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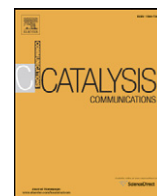
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Synergistic role of Lewis and Brønsted acidities in Friedel–Crafts alkylation of resorcinol over gallium-zeolite beta

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ABSTRACT

The role of Lewis and Brønsted acidities in alkylation of resorcinol is demonstrated through the gallium-zeolite beta by varying the amount of Lewis and Brønsted acid sites. The synergism of Lewis and Brønsted acid sites takes place heterogeneously in Friedel–Crafts alkylation of resorcinol with methyl *tert*-butyl ether to produce 4-*tert*-butyl resorcinol and 4,6-di-*tert*-butyl resorcinol as the major and minor products, respectively.

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1. Introduction

Alkylation of aromatics is an important reaction in organic chemistry as it is widely used in the synthesis of petrochemicals, fine chemicals, perfumeries, pharmaceuticals, dyes and agrochemicals [1]. One of the important reactions is Friedel–Crafts alkylation of resorcinol with methyl *tert*-butyl ether (MTBE). With an increase in the production of methyl *tert*-butylether (MTBE) for use as antiknock and octane number booster for gasoline, MTBE appears to be an attractive source for alkylation of resorcinol [2].

The use of solid acid catalysts for Friedel–Crafts alkylation reaction such as zeolites has generated great interests and wide applications in the industries nowadays [3]. In general, Friedel–Crafts alkylation is carried out conventionally with the use of homogeneous Lewis and Brønsted acid catalysts [3,4]. The disadvantages of these conventional acid catalysts lead to the research on replacement of the homogeneous catalyst with a heterogeneous type, predominantly zeolites [3,5]. Until now, the role of Brønsted and Lewis acids in the alkylation reaction is unclear as no research that systematically controlled the amount of Lewis and Brønsted on the surface of catalyst in alkylation reaction is carried out. Although few studies have been focused on the alkylation of resorcinol [1,6,7], the role and mechanism of Brønsted and Lewis acid sites have yet to be understood thoroughly. Here, we demonstrated the effect of Brønsted and Lewis acid sites on alkylation of resorcinol with methyl *tert*-butyl ether (MTBE) using zeolite beta impregnated with gallium. One suggests that Lewis and Brønsted acidities play a synergetic role in this reaction. The mechanism of this

reaction is also proposed in order to show the synergistic role of Lewis and Brønsted acidities.

2. Experimental

Gallium containing zeolite beta was prepared by impregnation of $\text{Ga}(\text{NO}_3)_3$ in water on BEA using the method described by Choudhary et al. [8]. The resulting sample was denoted as XGa-BEA (X is the percentage of Ga). Mesoporous alumina (MA) was prepared according to the literature [7]. All samples were characterized by powder X-ray diffraction (XRD) for crystallinity and phase content of the solid materials, using a Bruker Advance D8 diffractometer with the $\text{Cu K}\alpha$ ($\lambda = 1.5405 \text{ \AA}$) radiation as the diffracted monochromatic beam at 40 kV and 40 mA. The pattern was scanned in the 2θ ranges between 5° and 45° at a step 0.050° and step time 1 s. Infrared (IR) spectra of the samples were collected on a Perkin Elmer Spectrum One (FTIR) spectrometer, with a spectral resolution of 4 cm^{-1} , scans 10 s, at room temperature. For acidity evaluation, the wafer of the sample (10–12 mg) was prepared and locked in the cell equipped with CaF_2 windows and evacuated at 400°C under vacuum condition for 4 h. Infrared spectra of the samples were recorded at room temperature in the hydroxyl region of $4000\text{--}3000 \text{ cm}^{-1}$ and pyridine vibration region at $1700\text{--}1300 \text{ cm}^{-1}$. Catalytic activity of the catalysts in the alkylation of resorcinol with MTBE was performed at 80°C for 8 h under vigorous stirring. The reaction mixture containing resorcinol (40 mmol) and MTBE (60 mmol) was put in a round bottom flask equipped with a condenser. The catalyst (0.2 g) was then added to the solution. The reaction was carried out in an oil bath under stirring at 80°C . The products of the reaction were analyzed by a Hewlett-Packard 6890N gas chromatograph using an

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Ultra-1 column and a Hewlett-Packard GC-MSD instrument using a HP5 column.

