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Friedel-Crafts Alkylation of Resorcinol over Mesoporous Alumina Loaded with Sulfuric Acid

Sheela Chandren*

Zainab Ramli[†]

Hadi Nur[‡]

*Universiti Teknologi Malaysia, sheela83@gmail.com

[†]Universiti Teknologi Malaysia, zainab@kimia.fs.utm.my

[‡]Universiti Teknologi Malaysia, hadi@kimia.fs.utm.my

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Friedel-Crafts Alkylation of Resorcinol over Mesoporous Alumina Loaded with Sulfuric Acid*

Sheela Chandren, Zainab Ramli, and Hadi Nur

Abstract

Mesoporous alumina which contains only Lewis acidity was synthesized by sol-gel method and was then impregnated with sulfuric acid to generate Brönsted acidity. The catalyst was used in Friedel-Crafts alkylation of resorcinol with methyl *tert*-butyl ether to produce 4-*tert*-butylresorcinol and 4,6-di-*tert*-butylresorcinol as the major and minor products respectively. It was demonstrated that Lewis and Brönsted acidities play a synergetic role in this reaction.

KEYWORDS: mesoporous alumina, sulfuric acid, alkylation of resorcinol

*Please send correspondence to Hadi Nur, email: hadi@kimia.fs.utm.my, website: www.hadinur.com. This work was financially supported by the Ministry of Science, Technology and Innovation, Malaysia (MOSTI) and the Ministry of Higher Education, Malaysia (MOHE).

1. Introduction

Acid catalyzed reactions are among the most important in the chemical industry. Friedel-Crafts reactions are one of the examples which are of considerable importance in the productions of fine chemicals (DeCastro et al., 1988). Many industrial processes for the production of pharmaceutical products, fragrances, antioxidant, paint additives, cosmetics and others involve an intermediate step that is the Friedel-Crafts reaction. This type of reaction requires the presence of acidic catalyst in order to allow the reaction to proceed at a convenient rate. Unfortunately, the use of homogenous conventional Lewis and Brönsted acid catalyst such as AlCl_3 , BF_3 , FeCl_3 , ZnCl_2 , H_2SO_4 , HCl and HF lead to several problems such as they need more than stoichiometric amount because of complexation of reactant or product, disposal of potentially highly polluting and toxic wastes and corrosiveness (Smith, 1998). Homogeneous catalysts also involve problems in products separation as the catalyst is in the same phase with the products. Although a few researches have been focused on the alkylation of resorcinol (Devassy et al., 2004; Narayanan and Murthy, 2001; Yadaf et al., 2001), the role and mechanism of Brönsted and Lewis acid sites have yet to be shown clearly.

Mesoporous alumina is an interesting material with a large surface area and a narrow pore size distribution in a mesopore region, and has been synthesized using various templates such as polyethylene oxides, carboxylic acids and tetraalkylammonium salts (Čejka, 2003). While mesoporous alumina has been found in successful application as a catalytic material for a number of reactions involving epoxidation of olefins, hydrodechlorination, hydrodesulfurization, olefin methathesis, oxidation of methane to syngas, and oxidative dehydrogenation of ethane, the utility of mesoporous alumina as a solid catalyst in Friedel-Crafts alkylations is hindered by the existence of Lewis acidity only and the lack of Brönsted acid sites (Aguado, 2005; Čejka, 2003).

In this paper, in order to introduce Brönsted acidity to mesoporous alumina, the mesoporous alumina was modified by the impregnation of sulfuric acid (H_2SO_4). The catalytic activity of mesoporous alumina and the modified MA are tested in the alkylation of resorcinol with methyl *tert*-butyl ether (MTBE). It was demonstrated that Lewis and Brönsted acidities play a synergetic role in this reaction. The mechanism of this reaction is also proposed in order to show the role of Lewis and Brönsted acidities.

