DELAMINATED ZEOLITE, ITQ-6 AS HETEROGENEOUS CATALYST FOR FRIEDEL CRAFTS ALKYLATION

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Abstract

The ability of ITQ-6, a kind of mesoporous zeolitic material to replace microporous zeolite as catalyst has attracted particular attention. In this study, modification of a precursor of microporous ferrierite, PREFER to mesoporous material, ITQ-6 was carried out by delamination technique. The XRD results show that the crystalline phase of PREFER diminished for the sample after delamination. Porosity study of the ITQ-6 sample shows formation of homogeneous mesopores in the size between 3.5-4.0 nm. The acidity study indicates that ITQ-6 still contains appreciable amounts of Brönsted and Lewis acidities. Catalytic evaluation of the resulting material, ITQ-6 was carried out in the alkylation of resorcinol with methyl *tert*-butyl ether which gave 4-*tert*-butyl resorcinol and 4,6-*di-tert*-butyl resorcinol as main products. The conversion of resorcinol when using ITQ-6 was ten times higher than ferrierite, FER with similar selectivity of disubstituted product. It shows that the mesoporosity of ITQ-6 was responsible for the higher activity of the catalyst in the reaction.

Abstrak

Kebolehan ITQ-6 sejenis bahan zeolit berliang meso menggantikan zeolit berliang mikro sebagai mangkin telah menarik perhatian. Dalam kajian ini, pengubahsuaian bahan awal ferrierit berliang mikro, PREFER kepada bahan berliang meso ITQ-6 dilakukan melalui teknik penyahlaminan. Keputusan XRD menunjukkan yang fasa hablur PREFER musnah selepas proses penyahlaminan. Kajian keliangan terhadap sampel ITQ-6 menunjukkan pembentukan liang meso yang homogen dengan saiz liang antara 3.5-4.0 nm. Kajian keasidan menunjukkan yang ITQ-6 masih mengandungi keasidan Brönsted dan Lewis dengan amoun yang agak banyak. Kereaktifan bahan yang terhasil, ITQ-6 diuji dalam tindak balas pengalkilan resorsinol dengan metil *tert* butyl eter yang menghasilan 4-*tert*-butil resorsinol and 4,6-*di-tert*-butil resorsinol sebagai hasil utama. Pertukaran resorsinol apabila menggunakan ITQ-6 adalah sepuloh kali lebih tinggi daripada ferrierit, FER, dengan kepilihan yang sama bagi hasil dwitertukarganti. Ini menunjukkan yang ITQ-6 yang berliang meso bertanggungjawab ke atas kereaktifan mangkin dalam tindak balas.

Introduction

The Friedel Crafts alkylation of resorcinol with methyl *tert*-butyl ether or equivalent alkylating agents is known to give mono *tert*-butylated product (4-*tert*-butyl resorcinol) and further alkylation will lead to the formation of di-*tert*-butylated product (4,6-di-*tert*-butyl resorcinol) [1]. The products (butylated dihydroxybenzenes) are useful materials in the synthesis of antioxidants, polymer stabilizer and in the treatment of mitochondrial respiration ailments. Therefore this reaction has become industrially important.

Presently, Lewis acid type catalysts for aromatic alkylations include aluminum chloride, ferric chloride, and boron trifluoride. Those of the Bronsted-Lowry acid type are fluoride acid, sulfuric acid and phosphoric acid. However, these traditional catalysts have limitations such as environmental pollution hazards arising from the disposal of potential toxic wastes, reactor corrosion and difficulty in handling. In order to avoid these problems many efforts have been devoted in the search of solid acid and base catalysts more selective, safe, environment friendly, generable, reusable and which need not to be destroyed after reaction. Therefore acidic oxide catalysts of the silica alumina type especially zeolite and cation-exchange resins are becoming increasingly useful as heterogeneous catalysts.

