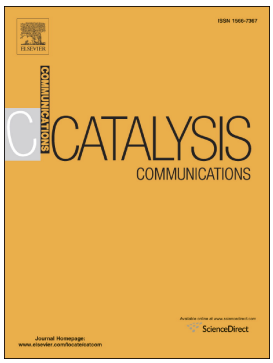
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Alkylation of resorcinol with tertiary butanol over zeolite catalysts: shape selectivity *vs* acidity

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Abstract

The catalytic performance of various zeolites such as H-ZSM-5, H-Y, H-beta, H-Mordenite in resorcinol alkylation with tertiary butanol demonstrated that pore characteristics have major influence on product selectivity, whereas acid strength and number of acid sites influenced resorcinol conversion. The passivation of external surface of H-beta zeolite by silylation and amine poisoning produced shape selectively O-alkylated resorcinol methyl tert butyl ether (RMTBE) and 4-tert butyl resorcinol (4-TBR). We propose that 4-TBR formation goes over external acid sites through RMTBE isomerization, whereas formation of 4-TBR takes place inside the pores through direct C-alkylation mechanism.

Keywords: Acidity; Alkylation; Shape selectivity; Resorcinol alkylation, Zeolite, Particle size.

1. Introduction

Alkylation of aromatics is an important reaction in organic chemistry due to its wide application in fine chemical, petrochemical, perfume, dye and pharmaceutical industries[1, 2]. Among different alkylation reactions, Friedel-Crafts butylation of resorcinol to produce mono-tert butylated products is one of the most noteworthy due to its involvement in the synthesis of

antioxidants, polymer stabilizers, therapeutics, and organic synthetic applications[3, 4]. The alkylation of resorcinol with tertiary butanol (TBA) gives a mixture of alkylated benzenediols and ethers. Being thermodynamically favoured (monoalkylated readily undergoes a consecutive alkylation), dialkylated 4,6-di-tert-butyl resorcinol (4,6-DTBR) is usually the major product[5]. However, 4-tert-butylresorcinol (4-TBR) is of particular interest as an antioxidant in food preservatives and in treatment of skin diseases. Therefore, selective synthesis of 4-TBR at a high conversion of resorcinol is a difficult and challenging task for catalyst design [6, 7].

Traditionally, homogeneous Lewis ($AlCl_3$, $FeCl_3$) and Brönsted acids (H_2SO_4, H_3PO_4) are used to catalyse the reaction[7]. However, limitations and hazardous nature of these soluble acid catalysts have led to replace them by heterogeneous catalysts[7]. There are a few solid acid catalysts that have been studied for the reaction so far, such as montmorillonite clay, zeolites, ZrO_2 supported phosphotungstic acid, dodecatungstophosphoric acid supported on K-10, sulphated mesoporous Al_2O_3, sulphated zirconia and heteropolyacid supported mesoporous materials[1-7]. However, reactions over these catalysts were carried out at high temperature and/or pressure, and allowed only moderate yields for 4-TBR. Zeolites with their tuneable acidity and high thermal stability are promising and were well explored in various alkylation, acylation, carbonylation, condensation and dehydrogenation reactions[8-12]. Among the zeolite catalysts H-Y, ITQ-6 and H-ZSM-5 were studied for the butylation of resorcinol but low selectivity for 4-TBR was reported, with only few details being given on the nature and location of active sites for the reaction and the influence of their respective pores on the product selectivity [1, 3].

Recently, we reported heteropolyacid supported SiO_2 and sulphated zirconia as active catalysts for the alkylation of resorcinol[6, 7]. In continuation of our quest for simple, efficient and robust active catalysts for this reaction, herein is reported the application of different zeolites

as solid acid catalysts for the conversion of resorcinol to 4-TBR. In this work, zeolites (H-ZSM-5, H-Y, H-beta, H-Mordenite) with different acidity, framework type, and particle sizes were studied. Insights on the origin of product selectivity was gained by a systematic modification of the zeolite catalysts by silylation and amine poisoning. The physicochemical properties of the catalysts, especially the porous characteristics, were correlated with catalytic activity in the alkylation reaction.

2. Experimental

2.1. Catalyst Preparation

The zeolites H-ZSM-5, H-Y, H-BEA and H-Mordenite with different SiO_2/Al_2O_3 ratios (SAR) were purchased from Zeolyst International, USA. The H-BEA (SAR 28) with bigger crystal size (Micro) obtained by TOSOH, Japan. Before the reaction, catalysts were pre-treated to 550 °C for 4 h in static air.

Silylation of H-BEA: Tetra butyl orthosilicate (TBOS) corresponding to loading of 15 wt % SiO_2 mixed with a 100 ml toluene in a round bottom flask. To this solution, around 5 grams of H-BEA zeolite was added and refluxed for 8 h followed by filtration. The solid obtained was dried at 120 °C for 12 h, and finally calcined in air at 550 °C for 4 h. The above procedure was repeated for successive SiO_2 depositions.

