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t-Butylation of 1,2-dihydroxybenzene over acidic zeolites

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Abstract

t-Butylation of 1,2-dihydroxybenzene (DHB) with isobutene as alkylating agent was carried out over various acidic zeolites such as USH-Y, H-beta, and H-ZSM-5. USH-Y zeolite exhibits the highest catalytic activity and considerable selectivity of 4-*t*-butylcatechol (4-TBC). The selectivity of 4-TBC is increased in the order of H-ZSM-5>USH-Y≅H-beta. 3-*t*-Butylcatechol (3-TBC) is well produced over catalyst with high SiO_2/Al_2O_3 ratio and large pore aperture. 3,5-Di-*t*-butylcatechol (3,5-DTBC) selectivity is maximum in zeolite which contains strong acidity and large pore channel. The influences of various reaction parameters such as reaction temperature, space velocity, reactant molar ratio are discussed. In order to improve 4-TBC formation and decrease in 3,5-DTBC selectivity simultaneously, USH-Y zeolite was silylated by tetraethylorthosilicate (TEOS) resulting in the decrease of 3,5-DTBC selectivity over modified catalysts by about 25%. USH-Y zeolite shows high stability in the *t*-butylation for at least 350 h. The coke formed during the reaction was identified by FT-IR and the USH-Y zeolite could be regenerated through oxidative thermal treatment. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Alkylation; Dihydroxybenzene; Isobutene; Zeolites; Coke; Regeneration; Silylation

1. Introduction

4-*t*-Butylcatechol (4-TBC) and its derivatives are used as raw materials for the synthesis of several polymerization inhibitors, dye developers, pharmaceuticals, and agricultural chemicals. Commercial alkylation of aromatics is carried out via electrophilic substitution, where Lewis acids such as $AlCl_3$, $ZnCl_2$ and HCl, and H_2SO_4 are the most commonly available catalysts [1]. The use of these catalysts gives rise to many problems concerning handling, safety, corrosion, and waste disposal.

Much effort has been put into developing an alternative technology based on heterogeneous catalysts [2]. The use of zeolites in organic reactions has grown over the last several years because of the shape selectivity, which zeolites impose on a reaction, together with lower environment pollution and higher purity of the product [3,4]. Hence, many reports on the aromatics alkylation over solid acid catalysts with alcohol or olefin as alkylating agent have been published [5–7], dealing with parameters which affect catalytic properties. For example, the reaction parameters in the shape-selective alkylation of naphthalene over large-pore zeolites were studied by Chu and Chen [5]. Bellussi et al. [6] reported benzene alkylation with light olefins catalyzed by beta zeolite and concluded that the catalytic activity and product selectivity are affected by the structure and particle size of zeolite. Cejka et al. [7] used silylated HZSM-5 in toluene alkylation, where conversion and selectivity were improved.

On the other hand, a number of scientists have tried to enhance the para-selectivity through various meth-

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ods [8–10]: lowering of the effective pore size of the zeolite, enhancement of the diffusional constraints, suppression of the non-shape-selective sites located on the external zeolite surface and control of the catalyst acid strength. Silylation has been considered the most effective method among the various modifications to give high para-selectivity in alkylation. This can be achieved via chemical modification of the zeolite crystal surface, by deposition of bulky silicon molecules that do not penetrate into the zeolite channels. This is ascribed to the blocking of active sites on the external surface and/or to decreasing the free diameter of channel entrance [11–13].

Although many articles about aromatics alkylation have been reported, only a few papers [14] and patents [15,16,27,28] on the butylation of dihydroxy-substituted aromatics were disclosed until now. We have reported the relationships between conversion/selectivity and acidic nature of the catalyst determined by FT-IR spectroscopy for *t*-butylation of 1,2-dihydroxybenzene (DHB) with *t*-butylalcohol over zeolites [14]. In a Japanese patent [15,27,28], 4-TBC was prepared from DHB and *t*-butylalcohol in the presence of Friedel–Crafts type catalysts, $ZnCl_2$, $FeCl_3$, and HCl, with low conversion and selectivity, and di-*t*-butylation of hydroquinone was achieved by isobutene over acidic resin with low conversion and selectivity [16].

