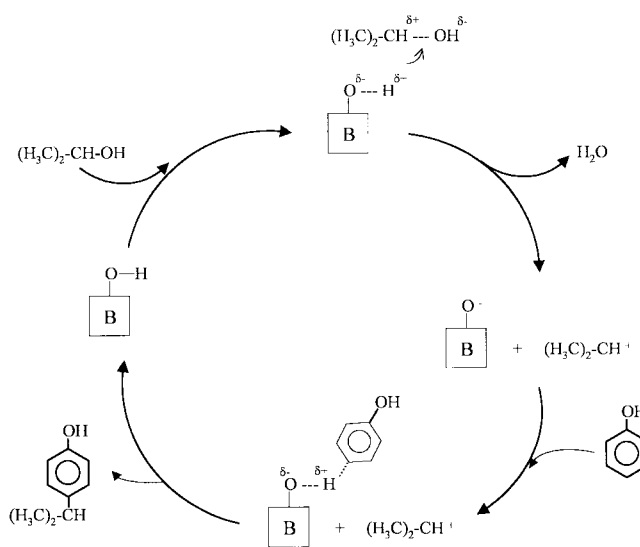
L: Lewis acid sites, B: Brønsted acid sites, WB: Weak Brønsted acid sites, SB: Strong Brønsted acid sites.



**Figure 3.** FT-IR spectra of HZSM-5 after various treatments. (a) evacuated at 450 °C for 2 h, (b) 2-propanol (3.5 Torr) adsorbed on (a) at room temperature, (c) evacuated (b) at 200 °C for 1 h, and (d) phenol (1.5 Torr) was introduced to (c), heated up and evacuated at 200 °C for 1 h.

sites concentration of 61NaHZSM-5 is almost cut in half compared with the concentration before ion-exchange with Na cation. Furthermore, the concentration of strong Brønsted acid sites falls to about 20% compared with the concentration of HZSM-5. While the concentrations of weak Brønsted and Lewis acid sites do not change remarkably, strong Brønsted acid sites are decreased markedly. Interestingly, it is observed that, over 61NaHZSM-5, the phenol conversion increases from 42% with 0.5 g catalyst to 78% with 1.0 g catalyst, but the product selectivity does not depend on the amount of catalyst. Strong Brønsted acid sites exhibit a closer proportionality against the activity compared with weak sites, which is further evidence that the main controlling factor in this reaction is strong Brønsted acid sites. 3-IPP and other products are well formed on strong acid sites, whereas 2-IPP is well produced on weak acid sites.

To understand the reaction pathway, reactants were adsorbed and analyzed by FT-IR, which yielded information about active sites as well as the reaction mechanism. As shown in Figure 3, the spectrum of HZSM-5 contains two main bands at 3612 and 3744  $\text{cm}^{-1}$  (spectrum a), where the former band is associated with the acidic OH groups (-Si-OH-Al-), and the latter with the terminal, nonacidic OH groups bound to silicon framework atoms (-Si-OH).<sup>12,13</sup> When 2-propanol was first chemisorbed on the activated HZSM-5, only the acidic OH group at 3612  $\text{cm}^{-1}$  completely disappeared (spectrum b), *i.e.*, 2-propanol was selectively adsorbed not on terminal, nonacidic OH groups at 3744  $\text{cm}^{-1}$  but on the Brønsted acid site at 3612  $\text{cm}^{-1}$ . And simultaneously, a new band at 1629  $\text{cm}^{-1}$  appeared, attributed to the bending vibration of water. In addition, characteristic bands of 2-propanol at 2956, 2931, and 2874  $\text{cm}^{-1}$  were also detected. These observations can be interpreted that chemisorbed 2-propanol is dehydroxylated by the Brønsted acid sites to form the 2-propyl cation and water. The water is produced through the interaction of the hydroxyl group dissociated from 2-propanol and a proton of a Brønsted acid site. When the sample



**Scheme 1.** Reaction mechanism for phenol isopropylation with 2-propanol over HZSM-5.

was evacuated at 200 °C for 1 h, a water band at 1629  $\text{cm}^{-1}$  disappeared (spectrum c). Subsequently, phenol was introduced into 2-propanol chemisorbed HZSM-5, the sample was heated and then evacuated at 100 °C. A new band at 2901  $\text{cm}^{-1}$ , which is a characteristic band of monoisopropylphenols, was observed (spectrum d). This phenomenon can be explained as follows. The 2-propyl cation dissociated from bonding with the Brønsted acid site and the 2-propyl cation is electrophilic alkyl substituted on the phenol ring. The proton generated by the 2-propyl cation substitution attacks the oxygen of the Brønsted acid site, which is regenerated and recycled as an active site for phenol isopropylation. Based on these observations the pathway for the reaction is proposed in Scheme 1.

## Conclusions

It has been investigated that catalyst acidity in the isopropylation of phenol with 2-propanol influences the phenol conversion and product selectivity except for 4-IPP. The formation of 4-IPP is governed mainly by the pore size of the zeolite. From the acid site investigation by XPS of the pyridine adsorption, we found that not only the conversion but also the selectivity for 3-IPP and other products increase with each increment of the strong acid sites, especially, for strong Brønsted acid sites. On the other hand, weak acid sites prefer the formation of 2-IPP. The Brønsted acid site can be considered an active site based on the results of selective adsorption of the reactant on the Brønsted acid site, as revealed by FT-IR. Finally a reaction pathway is suggested.

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