2. Experimental

The mesoporous alumina (MA) was prepared according to a literature (Aguado, 2005). The procedure consists of three steps. Firstly, the hydrolysis of aluminum

iso-propoxide ($\text{Al}(\text{C}_3\text{H}_7\text{O})_3$) by hydrochloric acid (HCl) at room temperature was carried out for 4 h in the presence of the surfactant cetyltrimethylammonium bromide (CTABr) and isopropyl alcohol ($\text{C}_3\text{H}_7\text{OH}$). The second step was the condensation of aluminum hydrolyzed species by heating the reacting mixture at 80 °C. Then the gel obtained underwent ultrasonic treatment for 30 min and then dried at 100 °C. Finally, the resulting material was calcined at 600 °C for 4 h.

Sulfated mesoporous alumina was prepared according to the literature (Ng et al., 2006). The desired amount of sulfuric acid was added to toluene before adding the pre-dried MA (200 °C for 24 h). The mixture was stirred at 50 °C for 1 h and dried at 130 °C for 12 h. The samples were designated as $x \text{H}_2\text{SO}_4/\text{MA}$, with $x\%$ sulfuric acid (H_2SO_4) in wt%.

The specific surface area and the pore size distribution of the synthesized mesoporous aluminas were determined by ASAP 2010 instrument. A JEOL JEM-2100 transmission electron microscope (TEM) was used for analyzing the particle size and distribution of mesoporous alumina. Infrared spectra of mesoporous aluminas prepared were recorded using Perkin Elmer Spectrum One FT-IR spectrometer. Samples were characterized by XRD for the crystallinity and phase content of the solid materials using Bruker Advance D8 diffractometer with $\text{Cu K}\alpha$ ($\lambda=1.5405 \text{ \AA}$) radiation as the diffracted monochromatic beam at 40kV and 40 mA. The patterns were scanned in the 2θ ranges between 5° to 85° at a step size 0.075° and step time 1 s at room temperature.

Acidity of the samples were determined by adsorption of pyridine (as probe molecule) on the evacuated sample at room temperature for a minute at 10 torr, followed by desorption of pyridine at 150 °C under vacuum for one hour. Infrared spectra of the pyridine vibration region were monitored in the range of 1700 – 1400 cm^{-1} .

The catalysts activities were evaluated under atmospheric pressure in a 50 ml round bottom flask as follows: resorcinol (40 mmol), MTBE (60 mmol) and nitrobenzene (20 mmol) as the internal standard were mixed in the flask and magnetically stirred. Freshly activated catalysts (0.2 g) were added and then the reaction was carried out under reflux in an oil bath at 80 °C for 8 h. For reusability test, the reaction condition for the first cycle is the same as described previously. However, for the subsequent runs the amount of substrates and solvent were scaled down according to the available amount of catalyst. The catalysts were filtered, washed with ethanol and reactivated before being used again. Products of reactions were separated and analyzed using gas chromatography equipped with FID detector and an Ultra-1 column.