In this study, we try to understand the influences of important variables affecting the conversion and selectivity of the reaction such as zeolite structure, reaction temperature, space velocity, and molar ratio of isobutene to DHB. In order to increase the para-selectivity, we modified USH-Y by silylation and applied it for the catalytic reaction. In addition, catalyst stability was examined and regeneration method for the catalyst was suggested.

2. Experimental

2.1. Catalyst preparation

Commercially available zeolites such as USH-Y, H-beta, and H-ZSM-5 were provided by Zeolyst.

Silylation was carried out as follows. USH-Y zeolite was dehydrated at 450°C for 2 h under 10^{-5} Torr, followed by cooling down to room temperature. Then TEOS (Aldrich 99+%) vapor was exposed to the sample. The sample was kept at 200°C for 20 h, followed by pumping at the same temperature for 2 h. The sample was calcined at 550°C for 6 h in air.

2.2. Catalytic reaction

The catalytic alkylation of DHB (Aldrich 99+%) with isobutene at 130°C was carried out at atmospheric pressure using a fixed-bed vertical flow reactor. DHB and isobutene with molar ratio of 1:1 were introduced into the reactor with WHSV=8.6 h^{-1} (based on the weight of reactant, i.e., DHB and isobutene). The liquid products were collected every hour, and analyzed by gas chromatography using a flame ionization detector and SE-30 30 m capillary column. Reaction products were identified by GC/MS (HP 5890 II GC–HP 5971 Mass Selective Detector) and ^{1}H NMR (GEMINI-2000, 200 MHz) as reported previously [14].

2.3. Characterization of catalysts

To study coke formation by FT-IR, 12 mg of USH-Y zeolites were pressed into self-supported wafers. These wafers were mounted in an infrared vacuum cell with calcium fluoride windows. The samples were degassed at 450°C for 2 h. All the FT-IR spectra were measured at room temperature. The IR peak intensities were normalized at the 1882 cm^{-1} band that is assigned to the Si–O overtone of the zeolite framework [17]. The FT-IR spectra were recorded by using a Nicolet Magna-IR 560 spectrometer over the range 1000–4000 cm^{-1} with 2 cm^{-1} resolution.

3. Results and discussion

Since olefins or alcohols can generally be used as alkylating agents in the alkylation of aromatic compounds, isobutene serves as the alkylating agent in this work. Isobutene has an advantage compared to *t*-butylalcohol. When isobutene is used in DHB *t*-butylation, the aimed product, 4-TBC is formed even at the low reaction temperature of 130°C and does not produce water. However, in case of *t*-butylalcohol, to achieve a similar activity, the higher reaction temperature of 170°C is required, and simultaneously water is produced stoichiometrically. This means that the isobutene is easily activated at lower reaction temperature to proceed *t*-butylation.

Acid-catalyzed alkylation is one type of Friedel–Crafts substitution reaction. Acidic zeolites can catalyze such a reaction due to the strong acidity of their protons. Because of the electrophilic nature of the alkylation over acidic catalysts, substitution at the para-position of DHB is favored. Three different reaction products which are identified by GC/MS and ^{1}H NMR can be produced in this reaction. Only C-alkylated derivatives such as 4-TBC, 3,5-di-*t*-butylcatechol (3,5-DTBC) and 3-*t*-butylcatechol (3-TBC) are produced.