Amine poisoning: The zeolite beta initially dehydrated by heating to 550 °C for 4 h in static air. For the amine poisoning, dehydrated H-beta zeolite was contacted with tri pentylamine, and then evacuated at 250 °C in vacuum to remove physiosorbed amine.

2.2. Catalyst characterization

The phase purity and crystalline properties of all the zeolites were determined by X-ray diffraction on a Siemens D5000 diffractometer equipped with a Cu Ka source. The samples were analysed in the 2-theta range of 5 to 80° with a scan rate of 0.02° s^{-1}. The amount of SiO_2 after silylation present on the catalyst was determined by ICP-OES analysis. The BET surface area, pore volume, and pore size distributions were obtained through N_2 sorption experiments performed using a Micrometrics 3flex. Before the measurements, catalysts were degassed overnight under a vacuum (6 Pa) at 300 °C. The measurements were performed at -196 °C with relative pressures in the range of 0.01–1.00 (p/p^0).

Acidity measurements of zeolite catalyst done by the pyridine adsorption technique. Wafers of the zeolite catalyst were prepared, weighed and then placed in a sample holder inside a Pyrex cell specially designed for a controlled heating of the sample under vacuum and equipped with a NaCl window. In a typical measurement, the catalyst was pre-treated at 300 °C under vacuum (between 10^{-4} and 10^{-5} Pa) for 2 h in order to remove impurities from the surface. After cooling under vacuum, 1000 Pa of pyridine sent at room temperature into the cell and adsorption was allowed for 30 min. The sample was then outgassed at 10^{-5} Pa at 100 °C. FT-IR spectra were taken in transmission mode before and after pyridine adsorption, using a spectrometer IFS55 Equinox (Bruker) equipped with a DTGS detector. The spectra were recorded with100 scans between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1}. NH_3 adsorption and subsequent temperature-programmed desorption (NH_3-TPD) were performed in a Hiden CATLABPCS combined micro reactor and mass spectrometer (MS) system as reported earlier. [7]

2.3. Catalytic studies

The alkylation of resorcinol with TBA was carried out in a liquid batch reactor. In a typical reaction, 2.2 g of resorcinol was dissolved in 6 ml of TBA, 0.9 ml of o-xylene (internal standard) and 2-5 ml of solvent in a 100 ml two neck round bottom flask fitted with a condenser. [7] The reactor is placed in an oil bath under magnetic stirring (1200 rpm) and heated to 80 °C. Then, 0.22 g of catalyst was added. The reaction was monitored by GC-FID analysis. For sampling, 10 µl of reaction mixture was mixed with 1.8 ml of methanol and was analysed by a gas chromatograph (Shimadzu- 2041, FID detector) equipped with an RTX-5 column (0.25 mm I.D. and 30 m length). All the products were identified by injecting the standard sample followed by NMR analysis as done in our previous work. [6, 7] The conversion and selectivity were directly calculated from GC peak areas in mol% using a multi-point calibration curve through the internal standard method. The mass balance calculated after the reaction is in the range 95–98%.

3. Results and discussion

The Friedel-Craft alkylation of resorcinol with TBA was carried out over different zeolitic frameworks such as H-ZSM-5, H-MOR, H-BEA and H-Y. The crystal structure using powder XRD and pore analysis (surface area, pore volume, pore shape) of all the zeolites using N_2 adsorption are shown in **Fig. S1**. The conversion and selectivity for the different products are shown in **Table 1** along selected physicochemical properties of the catalysts. The resorcinol conversion was not same for these zeolites although they have similar Si/Al ratio in the range 18-30, (**Entry 1-2, 7, 9**). Among the different tested zeolites, H-Y and H-BEA showed higher resorcinol conversions (46 and 50 %, respectively) compared to H-MOR (5%) and H-ZSM-5 (4 %) likely due to higher diffusion rates of reactants and products in their large pores. The selectivity for 4-TBR over both H-Y and H-BEA zeolites was ~85 %, however, they differ in their selectivity to 4,6-DTBR and RMTBE, which could be related to their different texture

and/or acidity. The selectivity for RMTBE was high for H-BEA, whereas selectivity for 4,6-DTBR was dominant in the case of H-Y. The NH_3-TPD profile of H-BEA and H-Y zeolite exhibited similar acid strength profiles (**Fig. S2**)**.** Hence, the texture of zeolites appears as crucial factor to explain the difference of selectivity to 4,6-DTBR and not the acidity. Our interpretation is that H-Y zeolite having super cages could form the 4,6-DTBR inside the pores or at the pore mouth, but for H-BEA zeolite, due to smaller pore size, 4,6-DTBR formation is hindered. The small amount of 4,6-DTBR (4%) formed on H-BEA would then have proceeded on its external surface.

