FT-IR 및 XPS를 이용한 1,2-이수산화벤젠의 부틸화반응 측면특성연구

유중환 · 이철위 · 박용기 · 박상연

FT-IR and XPS Study of Zeolite in the tert-Butylation of 1,2-Dihydroxybenzene

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ABSTRACT

tert-Butylation of DHB (1,2-dihydroxybenzene) is carried out over ZSM-5 with three different Na cation-exchange levels and SiO$_2$/Al$_2$O$_3$ ratios. When Na cation-exchange level or SiO$_2$/Al$_2$O$_3$ ratio of ZSM-5 increases, the conversion and DTBC (3,5-di-tert-butylicatechol) selectivity decreases and 3-TBC (3-tert-butylicatechol) selectivity grows. However, selectivity for 4-TBC(4-tert-butylicatechol) is not changed significantly. Variation of catalytic activity and product selectivity over ZSM-5 catalysts are compared and discussed in terms of the concentration and strength of acid site determined by FT-IR and XPS. From this result, stronger Bronsted acid site seems to be responsible for the tert-butylation of DHB.

1. Introduction

DHB alkylation is an industrially important reaction since 4-TBC and its derivatives are used as raw materials for the synthesis of several polymerization inhibitor, dye developer, pharmaceuticals, agricultural chemicals, etc. Commercial alkylation of aromatics is carried out via electrophilic substitution, where the metal halides, AlCl$_3$, FeCl$_3$, ZnCl$_2$, are the most commonly used catalysts [1]. The use of these catalysts give rise to many problems concerning handling, safety, corrosion, and waste disposal. Much effort has been put into developing alternative technology based on heterogeneous catalyst [2]. Hence, many reports on the aromatics alkylation using zeolites have been published [3-5], dealt with parameters affected in catalytic properties. In the aromatics alkylation using zeolites [3-5] catalytic activity was controlled by acidity (Al content in zeolite) and selectivity by pore structure and acid strength of zeolites. Although so many articles about aromatics alkylation has been reported, only a few patents on the butylation of dihydroxy-substituted aromatics were disclosed until now [6-7]. In Japanese patent [6], 4-TBC was prepared by DHB and tert-butanol in the presence of Friedel-Craft type catalysts, ZnCl$_2$, FeCl$_3$, and HCl, with low conversion and selectivity, and di-tert-butylation of hydroquinone was achieved by isobutylene over acidic resin with low conversion and selectivity[7].

In this study, we attempt to clarify the relationship between conversion/ selectivity and acidic nature of the catalyst for tert-butylation of DHB with tert-butanol over zeolites. Various zeolites such as NaHZSM-5 with different ion-exchange levels and H-ZSM-5 with three different SiO$_2$/Al$_2$O$_3$ ratios
are applied for the catalytic reaction. The concentration and strength of acid sites are determined by FT-IR and XPS.

2. Experimental

The catalytic alkylation of DHB (Aldrich 99+% with tert-butanol (Aldrich 99+% at 170°C was carried out at atmospheric pressure using a fixed-bed flow reactor. A mixture of DHB and tert-butanol with molar ratio of 1:3 was introduced into the reactor by means of a syringe pump with WHSV = 4.85h⁻¹. The liquid products were analyzed by GC using FID furnished with SE-30 30m capillary column.

For FT-IR study, self-supported wafer samples are degassed at 450°C for 2h. 1 torr of pyridine vapor was introduced and kept for 1h at 200°C, the samples were then evacuated at the same temperature for 1h. In order to investigate the acid strength, pyridine was desorbed by evacuation at 200, 300, and 400°C, respectively. The IR peak intensities were normalized with the 1882 cm⁻¹ band which is assigned to the Si-O overtone of zeolite framework [8]. For XPS measurements, the samples was adsorbed by pyridine vapor at 200 °C. The X-ray photoelectron spectra were obtained using a EACA LAB MK II spectrometer provided with a hemispherical electron analyzer and a Mg anode X-ray exciting source (MgKα = 1253.6 eV). A binding energy of 284.6 eV for C(1s) was chosen as an internal reference.

