# Desilication of NaZSM-5 and Utilization as Support of Fe for Phenol Hydroxylation

M. Pimsuta, A. Neramittagapong, S. Prayoonpokarach, and J. Wittayakun

***Abstract*—NaZSM-5 zeolite was synthesized by a hydrothermal method using rice husk silica and modified by desilication with NaOH solution to generate mesopores. The removal of silicon atoms was confirmed by the Si/Al ratio, analyzed by ICP-MS showing that the Si/Al ratio of the desilicated NaZSM-5 was lower than that of the parent. Both the parent and desilicated NaZSM-5 were used as support materials for Fe for phenol hydroxylation. All the supports and catalysts were characterized by XRD, TEM, and $N_2$ adsorption-desorption to confirm the zeolite structure, observe morphology and determine surface area and pore size distribution. Desilication did not change the zeolite structure but generated non-uniform mesopores with a broad range of mesopore size and increased surface area. The form of Fe, analyzed by XANES was in the oxidation state 3+. Catalytic performance of 5Fe/NaZSM-5 and 5Fe/NaZSM-5(D) for phenol hydroxylation in a batch reactor using $H_2O_2$ as an oxidant, gave phenol conversion of ca. 67% at 70°C [phenol:$H_2O_2$= 1:3]. The 5Fe/NaZSM-5(D) showed a faster phenol conversion to reach equilibrium. Products from both catalysts were catechol and hydroquinone with mole ratio about 2:1.**

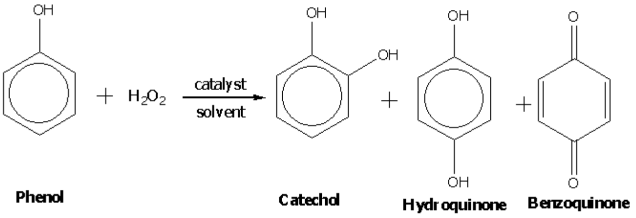
***Index Terms*—Phenol hydroxylation, Rice husk silica, ZSM-5, iron.**

## I. INTRODUCTION

Phenol hydroxylation is a reaction between phenol and hydrogen peroxide in a solvent with the presence of a catalyst (Scheme 1). The main products from this reaction are dihydroxybenzene isomers: catechol (CAT) and hydro-quinone (HQ). In addition, para-benzoquinone (PBQ) is also produced from over-oxidation. CAT and HQ are useful in several applications such as photographic chemicals, antioxidants, flavoring agents, polymerization inhibitors and starting reagents for pharmaceuticals [1].

Phenol hydroxylation is ecologically friendly and can be achieved by the presence of a catalyst [2]. When zeolites are used as catalysts, their strong acid sites would induce formation of coke which would block the zeolite pores and catalytic active sites, resulting in catalyst deactivation [3].

Fe is widely used as a heterogeneous catalyst in phenol hydroxylation, providing a high phenol conversion and product selectivity. The phenol conversion and product selectivity depended on the type of supports. The reaction of Fe (10 wt. %) supported on mordenite zeolite (MOR) gave a conversion of 20.0 % with only CAT as a product [4]. The conversion was increased to 60.0 % on Fe (5 wt. %) supported on modified MOR containing mesopores, but both CAT and HQ were produced [5].



Scheme 1. .Phenol hydroxylation reaction to produce catechol (CAT), hydroquinone (HQ), and benzoquinone (PBQ).

Product selectivity could be improved by changing to different types of zeolites, because their specific pore shape and size only allows molecules with similar a shape and size to pass though. This work focused on the use of *ZSM-5*.

The *ZSM-5* is widely used as a heterogeneous catalyst in various reactions such as catalytic cracking, alkylation, isomerization and phenol hydroxylation [6] because it has both Lewis and Brønsted acid sites. Furthermore, The *ZSM-5* zeolite is interesting as a support material for metal catalysts because it contains medium pore size of ~0.55 nm and a pore network composed of straight and zigzag channels [7]. There was a report that phenol hydroxylation over Fe/ZSM-5 gave a conversion of 23.0 % and selectivity for CAT and HQ at 73.6 % and 26.4 %, respectively [8]. The low conversion could be a result of the *Si/Fe* and *Si/Al* atomic ratio.

Diffusion of reactants to the metal active sites in zeolites could be improved by generating mesopores by desilication. The resulting materials are often called “hierarchical zeolites” which combine microporosity and mesoporosity. When mesopores were created in *ZSM-5* by desilication, the surface area of the zeolite was increased; large pores were created and the mass transport was improved [9] - [10].

In this work, the *NaZSM-5* was synthesized by using rice husk silica (*RHS*) and modified by desilication using *NaOH*. The parent and modified *NaZSM-5* zeolites were used as supports for the Fe catalyst. The catalysts were characterized by several techniques and tested for phenol hydroxylation which produced catechol and hydroquinone.