3.1. *Effect of zeolite structure*

The catalytic properties for DHB alkylation with isobutene over USH-Y, H-beta, and H-ZSM-5 are shown in Table 1. The DHB conversion is shown to have big differences according to the zeolite structure, in particular, pore size, which is proportional to the conversion. USH-Y and H-beta zeolites having pore size larger than 0.70 nm have high catalytic activities, 91.1 and 83.1%, respectively. USH-Y possesses a framework system consisting of supercages, connected by a three-dimensional array of large-diameter channels. This enables a much easier diffusion of reactants and products, thus favoring a high activity. However, H-ZSM-5 with 0.54 nm channels only exhibits a conversion of 45.0%. Though H-ZSM-5 possesses a high concentration of strong acid sites, a low activity is observed. This is attributed to the fact that the strong acid sites are located within the narrow pores, and thus these are difficult to access for the reactant. Generally, conversion in aromatics alkylation over zeolite catalysts can be controlled by acidity and diffusion rate. As shown in Table 1, the decisive factor in determining the catalytic activity in this reaction seems to be diffusion rate, because the SiO_2/Al_2O_3 ratio is independent of the conversion. The reason for the high activity of USH-Y with a high SiO_2/Al_2O_3 ratio and at lower reaction temperature is that isobutene is easily activated, and produces 4-TBC even at low reaction temperature.

Table 1
Catalytic activities and product selectivities over various zeolites[a]

	USH-Y	H-beta	H-ZSM-5
Pore size (nm)	0.74	0.70	0.54
SiO_2/Al_2O_3	80	25	30
DHB conversion (%)	91.1	83.1	45.0
Product selectivity (%)			
4-TBC	87.6	87.5	90.7
3-TBC	1.9	1.8	1.3
3,5-DTBC	10.5	10.7	8.0

[a] Reaction conditions: catalyst, 0.5 g; temperature, 130°C; isobutene/DHB (molar ratio), 1; WHSV, 8.6 h^{-1}.

The relative selectivity of 4-TBC increases in the order H-ZSM-5>USH-Y≅H-beta, which is inversely proportional to the size of the zeolite pore aperture. It can be interpreted that zeolite having narrower pore opening has advantage to produce 4-TBC selectively, which means the selectivity is controlled by zeolite pore size mainly. However, all zeolites adopted in this work are effective catalysts for the production of 4-TBC.

The 3-TBC selectivities are 1.9, 1.8, and 1.3% over USH-Y, H-beta, and H-ZSM-5, respectively. 3-TBC is produced well over the catalyst with the high SiO_2/Al_2O_3 ratio and large pore aperture. Based on our previous work [14], 3-TBC formation favors weak acid sites.

The selectivity of dialkylated product, 3,5-DTBC, shows a maximum for H-beta which has strong acidity and large pore channels. It seems that 3,5-DTBC is mainly formed on the external surface of the zeolite because 3,5-DTBC is too large to penetrate into the zeolite channels. Generally, the number of acid sites is inversely proportional to the SiO_2/Al_2O_3 ratio. Although, in this study, USH-Y (SiO_2/Al_2O_3=80) possesses a smaller acid concentration than H-ZSM-5 (SiO_2/Al_2O_3=30), the reason why USH-Y zeolite shows higher selectivity for 3,5-DTBC than H-ZSM-5 is due to the fact that USH-Y has larger pores than H-ZSM-5.

Although the selectivity of 4-TBC on USH-Y zeolite is somewhat less than that on H-ZSM-5, the high activity of this catalyst can overcome this weak point.

3.2. *Effect of reaction temperature*

The effect of reaction temperature in the range 110–170°C on the activity and selectivity of USH-Y zeolite is exhibited in Table 2. Basically, the DHB

Table 2
Effect of reaction temperature (110, 130, 150 and 170°C) on the DHB *t*-butylation with isobutene over USH-Y[a]

	110°C	130°C	150°C	170°C
DHB conversion (%)	62.0	91.1	91.4	95.5
Product selectivity (%)				
4-TBC	88.3	87.6	84.9	69.2
3-TBC	2.2	1.9	1.7	1.5
3,5-DTBC	9.5	10.5	13.4	29.3

[a] Reaction conditions: USH-Y, 0.5 g; isobutene/DHB (molar ratio), 1; WHSV, 8.6 h^{-1}.