To check this hypothesis, we separately measured the ability of the studied catalysts to achieve the butylation of 4-TBR to 4,6-DTBR. The conversion of 4-TBR over H-BEA was possible but with extremely low conversion (less than 1 %), indicating internal acid sites are not accessible in dialkylation reaction. At the opposite, H-Y zeolite exhibited 4-TBR conversion ~ 15 %, revealing that many of its acid sites are accessible and active for dialkylation. Besides, it is reported in the literature [2] that selectivity to 4-TBR *vs* 4,6-DTBR are dictated by the proportion of Brønsted *vs* Lewis acid sites present in the catalyst. Thus, considering this other factor, pyridine FT-IR measurements over H-Y and H-BEA were conducted as shown in (**Fig. S3**)**.** Both zeolites exhibit almost similar Brønsted to Lewis acid site ratio (B/L ratio), confirming that difference of acidity cannot be evoked to account for the difference in selectivity between the two catalysts, and, therefore, that this difference of selectivity should be more due to a textural effect as discussed earlier. The selectivity for 2-TBR being identical for all the different zeolites, suggests that on the contrary to the formation of 2-TBR, this is not related to the zeolite structure. Interestingly, ZSM-5 and H-Mordenite although with strong acid strength and large concentration of acid sites (**Fig. S2**) resulted in low activity due to constraint of reactants to

access acid sites inside their small pores. Hence, the low activity observed in these zeolites reflects the contribution of the reaction taking place on external surface acid sites.

The high selectivity for RMTBE over H-BEA zeolite is related to its pore characteristics. Reaction of resorcinol with TBA inside the pores could form RMTBE, but its isomerization to 4-TBR is not possible due to pore constraints. Such formed RMTBE coming out of zeolite pores could isomerize to 4-TBR on the external acid sites, and compete with resorcinol in the alkylation reaction. The resorcinol with its small molecular diameter (ca. 5.6 Å) can easily penetrate into the pores of H-BEA zeolite, whereas such diffusion is difficult for RMTBE[13]. As a result, the concentration of RMTBE increases with reaction time. It should be noted that the conversion of resorcinol to RMTBE is a reversible phenomenon, which dictates RMTBE selectivity in the reaction[6]. Therefore, RMTBE is shape selectively produced over zeolite H-BEA in the butylation reaction. The presence of supercages in H-Y zeolite makes the isomerization of RMTBE to 4-TBR feasible without any constraints, hence the low selectivity to RMTBE.

Further, we investigated the effect of Si/Al ratio (SAR) on the catalytic activity over H-BEA and H-Y (**Table 1**). As SAR increases for H-BEA and H-Y zeolites, total acidity decreases with as a result the decreasing conversion of resorcinol. The selectivity for 4,6-TBR decreases with the increase of SAR for H-Y and H-BEA zeolites, which could be due to the decrease in strength and number of strong acidic sites, in harmony with the TPD profiles (**Fig. 1**). The selectivity for RMTBE increases with SAR for BEA zeolite, whereas for H-Y zeolite it remains almost constant, which is attributed to pore characteristics of H-BEA as discussed earlier.

To further improve the selectivity for 4-TBR and to understand that RMTBE does form in BEA zeolite, pore engineering via silylation and amine poisoning was achieved on H-BEA

zeolites[14, 15]. The crystal structure and pore analysis (surface area, pore volume, pore diameter) of all the silylated H-beta zeolites using nitrogen adsorption are shown in Fig. **S4**. Successive systematic silylation of H-BEA using tetrabutyl orthosilicate progressively narrows the pore size distribution of zeolites along with passivation of external acid sites (Table S1). Small deposition of SiO_2 (3.7 wt%) at pore mouth and external surface improved the selectivity for 4-TBR from 83 to 88 % by decreasing 4,6-DTBR formation (**Fig. 2**). This decrease in the formation of 4,6-TBR could be due to the passivation of acid sites on the external surface of BEA zeolite. This shows that formation of 4,6-DTBR is not taking place inside the pores but on the external acid sites of zeolite. Further successive SiO_2 deposition (3.7 to 15 wt%) decreased resorcinol conversion from 41 to 10 % due to a decrease in the number of external acid sites, as seen from the TPD profiles (**Fig. 3.a, Fig. 2**). Moreover, with SiO_2 deposition pore mouths of zeolites were also narrowed (**Table S1**). SiO_2 deposition above 3.7 % had 4-TBR selectivity dropped from 88 to 45%, and RMTBE selectivity increased from 10 to 52 %, even though strength of acid sites remains similar for the pristine and silylated catalysts as seen in the TPD-NH_3 profiles **(Fig. 3b)**. Furthermore, Brønsted and Lewis acid sites (B/L ratio) of silylated H-BEA, determined by pyridine FT-IR, exhibits no variation in B/L ratio indicating that a variation of this feature might not be the reason for such a selectivity difference for RMTBE and 4-TBR. **(Fig. 3b).** This indicates that pore size of zeolites plays the major role in the present catalysis rather than their acidity. To further understand whether reaction is indeed undertaken inside the pores or outside, strong and bulky basic amine, namely tripentyl amine (not able to penetrate pores with a size of ~ 6.5 Å due to its large molecular diameter of 9-10 Å), was adsorbed on the surface of H-BEA, and catalytic activity after such modification will be limited to reactions proceeding only inside the pores of the zeolites. Doing so, resorcinol conversion dropped from

46 to 20 %, and selectivity for 4-TBR dropped from 85 to 43%. **(Table S1).** This indicates that half of the reaction was taking place inside the zeolite pores and half outside the pores. Similar resorcinol conversion (>15%) and 4-TBR selectivity (61%) values as obtained with 13.3 wt% SiO_2 deposition by silylation indicates that at this loading, the external surface of H-BEA is completely covered with SiO_2. The resorcinol conversion of 10-15% observed even after passivating the external acid sites by 13.3 wt% SiO_2 must originate from reaction taking place inside the pores of zeolites.