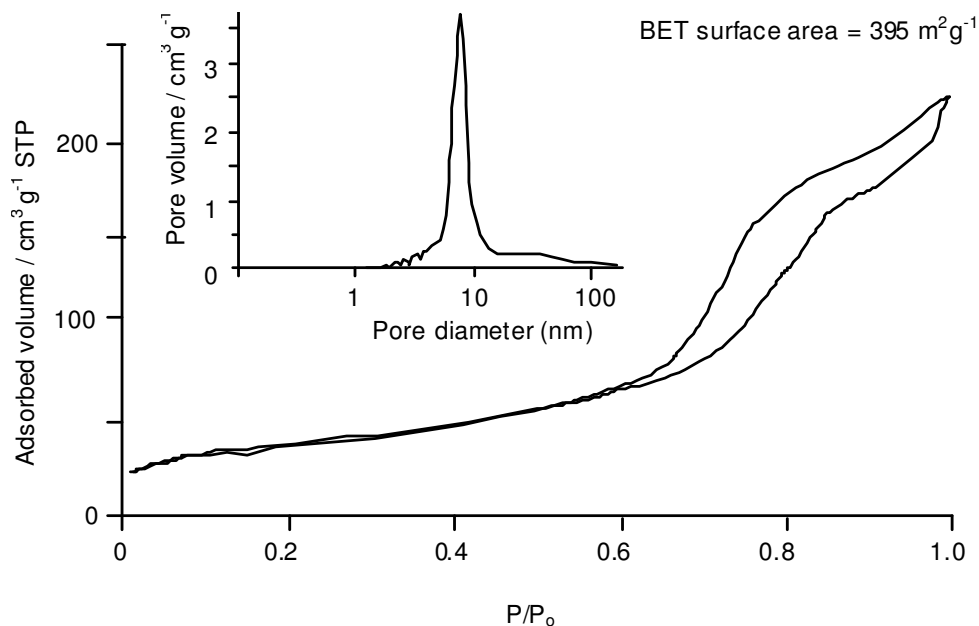


Figure 1. N_2 isotherms and pore size distributions (inset) of mesoporous alumina synthesized.

3. Results and discussion

The XRD patterns showed that the synthesized alumina was partially crystalline and exist in the phase of γ -alumina. The nitrogen sorption isotherm shown in Figure 1 for the prepared MA is of typical type IV as defined by IUPAC (Xu et al., 2006), which is the characteristic of mesoporous materials. The surface area recorded was $395 \text{ m}^2\text{g}^{-1}$, with a very narrow pore size distribution centred at 8.0 nm. The TEM image of the synthesized MA is shown in Figure 2. Similar TEM pictures were also reported by the other authors (Bagshaw and Pinnavaia, 1996). The particle size of the mesoporous alumina was in the range of 10 – 50 nm, which shows that the synthesized alumina consists of small particles.

The FTIR spectra in Figure 3 show that the synthesized mesoporous alumina can be distinguished by three bands. The broad band around $3450 - 3500 \text{ cm}^{-1}$ while deformational vibrations of adsorbed molecules cause the adsorption band at $1623 - 1640 \text{ cm}^{-1}$ (Kim et al., 2004). The peak at 740 cm^{-1} was due to the bending vibrations of Al-O. Apart from the bands mentioned, the spectra of sulfated mesoporous alumina nanoparticles displayed a few additional peaks. The additional band at around 1128 cm^{-1} caused by the stretching vibration of the S=O bond is clearly visible for all $\text{H}_2\text{SO}_4/\text{MA}$ samples (Ng et al., 2006; Nur et al., 2004).