Throughout the 1990s, environmentalism remains a foremost concern, with zeolite in the forefront as solutions to new challenges in the generation of "Green Chemistry". The versatility of zeolite has allowed its application particularly as heterogeneous catalyst in acid [2], base [3] and redox [4] reactions. Over a wide range of solid acids, zeolites hold high acidities on their surface and have received much attention in industry [5] and organic synthesis [6]. Uses of zeolite in the Friedel-Crafts reactions were extensively been studied [7, 8].

The productions of fine chemicals are frequently facing the problem of producing products much bulkier than reactants when using zeolite as catalyst. The products remain occluded in the zeolite blocking the pores and deactivating the catalyst. Efforts have been focused to prepare a catalyst which has the properties of zeolite with larger pores size.

Since the discovery of new method for modification of zeolite from micropore to mesopore through delamination [9], further research on it has enlarged the field of zeolites. Nowadays the research interest focus on characterization, the mechanism of the formation, and synthesis of new materials based on the zeolite synthesis concept and morphology control and technical application of modified mesopore zeolite.

The delaminated zeolite was proved to be active in the acetalization of phenylacetaldehyde with glycerol [10], epoxidation of 1-hexene [11] and hydroxyalkylation of 2-methoxynaphthalene with paraformaldehyde [12]. In addition, by using a type of delaminated zeolite known as ITQ-6 it opens an alternative route way in order to catalyze the reaction that involved bulky chemicals and products. Therefore a study on the ability of delaminated zeolite, ITQ-6 as catalyst in the Friedel Crafts alkylation was carried out in this work.

Experimental

Materials

The precursor of ferrierite type zeolite material was synthesized with the ratio of $10SiO_2:1Al_2O_3:15NH_4F:5HF:10R:100H_2O$ where R is the organic template (R=4-amino-2,2,6,6-tetramethylpiperidine) used following the method described by Schreyeck *et al.* [13]. The as-synthesised material denoted as PREFER (precursor of ferrierite).

ITQ-6 sample was prepared by swelling the laminar PREFER according to the procedure described by Concepcion *et al.* [14]. A portion of PREFER material was calcined at 550 ^{o}C to yield the formation of microporous FER type zeolite.

Catalytic reaction

The catalytic reactions were conducted batchwise in 25 mL round bottle flask equipped with a condenser and stirred well. In a typical run, 5 mmole of resorcinol, 15 mmole of methyl tert-butyl ether and 100 mg freshly activated at 200 ^{o}C catalyst were used. The reactor was introduced into the thermostated bath at 80 ^{o}C, 100 ^{o}C and 120 ^{o}C for 24 hours. The mixtures of the reaction were analyzed using gas chromatography (GC).

Apparatus and procedure

The extent of crystallization and phase purity was evaluated for all samples by recording X-ray diffractograms using Seimens 500 Kristalloflex with Cu Ka radiation, (? = 1.54056 A^{o}, 40 kV, 40 mA) in the 2? range of 2-40° at ambient temperature. Scanning was carried out in the step interval 0.05^{o} with counting time of 1 second per step.

Framework vibration, surface hydroxyl groups and acid sites were determined using Perkin Elmer Spectrum One FTIR spectrometer. The framework was characterized using KBr technique. On the other hand for surface hydroxyl group and acid sites study, self supported disc was prepared and placed in a glass cell equipped with CaF_2 windows. Sample was heated at 400 ^{o}C under vacuum condition (P ~ 1 x 10^7 mbar) overnight. Surface hydroxyl groups were recorded at room temperature. For acidity study, the sample was dehydrated at 400 °C under vacuum (P ~ 1 x 10^7 mbar). Adsorption of pyridine on dehydrated sample was carried out at room temperature followed by desorption under vacuum at 150 °C for 1 hour in order to determine the existence of the acid sites.

The specific surface area and the pore size distributions of samples were determined by BET technique using ASAP 2010 instrument.

Field Emission Scanning Electron Microscope (FESEM), Carl Zeiss Supra Series model was used to determine the morphology and crystal size of the samples.