Moreover, increased RMTBE selectivity with successive silylations also supports that the formation of RMTBE occurs inside the pores and its isomerization to 4-TBR on the external acid sites is inhibited. Not only external acid sites are blocked, but also pore mouth of BEA zeolite is narrowed by silylation, where this also restricts access of RMTBE inside the pores to form 4-TBR, hence RMTBE concentration in reaction increases. We suspect that weak hydrogen bonded silanol groups present after silylation on the zeolite surface could catalyse the formation of RMTBE [16]. To check this hypothesis, reaction of resorcinol with TBA over pure SiO_2 catalyst was studied. Formation of RMTBE was not observed, supporting the idea that silanol groups do not contribute to RMTBE selectivity. This indicates that formation of RMTBE shape selectively occurs inside the pores of zeolite, as due to pore constraints, it cannot be isomerized to 4-TBR. Still ~ 45% of 4-TBR selectivity obtained with surface passivated zeolite could be originated by direct C-alkylation of resorcinol with TBA and not through formation of RMTBE.

These studies show that part of the reaction (formation of 4-TBR) proceeds within the zeolite pores, but another part proceeds on its surface. Hence, reaction proceeding inside the BEA zeolite pores to form 4-TBR (in case of silylated catalysts) must go through a direct C-alkylation pathway (**Scheme 1**). In this case, TBA within the zeolite beta undergoes dehydration over acid

sites (to form either carbocation or isobutylene), then attacks resorcinol to form the 4-TBR directly through C-alkylation. The reaction over external acid sites may proceed through isomerization of RMTBE; initially RMTBE is formed inside or over the external surface of zeolite through O-alkylation of resorcinol and then isomerization to 4-TBR occurs over external acid sites.

To further support this, the effect of particle size of H-BEA on catalytic activity in the alkylation of resorcinol was studied. H-BEA with larger (sample named micro) particle size of ~ 400-500 nm and high acidity (1.2 mmol NH_3/g) exhibits lower catalytic activity compared to smaller (sample named nano) particle size of 20-50 nm (**Fig. 4 and Table 1**). This indicates that particle size effect is predominant over acidity in H-Beta catalyst. The resorcinol conversion and selectivity for RMTBE and 4-TBR depends on the particle size of the H-BEA zeolite. The lower resorcinol conversion in case of large particles of H-BEA is due to the reduced external surface acid density compared to smaller particles in size having large external surface acid density. Moreover, a large particle size of H-BEA could limit the diffusion of reactants along the long length of zeolite channels. The high selectivity of RMTBE in case of large particle sized H-BEA indicates that its isomerization to 4-TBR over fewer external acid sites is reduced and further conversion of RMTBE to 4-TBR by direct C-alkylation inside the zeolite pores of longer dimension is limited. This illustrates that particle size and pore characteristics of zeolite have enormous effect on the product selectivity over BEA zeolite.

TBA as alkylating agent in reaction produces water as byproduct and is known to poison acidity of catalyst during reaction leading to lower activity. Therefore, an effort to use different butylating agents such as tertiary butyl ether (MTBE) and di-tertiary butyl dicarbonate (DTBDC) was performed and results are provided in **Table S2**. MTBE produces methanol as by- product,

which resulted in a lower conversion, likely due to the blockage of acid sites. On the contrary, DTBDC produces CO_2 gas as by-product, without influencing the acidity of the catalysts, hence the relatively good conversion of resorcinol observed over DTBDC even at the lower temperature of 60 °C. Moreover, the complete inhibition of RMTBE, 2-TBR and other side-products formation indicates direct C-alkylation with DTDBC (**Table S2)**. The absence of side products formation also could be due to the lower reaction temperature that we were forced to apply with MTBE and DTBC as alkylating agent due to their low boiling points. Overall, H-BEA and HY zeolite in the present work exhibited good resorcinol conversion of ~70 %with 91-97% selectivity to 4-TBR at lower temperature (ca. 60 °C) using DTBDC as alkylating agent than most of the previously reported catalysts (**Table S2**). The 10% Ga-BEA zeolite and 20% DTP/K10 are the only catalysts exhibiting 100 % selectivity for 4-TBR. However, for the 20% DTP/K10 and Ga-Beta catalysts, reaction was carried out at higher temperature, namely 150 °C and 80 °C, respectively [1, 2]. Furthermore, the use of less abundant thus more expensive metal like Ga makes it a less attractive process. ITQ-6 zeolite showed 45 % resorcinol conversion with 78% selectivity to 4-TBR at 100 °C [3]. The other catalysts such as ZrO_2 supported phosphotungstic acid (PTA), acidified montmorillonite K-10, sulphated zirconia and heteropolytungstate (HPW) supported SBA-15 exhibited lower activity and selectivity in the alkylation reaction compared to H-Y zeolite in the present work [5-7]. The zeolites in the current study appear simple, efficient, and easily scalable, which makes them attractive catalysts for the alkylation reaction.