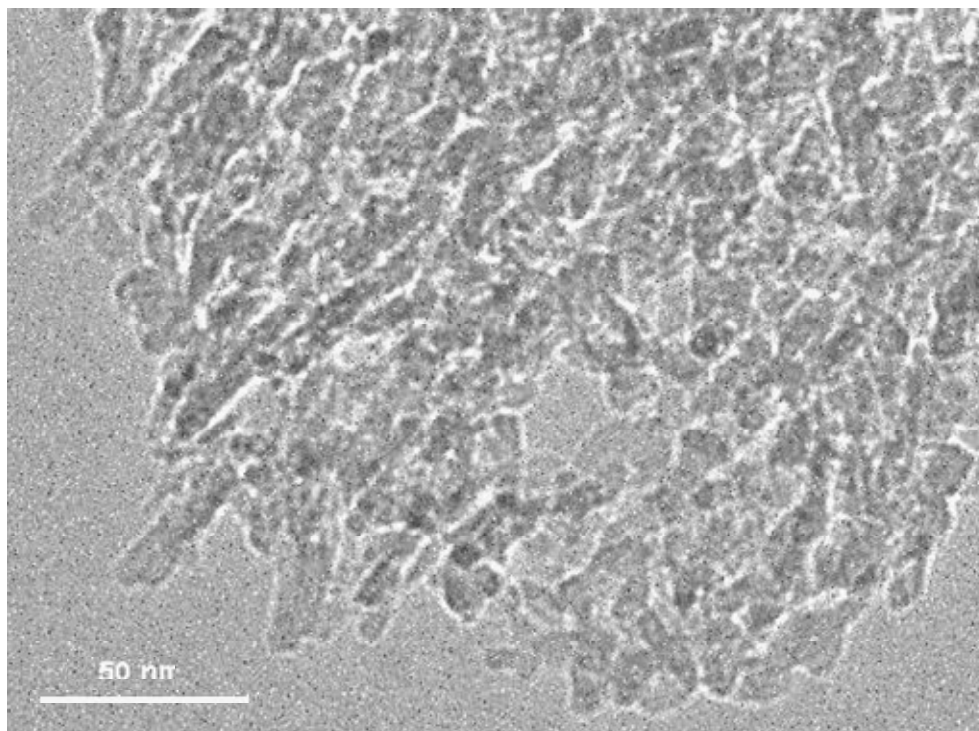


Figure 2. TEM image of the synthesized alumina.

Results obtained by pyridine adsorption on aluminas at temperatures between room temperature and 150 °C shows only the presence of Lewis type acidity. As expected, the FTIR results given in Figure 4 confirm the absence of Brönsted type acidity with the absence of adsorption bands near 1540 cm^{-1} , characteristics of Brönsted acid sites, whereas the characteristic bands at 1452 cm^{-1} that correspond to the vibration of pyridine in sites Lewis type are present. As for acid sample 15% $\text{H}_2\text{SO}_4/\text{MA}$ and 6% $\text{H}_2\text{SO}_4/\text{MA}$, it is apparent that Brönsted sites are present as the peak at 1542 cm^{-1} was clearly visible. However, the peak area of the Brönsted acidity for sample 15% $\text{H}_2\text{SO}_4/\text{MA}$ is much larger than that of sample 6% $\text{H}_2\text{SO}_4/\text{MA}$.

The catalytic activity and selectivity of modified mesoporous alumina were investigated in Friedel-Crafts alkylation of resorcinol. In the Friedel-Crafts alkylation of resorcinol with *tert*-butyl methyl ether, 4-*tert*-butylresorcinol and 4,6-di-*tert*-butylresorcinol were obtained as the major and minor products respectively. The results displayed in Table 1 show that the alkylation of resorcinol with MTBE required the presence of a catalyst. This proved that