Identifications of the reactants and desired products were carried out using GC, Model No: Agilent 6890N with Ultra 1 methyl siloxane capillary column (25 m length, 0.25 diameters with 0.2 µm wall thickness). Confirmation of the products was done by comparing the retention time of the authentic samples.

Results and Discussion

X-ray Diffraction (XRD)

ITQ-6 can be obtained through delamination process of layered zeolite ferrierite precursor. The PREFER sample was first swollen to form bulk material by intercalation of swelling agent, cetyltrimethylammonium bromide (CTABr) between the PREFER layers through ion exchange. This bulk material is assigned as preITQ-6. Then the preITQ-6 was delaminated through sonication to produce ITQ-6 followed by calcinations in order to remove the organic templates. This will lead to the formation of material called mesoporous ITQ-6. All the treatments done to the PREFER sample was monitored using XRD technique. ITQ-6 is formed by single layers organized in a "house of cards"-type structure, which is thermally stable and presents a well-defined and homogeneous external surface area. The schematic process of preparing ITQ-6 is illustrated in Figure 1.
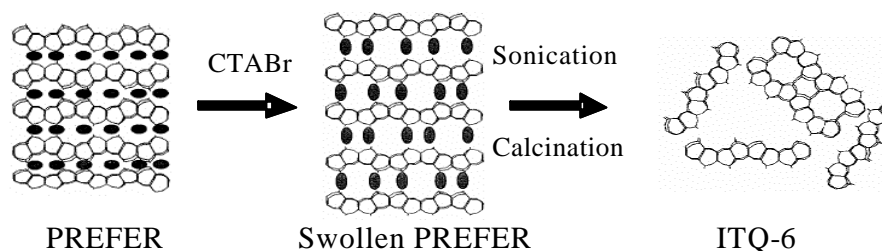

Figure 1: Scheme for preparing ITQ-6 material.

Figure 2 shows the X-ray diffractogram of PREFER samples after each treatment. As can be seen in Figure 2, the swollen material, preITQ-6 shows an increased in the d-basing of d_{200} plane in the range 1.31-3.00 nm compared to 1.30 nm for PREFER while the peaks corresponding to the individual layers decreased strongly. This indicates that the PREFER layers containing 4amino-2,2,6,6-tetramethylpiperidine templates had been expanded in the present of CTABr as swelling agent. When the delamination was completed as in sample ITQ-6-bc, the XRD peaks of the sample are much broader and less intense than that of PREFER and preITQ-6. A sharp peak was observed at 2θ 6.8^{o} indicating the presence of a small amount of PREFER that had not been swollen and delaminated.

Upon calcinations of the delaminated ITQ-6-bc sample, much broader and less intense peaks were observed in the X-ray diffractogram of ITQ-6 sample compared to the ITQ-6-bc sample. The X-ray diffractogram of ITQ-6 sample also shows a sharp peak at 2θ 9.4^{o} which is due to the existence of FER type zeolite due to the removal of templates in the delaminated ITQ-6-bc sample that contain a small amount of PREFER.
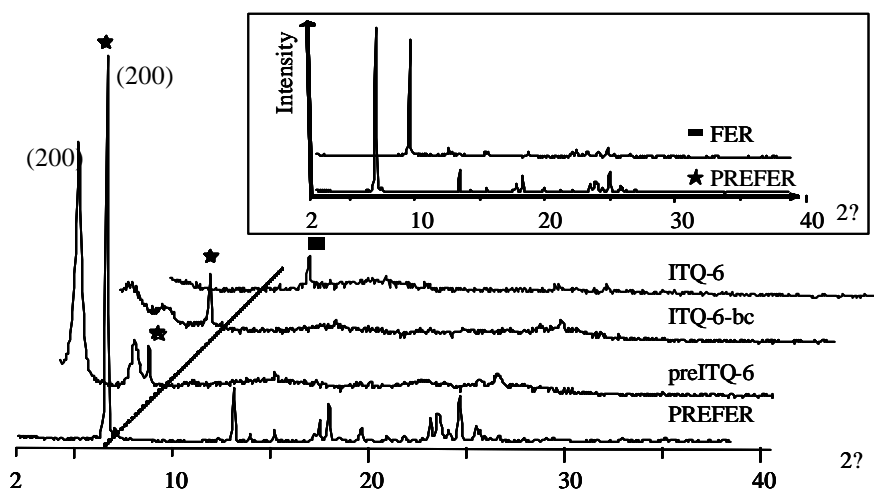