4. Conclusions

The difference of pore size in zeolites H-ZSM-5, H-Y, H-beta, H-Mordenite brings tremendous effect on resorcinol conversion and product selectivity compared to their acidity. H-BEA and H-Y zeolites with large pore size exhibit high resorcinol conversion compared to the H-ZSM-5 and H MOR zeolites. The pore characteristics of H-BEA increases the formation of RMTBE, whereas that of H-Y zeolite increases dialkylation and produces more 4, 6-TBR. The external acid sites passivation by silylation and amine poisoning of H-BEA shows that part of reaction goes outside the pores (O-alkylation followed by isomerization) and another part goes inside the pores (direct C-alkylation) with different plausible mechanisms as supported by studying catalysts with different particle sizes. The use of DTBDC butylating agent has shown large catalytic activity via the direct C-alkylation route without formation of either RMTBE, or 2-TBR. H-BEA zeolite with DTBDC as alkylating agent exhibits 68% of resorcinol conversion with 97% of 4-TBR selectivity at the mild reaction temperature of 60 °C, which competes very well with previously reported catalysts.

Supporting information: Py-FTIR spectra of H-Y and H-BEA, catalytic activity over silylated H-BEA and different alkylating agents.

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Eric M Gaigneaux: Investigation, Supervision, Reviewing and Editing, Validation.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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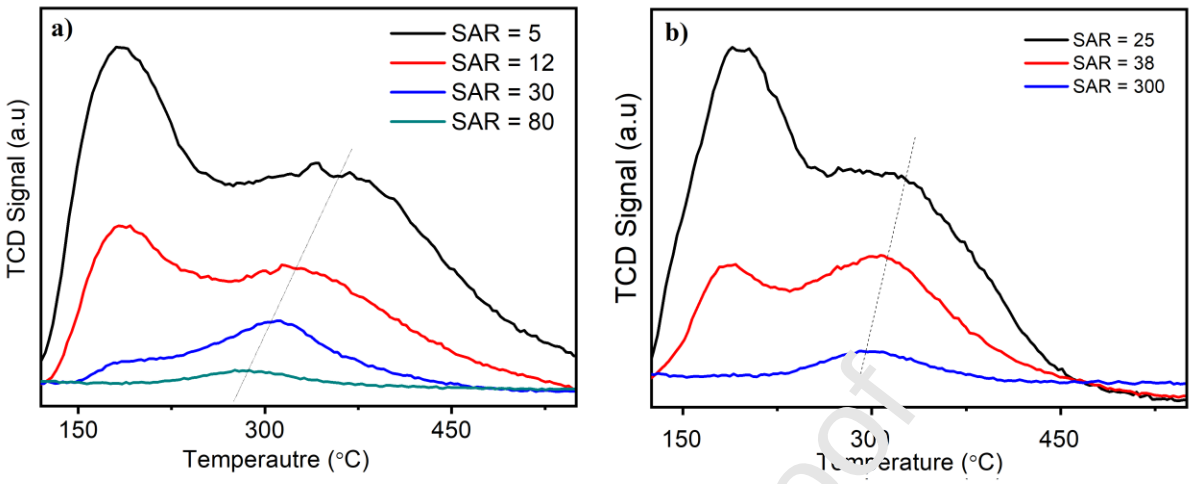


Figure 1. NH_3-TPD profiles of a) H-Y and b) H-BEA zeolites with different Si/Al ratio (SAR).