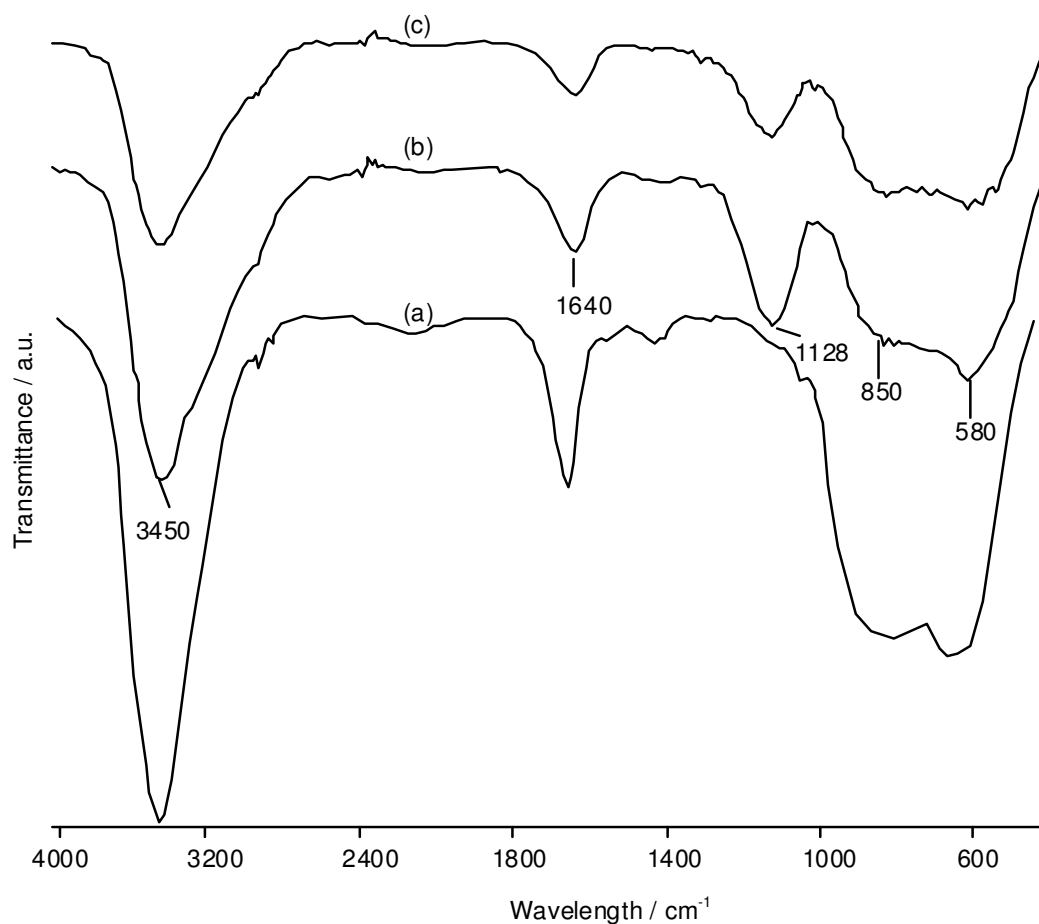


Figure 3. FTIR spectra of (a) MA, (b) 15% $\text{H}_2\text{SO}_4/\text{MA}$ and (c) 6% $\text{H}_2\text{SO}_4/\text{MA}$.

without the presence of catalyst, the reaction did not produce any product because MTBE was not converted into the reactive species (electrophile).

For MA modified with sulfuric acid, both monobutylated and dibutylated resorcinol were produced, even with loading as low as 6%. The yield of the products increased as the loading percent of sulfuric acid increased. This indicates that the amount of Brønsted acid sites plays a role in alkylation of resorcinol with MTBE. Sample 15% $\text{H}_2\text{SO}_4/\text{MA}$ produced considerable amount of the monobutylated and dibutylated products. When homogenous catalyst sulfuric acid (H_2SO_4) was used, the yields obtained for both products were lower than those when 15% $\text{H}_2\text{SO}_4/\text{MA}$ was used as the catalyst. Employing a filtered homogeneous reaction mixture as catalyst in the Friedel-Crafts alkylation of

Table 1 Catalytic alkylation of resorcinol to 4-*tert*-butyl resorcinol and 4,6-di-*tert*-butyl resorcinol^a

Entry	Catalysts	Products Yield / mmol		TON per H ₂ SO ₄
		Mono-alkylated	Dialkylated	
1	None	0	0	-
2	MA	0	0	0
3	6%H ₂ SO ₄ /MA ^b	3.5	0.9	37
4	15%H ₂ SO ₄ /MA ^b	6.1	4.2	34
5	H ₂ SO ₄ ^c	2.5	0.1	9
6	MA + H ₂ SO ₄ ^d	2.4	0.1	9

^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 percentage of H₂SO₄ is calculated by using the peak area of S=O at IR wavenumber of 1128 cm⁻¹.

^c The amount of H₂SO₄ is the same as entry 4.

^d The MA in a solution containing H₂SO₄. The amount of MA and H₂SO₄ are similar as entries 2 and 5, respectively.

resorcinol provides no significant turnover number (TON), suggesting that the catalysis occurs heterogeneously.