Figure 2: X-ray diffractograms of PREFER samples after every treatments (insert shows XRD pattern of FER and PREFER)

Microporous FER type zeolite can be obtained through complete removal of template by calcination of PREFER material at 550 ^{o}C. During calcinations of two-dimensional sheets of PREFER, the condensation of the silanol groups and elimination of the organic template occur; this accompanied by a decrease of the interlayer spacing to form three-dimensional FER type material.

X-ray diffractogram of PREFER material and FER type zeolite (calcined PREFER) is presented in Figure 2 (small box). The XRD patterns of both samples are practically identical and characteristic of highly crystalline products accept for the peak at d_{200}.

Table 1: Values of unit cell parameters for PREFER and FER type zeolite.

	a (Å)	b (Å)	c (Å)
PREFER	26.09	13.94	7.42
FER	18.68	13.99	7.49

As shown in Table 1 the values of the parameter *b* and *c* are unchanged, whereas the *a* parameter decreased drastically upon remo val of templates by calcinations. Finally all these observation suggest that the structural changes leading from the PREFER structure to the FER type structure involved essentially the *a* axis.

Fourier Transform Infrared (FTIR)

Framework
The IR spectra of the ITQ-6 framework and hydroxyl group are presented in Figure 3. The framework of ITQ-6 was found to be similar to the amorphous silica and in agreement with X-ray diffractogram findings. The band at 430 cm^{-1} assigned for pore structure of ferrierite framework diminished and the intensity of the characteristic peaks of ferrierite framework at 721 cm^{-1} and 580 cm^{-1} decreased upon delamination process. It can be observed from the IR spectra that the strongest band corresponding to asymmetric stretching around 1080 cm^{-1} has becomes broaden.

Hydroxyl species and the acidity property
Acidity measurement, type of acid sites and hydroxyl groups in FER and ITQ-6 were characterized by infrared spectroscopy and pyridine molecule was used as probe base.

After the dehydration of FER type material at 400 °C, three bands were observed in the hydroxyl region of FER spectrum. The bands are assigned for vibration external terminal silanol (Si-OH) groups (3746 cm^{-1}), Al(OH) groups (3664 cm^{-1}) and bridging OH (Si-OH-Al) groups at (3598 cm^{-1}). IR spectrum of delaminated ITQ-6 material evacuated at 400 ^{o}C shows the formation of large amounts of silanol groups at 3742 cm^{-1} (Figure 3a) assigned to external silanol groups in accordance with the proposed structure. The total acidity results of the samples are summarized in Table 2. Delaminated ITQ-6 appears to have both Brönsted and Lewis acid sites even after delamination process.

Table 2 : Acid sites of ITQ-6 measured by Adsorption Desorption of Pyridine at 150 ^{o}C

	Brönsted, 1545 cm^{-1} (μmoleg^{-1})	**Lewis,** 1454 cm^{-1} (μmoleg^{-1})
FER	3.12	1.09
ITQ-6	10.14	9.87