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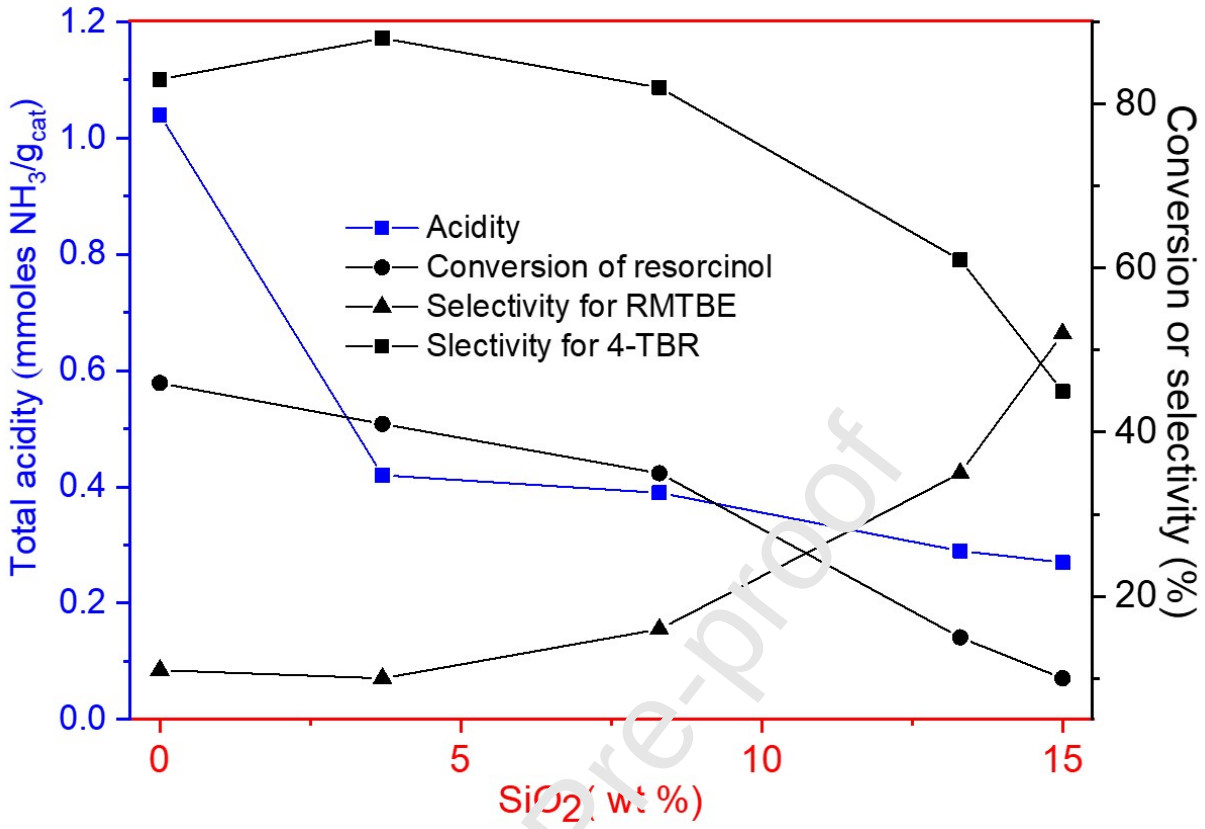


Figure 2. Total acidity and catalytic activity and selectivity (%) of silylated H-beta zeolite for the resorcinol alkylation with tertiary butanol reaction.

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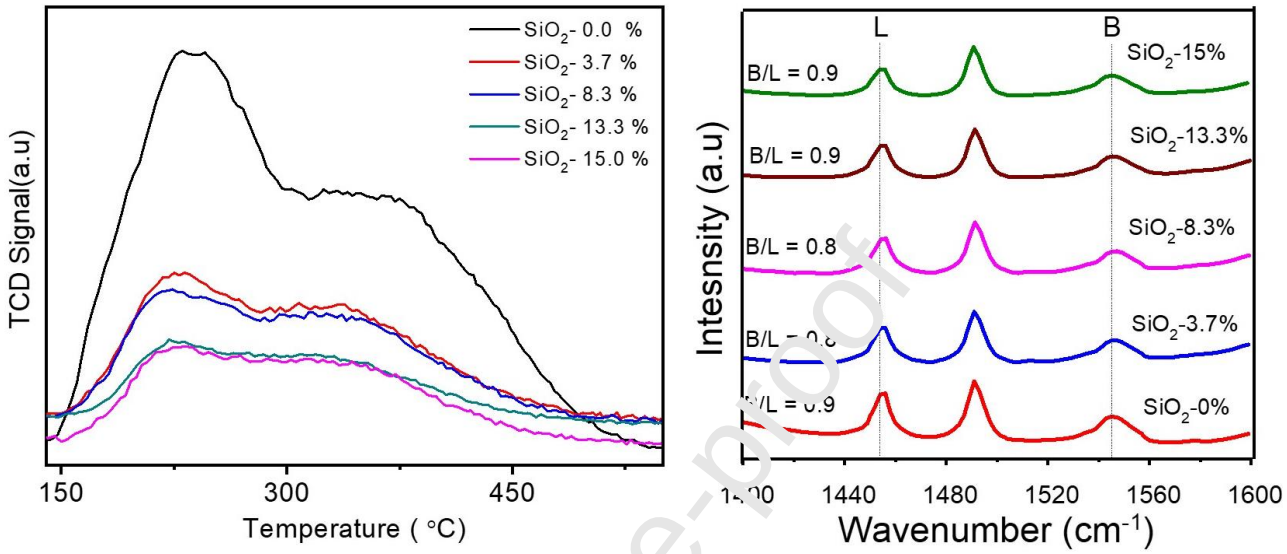


Figure 3. a) NH_3-TPD, and b) pyridine FT-IR spectra over silylated H-BEA catalysts of different wt% SiO_2.