3. Results and discussion

Impregnation of gallium on zeolite beta was done at different wt.% of Ga which varies from 3 to 25 wt.%. The XRD patterns for all XGa-BEA ($X = 3\text{--}25$ wt.% Ga) samples (Fig. 1) showed that the structure of zeolite beta is maintained even at high Ga loading without the formation of Ga_2O_3 crystal phases. X-ray diffractograms of the impregnated gallium on zeolite beta showed no evidence of any crystalline Ga containing compounds suggesting that the Ga species is either in the amorphous form or was highly dispersed as very small particles on the zeolite support.

Fig. 2 shows the FTIR spectra of the gallium-zeolite beta samples after evacuation at 400°C for 4 h under vacuum. In the region of hydroxyl groups, two bands were observed at 3608 and 3740 cm^{-1} . The former had been assigned to acidic bridging OH from the Si–O(H)–Al band while the latter is attributed to the defect sites and terminal Si–OH [9]. Bands at 3740 cm^{-1} can be clearly seen in all samples. However, the band assigned to the bridging hydroxyl group, at 3608 cm^{-1} , can be seen with different intensities of peak area in all samples. As shown in Fig. 2, it is clearly observed that the peak area at 3608 cm^{-1} decrease with an increase in the amount Ga impregnated on the surface of zeolite beta. This suggests that the gallium atoms have interacted with the Brønsted acid of zeolite beta. Mesoporous alumina (MA) was also used for comparison. The absence of peak at 3608 cm^{-1} in the FTIR spectrum of MA suggests that this sample did not have the acidic bridging hydroxyl groups (see Fig. 2a).

The acidity of the XGa-BEA and MA catalysts was further monitored by FTIR using pyridine as a probe molecule. The purpose of this experiment is to determine the amount and type of acid in the catalyst. Fig. 3 shows the IR spectra of samples after the adsorption of pyridine. The bands at 1450 cm^{-1} in the spectra are attributed to adsorbed pyridine bound coordinative with Lewis acid sites [10]. The

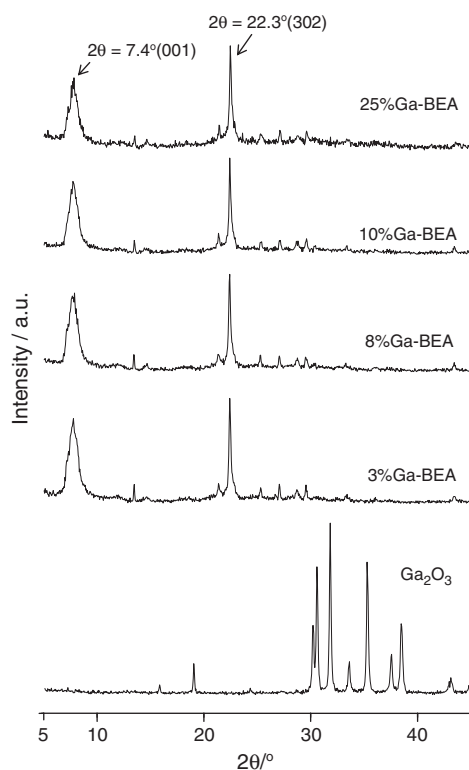


Fig. 1. X-ray diffractograms of gallium-zeolite beta and Ga_2O_3 .

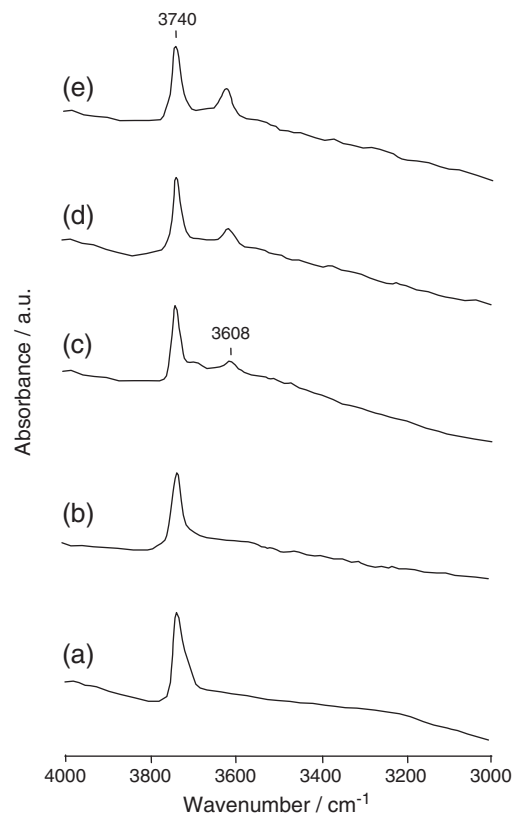


Fig. 2. The FTIR spectra of hydroxyl group of (a) MA, (b) 25%Ga-BEA, (c) 10%Ga-BEA, (d) 8%Ga-BEA and (e) 3%Ga-BEA.