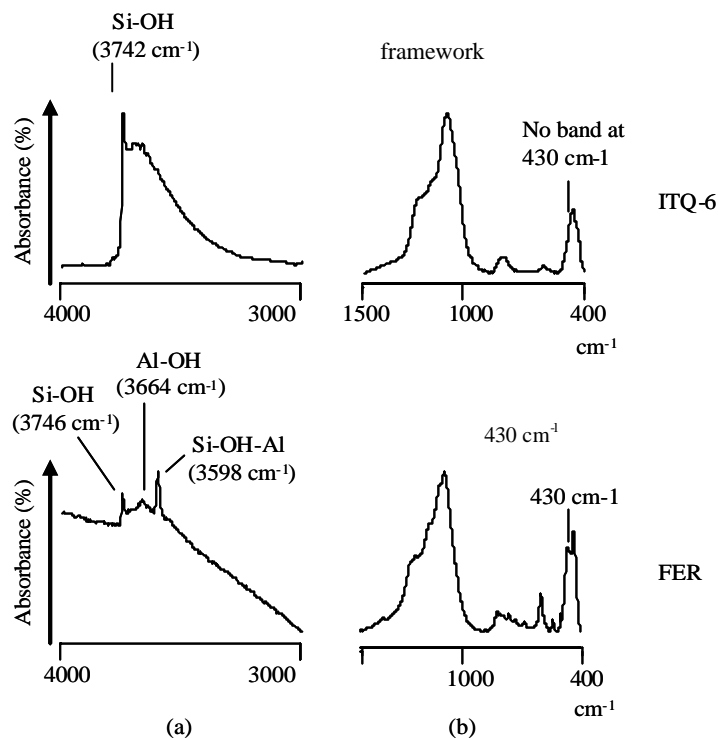Figure 3: FTIR spectra of ITQ-6 and FER samples (a) hydroxyl vibration (P = ~ 10^{-7} mBar) and (b) framework structure.

Nitrogen adsorption

Figure 4 exhibits (a) nitrogen adsorption-desorption isotherms and (b) pore size distribution plot of ITQ-6 and FER samples. The ITQ-6 exhibits the adsorption-desorption isotherm of Type IV and hysteresis loop of Type H3 which characterized it as mesoporous material. Hysteresis loop of Type H3 in the range 0.40-1.00 shows that capillary condensation occurred in the slit shape pores with non-uniform size. This proved that the layered structure in the ITQ-6 material had destroyed. FER exhibits the adsorption-desorption isotherm of Type I with hysteresis loop of Type H4. This indicates the presence of micropores in the FER-type material. Since FER is having micropore type material, interaction between the solid and gas molecule was enhanced leading to high volume of nitrogen adsorbed at low relative pressure.

From the pore size distribution plot, ITQ-6 gives a sharp peak in the mesoporous region centered at Ca = 4 nm indicates a uniform pore size distribution. Whereas the FER sample shows non-uniform pore size distributions having micropores as dominant pore with meso and macropore exist on the external surface of the crystal.

Table 3 summarises the values obtained by applying the BET equation to the values of the nitrogen adsorption isotherm for ITQ-6. The micropore surface area, external surface area and micropore volume were determined from the 't-plot' by using Harkin-Jura equation. From the table it can be proved that the pore with meso size has been formed by delamination process of PREFER to ITQ-6 leads to material with higher external surface. ITQ-6 with higher external area is more accessible for bulk molecule to the acid sites compared to the micropore FER type material.

Table 3 : Specific surface areas, S (m^2g^{-1}) and micropore volume, V (cm^3g^{-1}) determined from nitrogen adsorption isotherm.

	S_{Total} (BET)	S_{Micro} (t-plot)	$S_{External}$ (t-plot)	V_{Micro} (t-plot)
ITQ-6	153.94	59.48	94.46	0.025
FER	290.17	260.78	29.39	0.120