It is generally accepted that the alkylation reaction can be catalyzed by the Lewis acid sites. As shown in Table 1, no product was obtained when MA alone which contains only Lewis acidity was used as the catalyst in the reaction. This suggests that the Lewis acid sites in MA are weak acid sites. However, their presence undoubtedly influences the performance of sulfated MA in alkylation. This is supported by the fact that TON of 15%H₂SO₄/MA (entry 4 in Table 1) is higher than that of H₂SO₄ (entry 5 in Table 1). This indicates that the presence of Lewis sites increase the formation of reaction products in alkylation of resorcinol.

In order to confirm the important of synergism between Lewis and Brönsted sites, we compared the activity of sulfated MA with that of unsulfated MA in a solution containing H₂SO₄ (see entries 2 and 6 in Table 1). It shows that

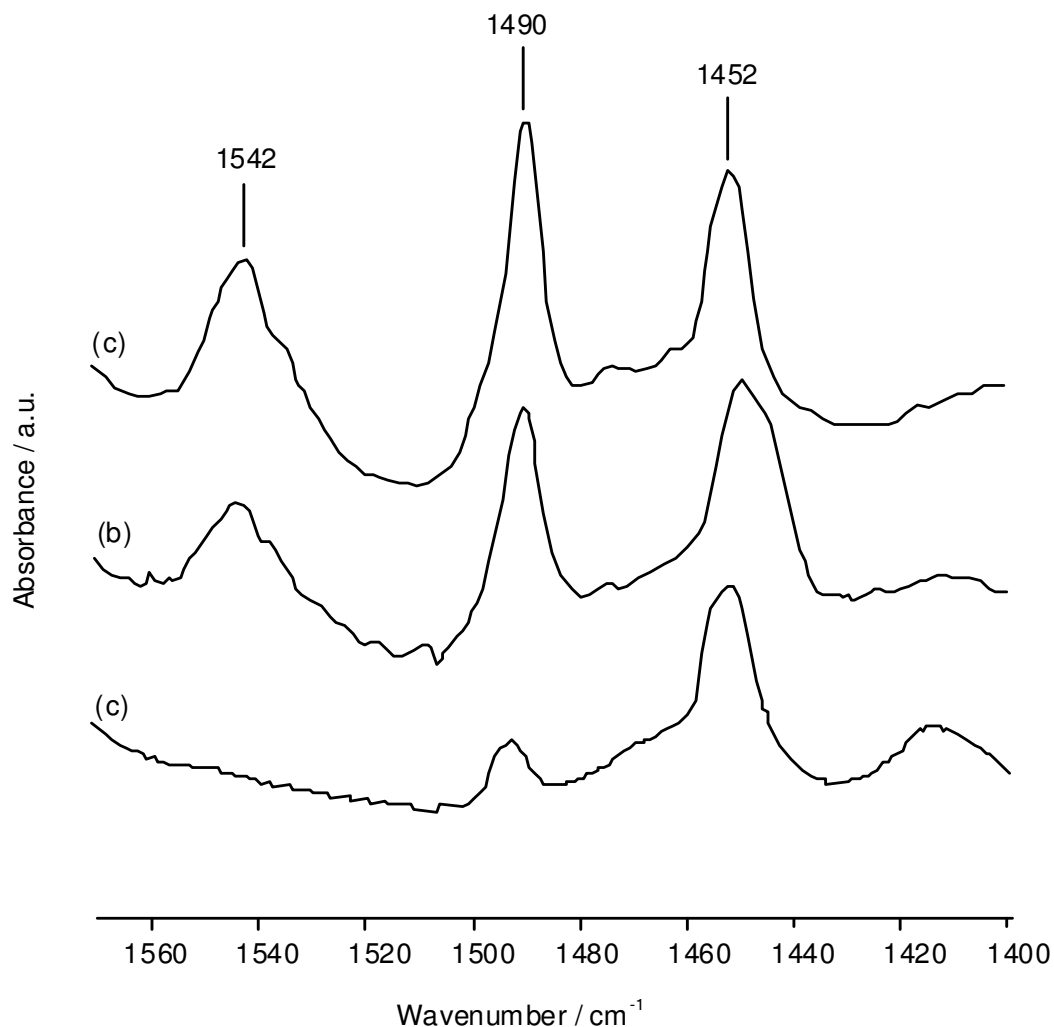


Figure 4. The FTIR spectra of (a) MA, (b) 6% H_2SO_4 /MA (c) 15% H_2SO_4 /MA after desorption of pyridine at 150 °C for 1 h.