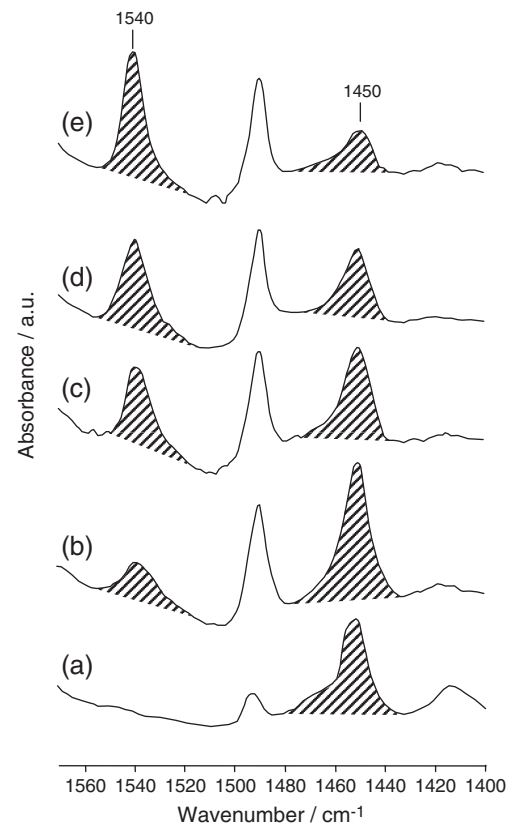


Fig. 3. The FTIR spectra of pyridine adsorbed on (a) MA, (b) 25%Ga-BEA, (c) 10%Ga-BEA, (d) 8%Ga-BEA and (e) 3%Ga-BEA after desorption of pyridine at 150°C for 1 h.

absorption bands at 1540 cm^{-1} correspond to pyridine interacting with Brönsted acid sites [10]. The presence of these bands for all samples indicates that all samples contain both Lewis and Brönsted acid sites. For calculation of the pyridine concentrations adsorbed on Brönsted site and Lewis site, the values of integrated molar extinction coefficients chosen are 1.67 and $2.22\text{ cm}^2/\text{mmol}$, respectively [12]. As shown in Fig. 3, it is observed that the number of Lewis acid sites of XGa-BEA increases with increasing Ga loading. On the contrary, the number of Brönsted acid decreases with increasing Ga loading. When the acidity of XGa-BEA is compared with MA, as expected, only the Lewis acid is observed in the MA sample (Fig. 3a).

From Fig. 3, it was also proposed that the presence of Brönsted acid is more dominant than Lewis acid at a low amount of Ga loading (ca. 3 wt.% Ga). However, the amount of Lewis acid is significantly higher than Brönsted acid when the amount of Ga is 25 wt.% Ga. The increase in Lewis acid sites in the samples is suggested to originate from the agglomeration of Ga_2O_3 particles, creating Lewis acid sites [11].