Table 4
Effect of isobutylene/DHB (0.6, 0.8, 1.0, 1.2 and 1.4 molar ratio) ratio on the DHB *t*-butylation with isobutene over USH-Y[a]

	0.6	0.8	1.0	1.2	1.4
DHB conversion (%)	37.9	72.1	81.0	84.5	89.4
Product selectivity (%)					
4-TBC	96.4	94.3	91.0	89.2	87.4
3-TBC	2.1	2.7	2.9	2.5	2.0
3,5-DTBC	1.5	2.9	6.1	8.3	10.6

[a] Reaction conditions: USH-Y, 0.5 g; temperature, 130°C; WHSV, 34.4 h^{-1}.

conversion increases with increasing reaction temperature. The conversion of DHB increases drastically from 62.0 to 91.1% as the temperature is raised from 110 to 130°C. The reason for the low activity at low reaction temperature is attributed to severe diffusion limitation even with the ultrastable Y zeolite [18]. However, at higher temperature, the 4-TBC selectivity is quickly reduced due to the increase of 3,5-DTBC, because once 4-TBC is formed it reacts with isobutene to 3,5-DTBC. Therefore, 4-TBC formation is favored at lower reaction temperature. 3-TBC indicates an inverse trend compared to that of 3,5-DTBC, so that 3-TBC is formed well at lower temperature. Considering the DHB conversion and 4-TBC selectivity, the proper reaction temperature is about 130°C.

3.3. *Effect of space velocity*

Table 3 shows the effect of the space velocity of the feed on the catalytic properties of USH-Y zeolite. The conversion of DHB slowly decreases with increasing space velocity from 8.6 to 43 h^{-1}, while the 4-TBC selectivity increases. 3,5-DTBC selectivity is quickly reduced at high space velocity, which might be attributed to shorter contact time. The proper space velocity for obtaining high 4-TBC yield is 34.4 h^{-1}.

Table 3
Effect of space velocity (8.6, 17.6, 25.8, 34.4 and 43.0 h^{-1}) on the DHB *t*-butylation with isobutene over USH-Y[a]

	8.6 h^{-1}	17.6 h^{-1}	25.8 h^{-1}	34.4 h^{-1}	43.0 h^{-1}
DHB conversion (%)	91.1	90.9	85.6	81.0	70.2
Product selectivity (%)					
4-TBC	87.6	88.4	88.9	91.0	93.1
3-TBC	1.9	2.3	2.7	2.9	3.2
3,5-DTBC	10.5	9.3	8.4	6.1	3.7

[a] Reaction conditions: USH-Y, 0.5 g; temperature, 130°C; isobutene/DHB (molar ratio), 1.

3.4. *Effect of isobutene/DHB ratio*

DHB conversion and product selectivity were measured as a function of isobutene/DHB molar ratio and are summarized in Table 4. DHB conversion is proportional to the reactant molar ratio. A higher reactant ratio is helpful for improving the conversion due to the higher concentration of isobutene, which also results in further 4-TBC alkylation to 3,5-DTBC. But the formation of 4-TBC is dominant at lower reactant ratios.

3.5. *External surface modification by silylation*

It is observed that 3,5-DTBC is produced on the external surface of the zeolite mainly; its formation is closely related to the acid sites of the catalysts. In order to reduce the formation of 3,5-DTBC, a silylated USH-Y zeolite was prepared and its catalytic properties are plotted in Fig. 1.

The external surface of USH-Y zeolite was modified in situ with TEOS, according to the literature [19]. DHB conversion over the modified USH-Y is slightly reduced compared to that over the unmodified catalyst, which means that the modifications do not change the concentration of acid sites located in the pores. Also, an increase in the 4-TBC selectivity (87.6%→89.1%) and a reduction in the 3,5-DTBC selectivity (10.5%→7.8%) are observed over external surface modified USH-Y zeolites. Removal of external acid sites can be achieved by depositing the vapor of a bulky chemical whose molecular size is