the catalytic activity of reaction system containing unsulfated MA and liquid H_2SO_4 is similar to those observed for homogeneous catalyst H_2SO_4 (entry 5 in Table 1). This implies that the synergism between Lewis and Brønsted acid sites takes place heterogeneously on the surface of sulfated MA in the Friedel-Crafts alkylation of resorcinol.

Based on the results obtained, the mechanism of alkylation of resorcinol with MTBE is proposed (see Figure 5). MTBE and resorcinol gets preferentially adsorbed on Brønsted and Lewis acid sites, respectively. The activation of MTBE is initiated by hydrogen bonding between Brønsted hydroxyl proton and oxygen

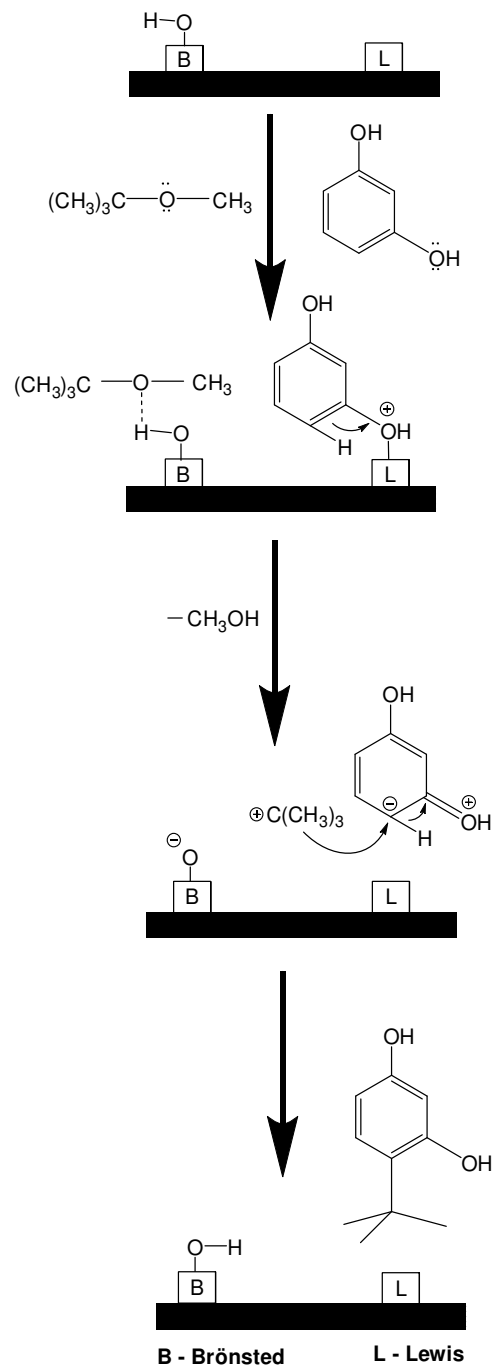


Figure 5. Proposed mechanism of the alkylation of resorcinol with MTBE.

of MTBE. It leads to the MTBE releasing the carbocation. The formation of carbocation from MTBE is necessary in order to begin the alkylation. The carbocation is only formed if the MTBE is adsorbed on Brønsted acid sites. On the Lewis site, high electronegativity of oxygen of resorcinol leads to bonding with Lewis acid site. The mechanism is consistent with our proposal that both Lewis and Brønsted acidities play a synergetic role in this reaction.

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