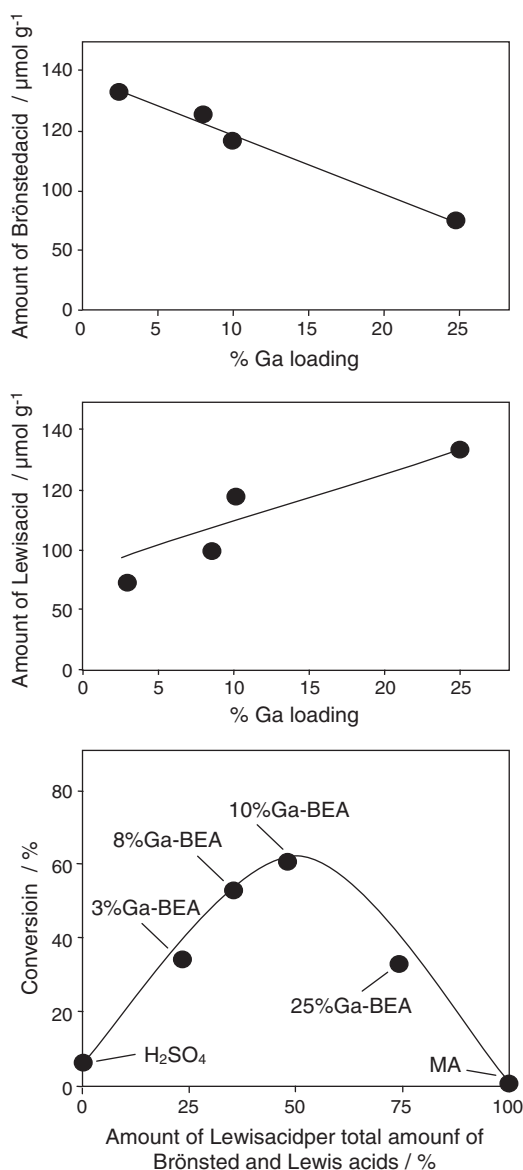


Fig. 4. Calculated amount of Brönsted and Lewis acid sites after thermodesorption of pyridine for samples with different wt.% of Ga loadings and the effects of Lewis and Brönsted acids in gallium-zeolite base to the conversion of resorcinol.

The calculated amount of Brönsted and Lewis acid sites after thermodesorption of pyridine for samples with different wt.% of Ga loadings and the effects of Brönsted acid in gallium-zeolite base to the conversion of resorcinol are shown in Fig. 4. An interesting effect of Lewis and Brönsted acids to the alkylation of resorcinol is demonstrated in this figure. The maximum conversion of resorcinol to 4-*tert*-butyl resorcinol and 4,6-di *tert*-butyl resorcinol by using 10%Ga-BEA is observed when the amount of Lewis and Brönsted acid is one to one ratio. This includes the amount of Brönsted and Lewis acids of MA and sulfuric acid which are also considered in the calculation.

Table 1 summarized the catalytic alkylation of resorcinol over XGa-BEA, MA and sulfuric acid. All Ga impregnated samples were found active as a catalyst in the Friedel–Crafts alkylation of resorcinol, giving 4-*tert*-butyl resorcinol and 4,6-di-*tert*-butyl resorcinol as major and minor products, respectively. Interestingly, as shown in Fig. 3 and Table 1, MA and sulphuric acid which possess 100% of Lewis and Brönsted acids, respectively, did not provide significant activities in the alkylation of resorcinol with MTBE while 10%Ga-BEA possessing both Brönsted and Lewis acids showed high catalytic activity. These results indicated the possibility of synergism between Brönsted and Lewis acids in the Friedel–Crafts alkylation of resorcinol.

In order to confirm the importance of synergism between Lewis and Brönsted sites, we compared the activity of MA with MA in a solution containing H_2SO_4 (see entries 1 and 7 in Table 1). It shows that the catalytic activity of the reaction system containing MA and liquid H_2SO_4 (entry 7 in Table 1) is similar to those observed for the H_2SO_4 homogeneous catalyst (entry 6 in Table 1). Although H_2SO_4 has a stronger acid strength than those of zeolite beta, HZSM-5 and HY zeolite [13,14], the yield of products from the Friedel–Crafts alkylation of resorcinol using H_2SO_4 as a catalyst is lower than that of XGa-BEA indicating the occurrence of the synergism between Brönsted and Lewis acids in Friedel–Crafts alkylation of resorcinol. Based on these results, one suggests that the presence of only Brönsted acid in the liquid form, even though with a high acid strength, is not suitable for catalyzing the alkylation of resorcinol with MTBE. In our previous paper, H_2SO_4 was heterogenized on the surface of mesoporous alumina ($6\%\text{H}_2\text{SO}_4/\text{MA}$) [7]. The catalytic activity of $6\%\text{H}_2\text{SO}_4/\text{MA}$ is

Table 1

Catalytic alkylation of resorcinol to 4-*tert* butyl resorcinol and 4,6-di *tert*-butyl resorcinol ^a.

Entry	Catalysts	Conversion/%	Product yield/ mmol	Selectivity/%		Ratio of Lewis acid to Brönsted acid ^b
				4- <i>tert</i> - butyl resorcinol	4,6-di- <i>tert</i> -butyl resorcinol	
1	MA	0	0	0	0	0
2	3%Ga-BEA	38.0	15.6	97.4	2.6	0.5
3	8%Ga-BEA	54.4	21.7	95.8	4.2	0.7
4	10%Ga-BEA	59.1	23.6	100	0	1.0
5	25%Ga-BEA	32.2	12.9	100	0	1.5
6	H_2SO_4 ^c	6.5	2.6	96.0	4.0	contain only Brönsted acid
7	MA + H_2SO_4 ^d	6.0	2.4	96.0	4.0	1.0
8	$6\%\text{H}_2\text{SO}_4/\text{MA}$ ^e	11.0	4.4	80.0	20.0	1.5

^a All reactions were carried out at 80°C for 8 h with resorcinol (40 mmol), MTBE (60 mmol) and catalyst (0.2 g) with vigorous stirring.