Field Emission Scanning Electron Microscope (FESEM)
The morphologies of the PREFER, ITQ-6 and FER samples are shown in Figure 5. The crystals of PREFER and FER (Figures 5a and 5c) had a plate-like morphology with a very homogeneous distributions. The aggregates are made of very thin stacked crystals (about 60 x 10 x 0.5 µm).
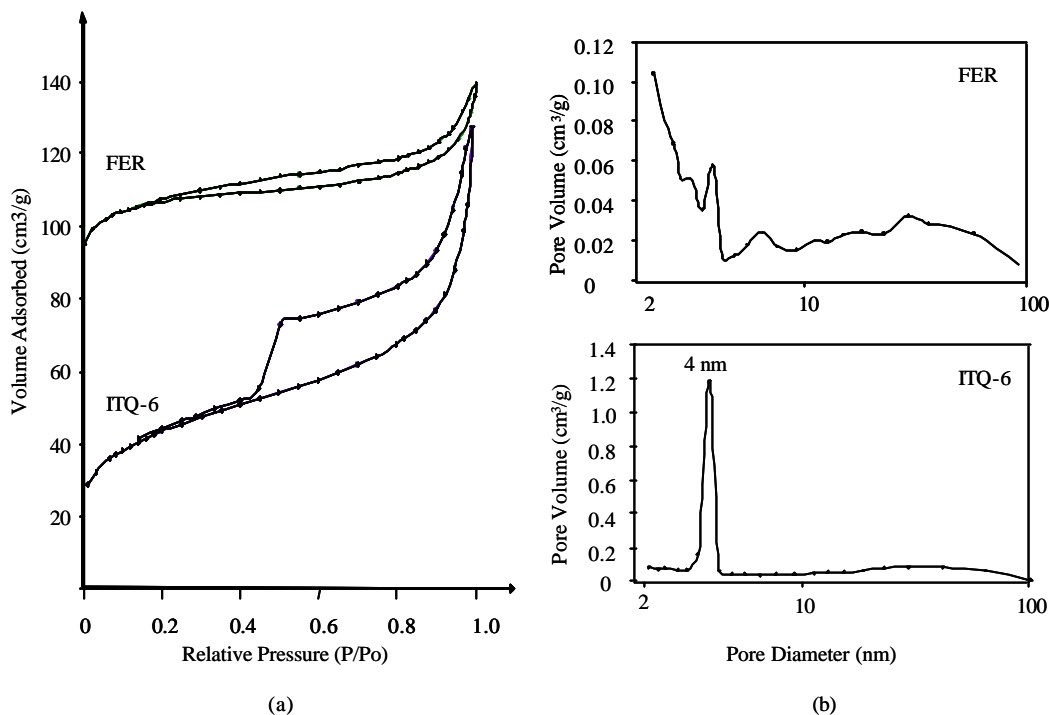

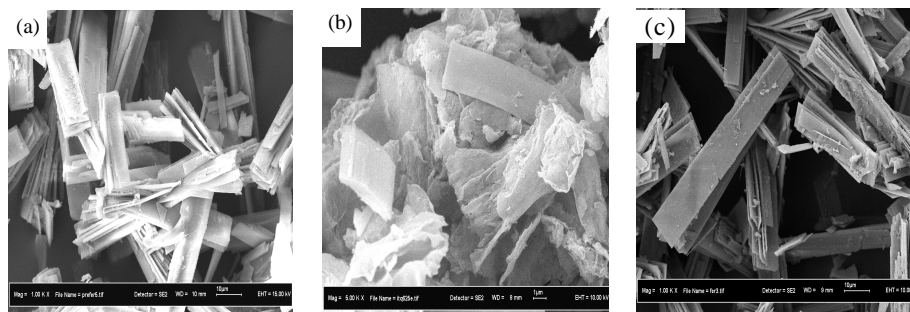Figure 4: (a) Nitrogen adsorption-desorption isotherm and (b) pore size distribution of ITQ-6 and FER

Figure 5: FESEM micrographs of (a) PREFER (magnification 1000x) (b) ITQ-6 (magnification 5000x) and (c) FER (magnification 1000x)

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The FESEM micrographs of ITQ-6 (Figure 5b) material clearly indicates that the crystal size and morphology of PREFER is strongly influenced by the delamination process. The plate-like crystal was destroyed upon the delamination process. There are no specific structure was observed in ITQ-6 micrographs. The plate-like crystals of FER is still present in the ITQ-6 material. This was proved by XRD of ITQ-6 where a sharp peak at 2θ 9.8° indicates the present of small amount of crystal material in ITQ-6 sample.