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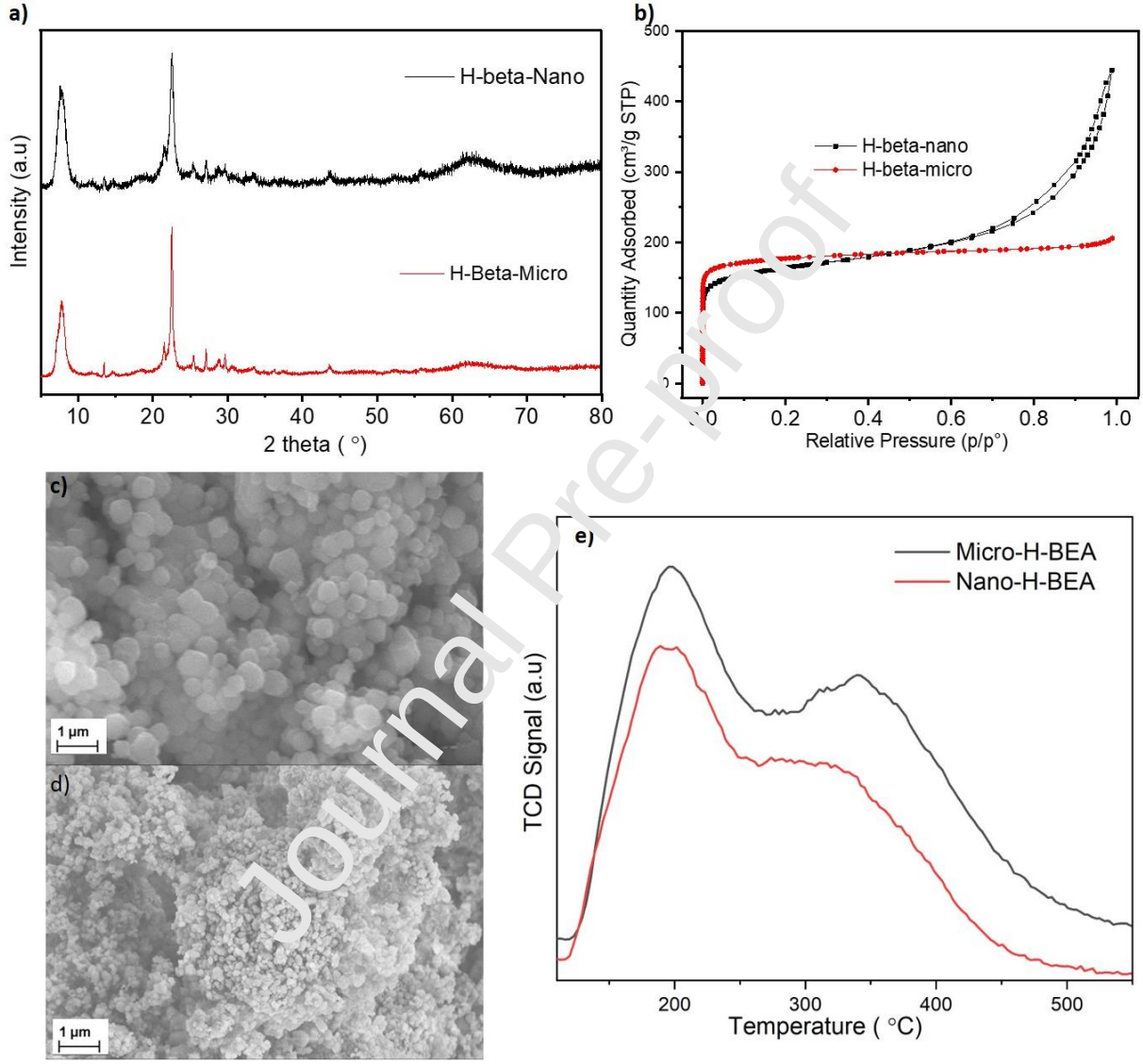


Figure 4. XRD pattern (a), nitrogen adsorption isotherms (b), Scanning Electron Microscopy (SEM) images of Nano (c), and Micro (d) H-beta zeolite. TPD-NH_3 profiles (e) of H-BEA zeolite with two different particle sizes, Nano and Micro. The broad peak for Nano H-beta at 2theta=23° clearly differentiates it from the conventional micro H-Beta, which has very narrow peak width. This is further supported by the SEM images.