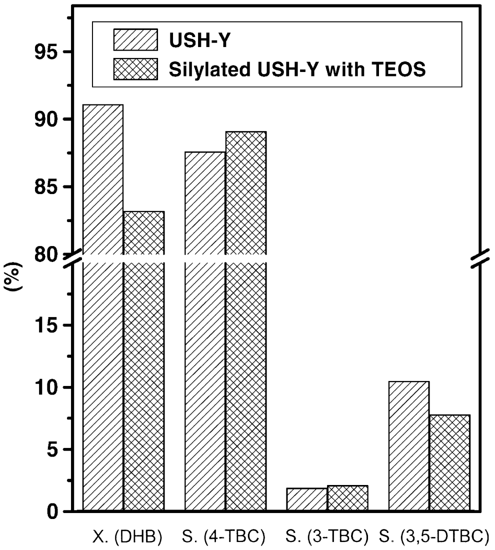

Fig. 1. Comparative catalytic activities and product selectivities over USH-Y and silylated USH-Y. X: conversion; S: selectivity.

larger than the USH-Y pore opening, while the internal structure of the zeolite remains unaffected. Since the 3,5-DTBC selectivity over modified catalysts is decreased by about 25%, it seems that the modification induces partial removal of acid sites on the external surface. Improved 4-TBC formation with high activity can be achieved via silylation of the zeolite external surface by TEOS. The 3-TBC selectivity is almost constant before and after silylation, which implies that the formation of 3-TBC is not related to the external acid sites.

3.6. Deactivation and regeneration of catalyst

The time dependence of activity and selectivity of USH-Y for DHB *t*-butylation with isobutene are indicated in Fig. 2. Reduction of DHB conversion (89.2%→80.5%), 4-TBC selectivity (85.9%→77.3%) and an increase of 3,5-DTBC selectivity (12.5%→18.1%) are observed after a reaction time of 350 h. The reason for the decrease of the conversion and 4-TBC selectivity is probably the formation of heavy reaction products and coke during the reaction. These phenomena are well explained by Guisnet and Magnoux [20]. Formed coke blocks the active sites and pore aperture partially, so that the reactants have

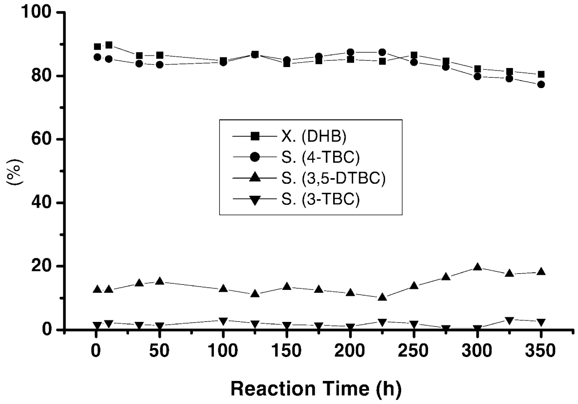

Fig. 2. Reaction time dependence of DHB conversion and product selectivity in DHB *t*-butylation with isobutene.

difficulty in accessing the internal acid sites. As indirect evidence, the color of the USH-Y zeolite slowly changed to dark red in the initial reaction time and when the catalyst is fully deactivated the color turned from red to dark brown. According to the literature [21,22], zeolite catalysts used in isobutane alkylation are rapidly deactivated. Especially when the reaction is carried out in a fixed-bed reactor, oligomerization dominates and the catalysts deactivated within a few minutes time on stream. Furthermore, it is reported that large-pore zeolites show rapid deactivation [23]. However, USH-Y zeolite shows higher stability in this *t*-butylation than catalysts used in other alkylations.

FT-IR spectroscopy was used to obtain information about the nature of the species present in the coke deposited on zeolites. The spectrum of the fresh USH-Y zeolite evacuated at 450°C for 2 h contains three bands at 3740, 3629 and 3564 $\mathrm{cm^{-1}}$ in the range 3500–4000 $\mathrm{cm^{-1}}$ (Fig. 3(a)). The bands at 3629 and 3564 $\mathrm{cm^{-1}}$ are associated with the acidic OH groups (–Si–OH–Al–) and the 3740 $\mathrm{cm^{-1}}$ band with the terminal, non-acidic OH groups bound to silicon framework atoms (–Si–OH) [24,25]. When USH-Y was deactivated, the pattern of the FT-IR spectrum changed completely (Fig. 3(b)). New bands at 2966, 2911, and 2873 $\mathrm{cm^{-1}}$ are characteristic of highly branched multiple alkylated species formed during the alkylation reaction. Bands between 3000 and 3200 $\mathrm{cm^{-1}}$, generally attributed to aromatic deposits, are observed. The FT-IR absorption bands at 1598 and 1505 $\mathrm{cm^{-1}}$, which can be assigned to polyalkylated aromatics and