^b The ratio of Lewis acid to Brönsted acid is calculated by using the peak area of peaks at wavenumber of 1540 cm^{-1} and 1450 cm^{-1} for Brönsted and Lewis acids, respectively (see Fig. 3). For calculation of the pyridine concentrations adsorbed on Brönsted site and Lewis site, the values of integrated molar extinction coefficients chosen are 1.67 and $2.22\text{ cm}^2/\text{mmol}$, respectively [12].

^c The amount of H_2SO_4 is 25 μmol .

^d The MA in a solution containing H_2SO_4 . The amount of MA and H_2SO_4 is similar as entries 1 and 6, respectively.

^e The catalyst is the same as those reported in our previous publication [7].

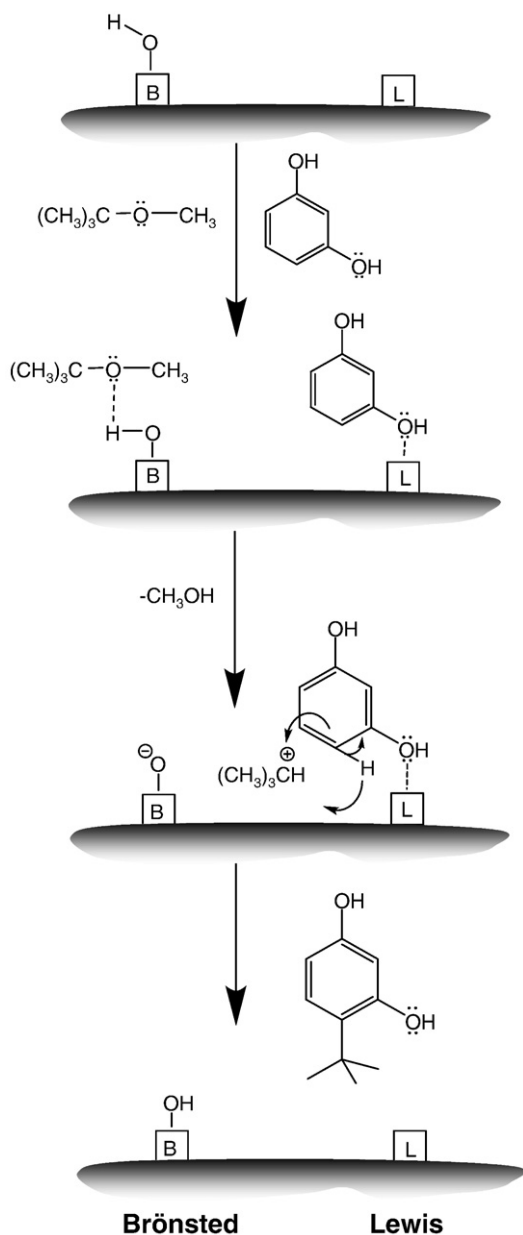


Fig. 5. Proposed mechanism of the alkylation of resorcinol with MTBE.

much higher than that of H_2SO_4 . This also implies that the synergism between Lewis and Brønsted acid sites take place heterogeneously on the surface of solid catalysts in the Friedel–Crafts alkylation of resorcinol.

In order to clarify the effect of the pore structure of zeolite beta in Friedel–Crafts alkylation of resorcinol, a comparison has been made with mesoporous alumina loaded with sulphuric acid (entry 8 in Table 1) [7]. Although the amount of Brønsted and Lewis acid sites of 6% $\text{H}_2\text{SO}_4/\text{MA}$ is similar to those of 25%Ga-BEA, the catalytic activity of 25%Ga-BEA is higher than that of 6% $\text{H}_2\text{SO}_4/\text{MA}$ (see entries 5 and 8 in Table 1). This suggests that the pore structure of zeolite beta plays a role in the catalytic reaction.

Based on the results obtained, the mechanism of alkylation of resorcinol with MTBE is proposed (see Fig. 5). MTBE and resorcinol preferentially adsorbed on Brønsted and Lewis acid sites, respectively. The activation of MTBE is initiated by hydrogen bonding between Brønsted hydroxyl proton and oxygen of MTBE. It leads to the releasing of carbocation by MTBE. The formation of carbocation from MTBE is necessary in order to initiate the alkylation. The carbocation can only form if the MTBE is adsorbed on Brønsted acid sites. On the Lewis site, high electronegativity of oxygen of resorcinol coordinated weakly with Lewis acid site. The proposed mechanism clearly shows that both Lewis and Brønsted acidities play a synergetic role in this reaction.

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