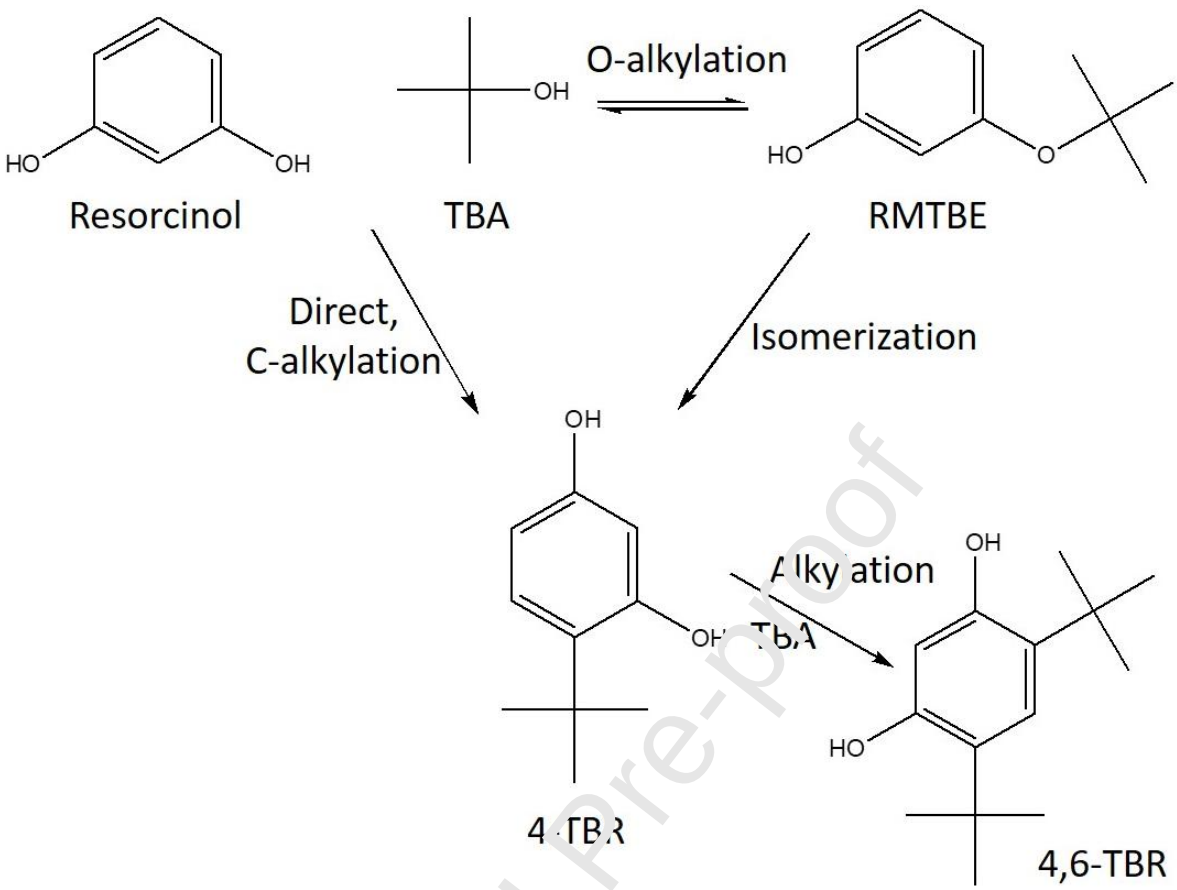
Table 1. Physicochemical properties and catalytic activity/selectivity of zeolites for the resorcinol alkylation reaction.

Entry	Zeolite	SiO_2/Al_2O_3 (SAR)	SSA[a] (m^2/g)	Micropore Volume[b] (cm^3/g)	Pore size[c] (Å)	Acidity (mmol/g)	Resorcinol Conversion (%)	Selectivity (%)					
								RMTBE	2-TBR	4-TBR	4,6-DTBR	Others	TON*
1	ZSM-5	23	414	0.122	5.7	0.65	04	08	02	90	00	00	6
2	H-BEA (nano)	25	607	0.163	6.8	1.04	46	11	01	83	04	01	40
3	H-BEA	38	677	0.197	6.8	0.39	34	13	01	84	00	02	79
4	H-BEA	300	656	0.186	6.9	0.05	17	36	04	57	00	01	309
5	H-Y	5	903	0.324	7.7	1.52	60	03	01	81	15	00	36
6	H-Y	12	763	0.242	7.5	0.78	54	02	01	81	14	02	62.9
7	H-Y	30	833	0.241	7.7	0.18	50	02	01	84	11	02	252
8	H-Y	80	920	0.265	7.7	0.03	40	04	03	86	06	01	1212
9	H-MOR	20	561	0.189	6.0	0.83	05	13	02	85	00	00	5
10	H-BEA(Micro)	28	688	0.224	6.7	1.23	31	16	03	77	03	01	23

Reaction conditions: Resorcinol =2.2 g, TBA = 4 ml, Chlorobenzene= 5 ml, T = 80 °C, Reaction Time =14 h, *o*-xylene (internal standard) = 0.9 ml, Amount of Catalyst = 0.22g; *TON: calculated by mmol of resorcinol converted per mmol of acid sites; [a] Specific surface area determined by BET method; [b]Micropore Volume obtained from t-plot, [c] Average Pore Diameter determined by Horvath-Kawazoe method.

Scheme 1. Plausible reaction mechanism for the butylation of resorcinol.

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HIGHLIGHTS

- H-Beta and H-Y zeolite exhibited higher catalytic activity than H-ZSM-5 and H-MOR.
- Pore characteristics of zeolites play a major role on the product selectivity.
- 4-TBR forms on the external surface of H-Beta zeolite by RMTBE isomerization.
- 4-TBR is also formed inside the pore of H-Beta zeolite by direct C-alkylation.
- Di-tert-butyl dicarbonate is an excellent alkylating agent compared TBA and MTBE.