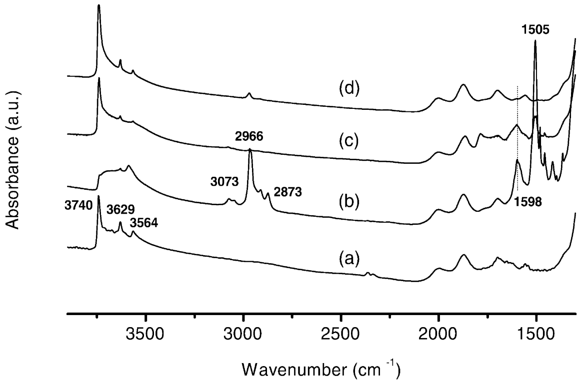

Fig. 3. FT-IR spectra of: (a) fresh USH-Y; (b) deactivated USH-Y evacuated at 400°C for 2 h; (c) calcined (b) at 400°C for 6 h in air and (d) recalcined (c) at 550°C for 6 h in air.

coke bound to bridging Si–OH–Al groups, are similar to those previously reported [7]. According to the report by Blackmond and Goodwin [26], the appearance of a band at around 1585 cm^{-1} is related to the presence of polyaromatic species, its intensity being proportional to the coke content. Similar phenomena were also observed in toluene alkylation by Cejka et al. [7]. The bands related to coke are strongly adsorbed on USH-Y catalyst even after evacuation at 400°C for 2 h. To regenerate deactivated USH-Y, the catalyst was treated at 400°C for 6 h in air, after which the peaks at 1598 and 1505 cm^{-1} are almost removed and the acidic OH groups are partially regenerated at 3629 and 3564 cm^{-1} (Fig. 3(c)). As shown in Fig. 3(d), by calcining at 550°C coke is completely eliminated and acidic OH groups reappeared. Regeneration of the USH-Y zeolite seems to be achieved through oxidative thermal treatment.

4. Conclusions

t-Butylation of DHB with isobutene was carried out over various forms of H-zeolites, USH-Y, H-beta, and H-ZSM-5. From this reaction, 4-TBC is obtained as major product, and 3,5-DTBC and 3-TBC as by-products. We have investigated the influences of important variables governing the conversion and selectivity of the reaction such as zeolite structure, reaction conditions, and zeolite modification. Catalyst stability was evaluated and a catalyst regeneration method was suggested. The conclusions from the present results can be summarized as follows:

1. Isobutene as alkylating agents has merit compared to *t*-butylalcohol because isobutene is more active at lower reaction temperature with a high selectivity for 4-TBC and does not produce by-products like water.
2. USH-Y exhibits the highest catalytic activity among catalysts. The selectivity of 4-TBC increased in the order H-ZSM-5>USH-Y≅H-beta. However, when taking both activity and selectivity into account, USH-Y zeolite was the best candidate among the catalysts in this study. On the other hand, 3,5-DTBC production favors strong acidic sites of large-pore zeolite and the outer surface of zeolites.
3. A reaction temperature of 130°C, a high space velocity of WHSV=34.4 h^{-1}, and equi-molar reactants are helpful in producing 4-TBC selectively.
4. Silylation of USH-Y zeolite with TEOS enhances the 4-TBC selectivity compared to the parent USH-Y, which is the result of modification of the pore entrance and reduction of the number of external surface acid sites.
5. Blocking of acid sites by coke and polyalkylated aromatics which are formed during the reaction might be a reason for the deactivation of catalyst. The deactivated catalyst can be regenerated through oxidative calcination.

Acknowledgements

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