Catalytic testing

The reaction was carried out by refluxing a mixture of methyl *tert* butyl ether and resorcinol using ITQ-6 and FER as catalysts. The reaction equation is shown in Eq. 1.

resorcinol	Methyl *tert*-butyl ether		4-*tert*-butyl resorcinol	4,6-di-*tert*-butyl resorcinol	Eq. 1
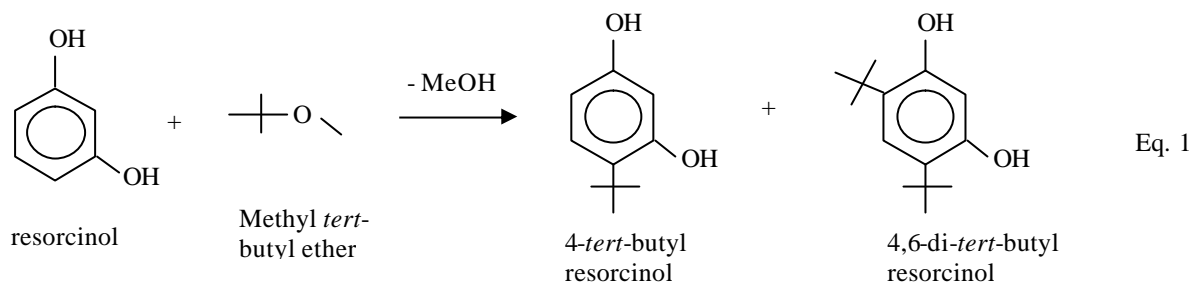
The differences in the conversion of resorcinol, selective formation of 4-tert-butyl resorcinol and 4,6-di-tert-butyl resorcinol over both catalysts in the influence of temperature is shown in the Figures 6 and 7. The conversion of resorcinol increase from 11% to 55% as the reaction temperature increases from 80 ^{o}C to 120 ^{o}C. Basically, the selectivity of the products is not influenced by the reaction temperature. When the reaction was carried out at 120 ^{o}C, the selectivity of dialkylated product (bulkier molecule) show the highest selectivity compared with other temperature with high activity. Therefore as a comparison, FER was used as catalyst in order to study the effect of the pore size. The results show the activity of FER is much lower than ITQ-6. ITQ-6 was also found to have higher yield for both products compared to FER (Figure 8). This may be due to the pore restriction whereby the accessibility of the reactants to the active acid side is limited and the property of ITQ-6 which have higher external surface area compared to FER
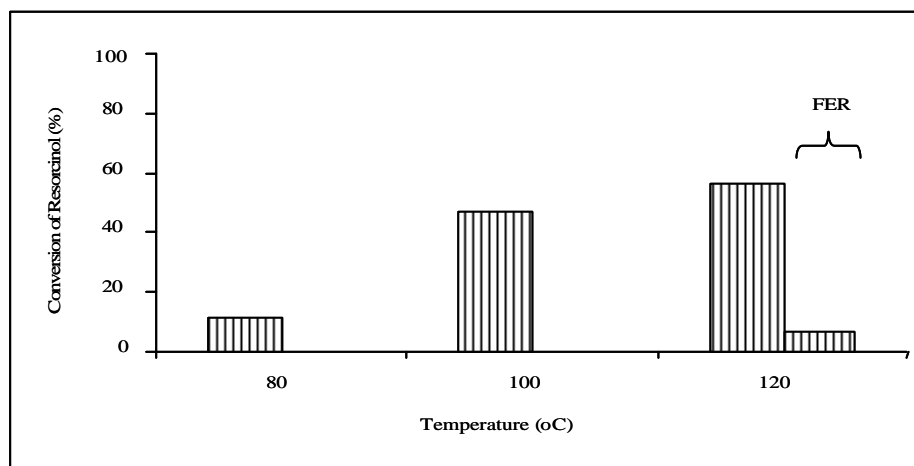