3. Results and discussion

Table 1 exhibits catalytic property over ZSM-5 with different Na ion-exchange level and SiO₂/Al₂O₃ ratio in the DHB alkylation.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>Xₐ (DHB)</th>
<th>4-TBC selectivity</th>
<th>Yₐ (4-TBC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM-5 (30)</td>
<td>90.8</td>
<td>84.8, 12.7, 2.5</td>
<td>77.0</td>
</tr>
<tr>
<td>27NaH-ZSM-5 (30)</td>
<td>57.2</td>
<td>87.3, 7.3, 5.4</td>
<td>49.9</td>
</tr>
<tr>
<td>61NaH-ZSM-5 (30)</td>
<td>24.2</td>
<td>86.5, 2.2, 11.3</td>
<td>21.0</td>
</tr>
<tr>
<td>H-ZSM-5 (50)</td>
<td>82.3</td>
<td>87.7, 9.0, 3.3</td>
<td>72.2</td>
</tr>
<tr>
<td>H-ZSM-5 (80)</td>
<td>80.2</td>
<td>88.5, 8.1, 3.4</td>
<td>71.0</td>
</tr>
</tbody>
</table>

Numbers in parenthesis indicate SiO₂/Al₂O₃ ratio

Catalytic properties such as DHB conversion, selectivities of DTBC and 3-TBC are very sensitive in ZSM-5 having different Na exchange level, but not sensitive in ZSM-5 with different SiO₂/Al₂O₃ ratio. 4-TBC selectivities are not changed significantly in both catalysts, indicating that 4-TBC formation is controlled by zeolite pore mainly.
Fig. 1 FT-IR spectra of pyridine adsorbed (a) H-ZSM-5 (30), (b) 27NaH-ZSM-5(30), (c) 61NaH-ZSM-5(30), (d) H-ZSM-5 (50), and (e) H-ZSM-5 (80)

More acidic zeolite shows higher DHB conversion. DTBC will be formed over zeolite having higher acidic property, high Al contents, which is proportional to the number and strength of acid sites on the external surface. 61NaH-ZSM-5 (30) exhibits about 5 times higher 3-TBC selectivity than that of H-ZSM-5 (30). 3-TBC formation is proportional to Na contents in zeolite, indicating that 3-TBC formation favors on weak acid sites.

Fig. 1 shows the FT-IR spectra of pyridine adsorbed ZSM-5 zeolites. The band at 1490 cm\(^{-1}\) is due to the pyridine adsorbed on both Bronsted and Lewis acid sites, while bands at 1546 and 1455 cm\(^{-1}\) are due to protonated pyridine molecule by Bronsted acid sites and that of Lewis acid sites, respectively. In order to understand the relationship between catalytic properties and acidity of catalyst, we compare each other. The DHB conversion is closer proportional to Bronsted one rather than Lewis acid sites, i.e. DHB alkylation seems to be controlled mainly by Bronsted acid sites. But the DHB conversion is not proportional to the concentration of Bronsted acid site in any case; for example, upon evacuation at 200\(^{\circ}\)C, the concentration of Bronsted acid sites for 27NaH-ZSM-5 (30) and H-ZSM-5 (80) show 117 and 112 \(\mu\) mol/g, respectively, which is not coincidence with the DHB conversion. However, upon
evacuation at 400°C, the concentration of Bronsted acid site for 27NaH-ZSM-5 (30) and H-ZSM-5 (80) show 19 and 70 μ mol/g, which shows same trend as the DHB conversion. To distinguish acid strength, pyridine adsorbed samples were analyzed by XPS (Fig. 2). Deconvolution of the N_{1s} XPS lines of chemisorbed pyridine can be used for the identification and quantitation of Bronsted and Lewis acid sites in zeolite. Compared with the infrared spectra, the XP spectra of chemisorbed pyridine are more sensitive in distinguishing Bronsted acid sites of different strengths: i.e., the strong and weak Bronsted acid sites. 398.7 eV was assigned to the nitrogen atom of pyridine associated with Lewis sites, and the peaks corresponding to E_{0} values of 400.3 and 401.8 eV to the nitrogen atoms of pyridine associated with relatively weak and strong Bronsted acid sites, respectively [9]. When the degree of Na ion exchange increase, strong Bronsted acid site decrease quickly. However as increasing SiO_{2}/Al_{2}O_{3} ratio, rapid reduction of strong Bronsted acid site is not observed. These results is consistent with those of FT-IR. From the above result, 27NaH-ZSM-5 (30) and H-ZSM-5 (80) possess weaker and stronger Bronsted acid site, respectively. This might be the reason why H-ZSM-5 (80) displays higher DHB conversion by 20% than 27NaH-ZSM-5 (30). Hence, it can be proposed that tert-butylation of DHB is associated with the stronger acid sites.

4. Conclusions
Catalytic activity is closely related to stronger Bronsted acid site rather than Lewis acid sites, and DHB conversion depends on the number and strength of stronger Bronsted acid sites. Higher concentration and stronger acid site of catalyst produce higher DHB conversion. 4-TBC selectivity is independent upon acidity of the catalyst, but controlled by zeolite pore size and its structure. By-product, 3-TBC formation is likely favored on weakly acidic catalysts more than on strongly acidic catalysts. On the other hand, DTBC is easily formed over the catalyst having stronger acidic sites on the external surface of the catalysts.

References