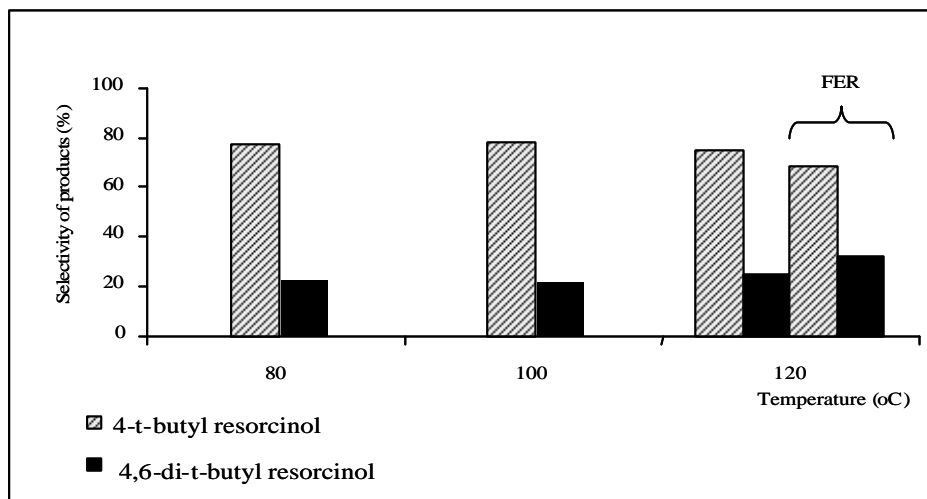Figure 6 : Effect of reaction temperature on the conversion of resorcinol over ITQ-6 and FER

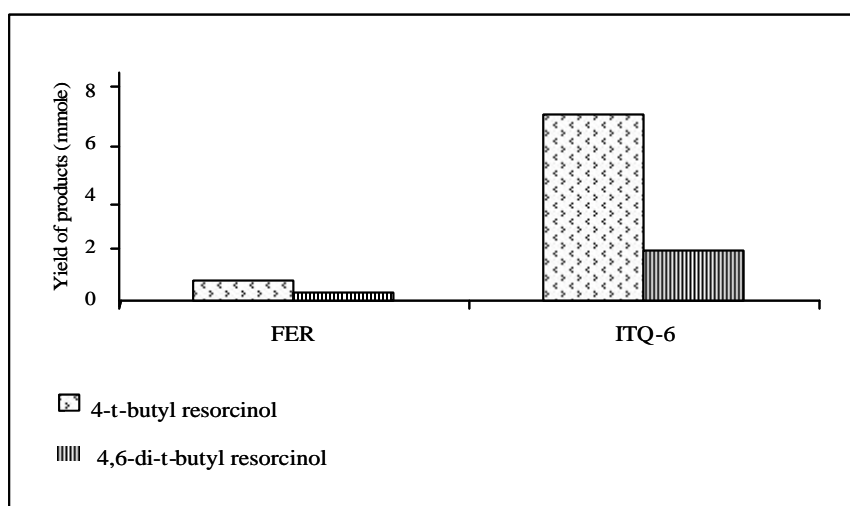Figure 7: Effect of reaction temperature on the products selectivity over ITQ-6 and FER

Figure 8: Yield of products over ITQ-6 and FER

Conclusion

Delamination of layered PREFER material leads to the formation of new mesoporous zeolitic material known as ITQ-6. Modification of PREFER to the delaminated ITQ-6 can be done by intercalation of bulk molecule in this case CTABr between the layers followed by sonication of swollen material and calcinations to remove the organic templates. Besides its amorphous phase, ITQ6 is having mesopores size channel. The ITQ6 material also appears to have appreciable amount Brönsted and Lewis acid sites. The acidity of zeolite and mesopore size shown by ITQ-6 was proved to be active as heterogeneous acid catalyst for Friedel crafts alkylation.

Acknowledgements

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