## II. EXPERIMENTAL

### A. Synthesis and Modification of NaZSM-5 Zeolite

Rice husk silica (RHS) was prepared by refluxing with 3 M HCl solution for 6 h and calcination at 550 ℃, as reported in

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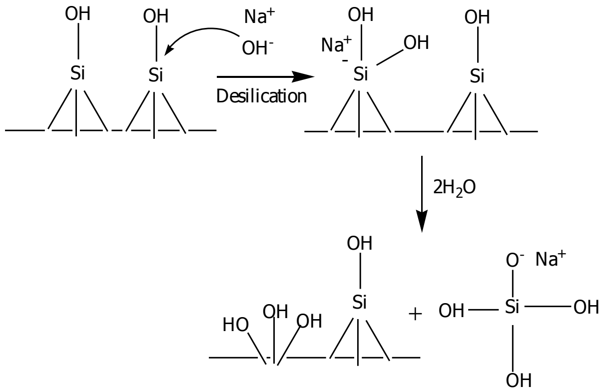
reference [11]. It was used as a silica source for the synthesis of *ZSM-5* in sodium form (*NaZSM-5*).

The *NaZSM-5* was synthesized by hydrothermal method with a method modified from literature [12]. The RHS was dissolved in 0.27 M of *NaOH* ( 97 %, Carlo ERBA) solution, mixed with $NaAlO_2$ ($Al_2O_3$ ~ 50-56 % of $NaAlO_2$, Riedel-de Haën$^{®}$) solution and 0.18 M TPABr (98 wt. %, *ACROS*) solution in a polypropylene bottle and continuously stirred for 24 h to ensure a complete dissolution. Then *pH* of the solution was adjusted to 11 by adding 1 M $HNO_3$, the solution was transferred into a Teflon-lined autoclave and crystallized under hydrothermal condition at 150 ℃ for 48 h in a muffle furnace. The product, *NaZSM-5* was centrifuged, washed with DI water, dried at 80 ℃ for 12 h and calcined at 550 ℃ for 5 h to remove the organic template.

Desilication of *NaZSM-5* was done by mixing with 0.2 M NaOH solution under a reflux setup at 65 ℃ for 30 min. The zeolite suspension was then cooled down in an ice-water bath, filtered, washed until the *pH* of the filtrate was neutral and dried at 100 ℃ overnight [10]. The final product is named *NaZSM-5(D)*, (D; desilication). A possible mechanism of desilication from the zeolite framework was proposed in the equation below (see Scheme 2.).



Scheme. 2. .Possible desilication from zeolite framewoke by alkaline treatment (0.2 M NaOH solution).

The molar ratios of *Si/Al* of the parent *NaZSM-5* and modified *ZSM-5* were determined by inductively coupled plasma-mass spectrometry *(ICP-MS)* on an Agilent 7500CE series instrument.

## *B. Preparation of Supported Fe Catalysts*

The supported Fe catalysts were prepared by incipient wetness impregnation. Both *NaZSM-5* and *NaZSM-5(D)* were dried at 100 ℃ overnight and cooled-down in a desiccator before being impregnated with a solution of $Fe(NO_3)_3{\bullet}9H_2O$ *(98.5 wt. %, QRëC).* The amount of loaded Fe was 5 wt. %. The samples were dried overnight at 105 ℃ and calcined at 500 ℃ for 3 h.

Both *NaZSM-5* and *NaZSM-5(D)* and Fe catalysts were characterized by *XRD* (Bruker axs diffractometer D5005) using Cu $K_{\alpha}$ radiation to confirm the zeolite structure. Intracrystalline mesopores and particle size were determined by transmission electron microscopy (TEM) (JEOL JEM 6400). Their surface area, pore volumes and pore sizes distribution were determined from $N_2$ adsorption-desorption data obtained from a Micromeritics Analyzer ASAP 2010 using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. The catalysts were characterized by X-ray absorption near edge structure (XANES) at Beamline 8 of the Synchrotron Light Research Institute, Thailand (Fe K-edge at 7112 eV) to determine the oxidation state of Fe compared with Fe standards (*Fe foil, FeO,* $Fe_3O_4$*, and* $Fe_2O_3$).

## *C. Catalytic Testing for Phenol Hydroxylation*

Both *5Fe/NaZSM-5* and *5Fe/ZSM-5(D)* were tested for phenol hydroxylation [13]. A 100 ml two-neck round bottom flask containing the reaction mixture was connected to a reflux condenser and a thermometer. The reaction mixture consisted of catalyst powder (0.05 g), phenol (99.5 wt. %, BDH) and $H_2O_2$ solution (30 w/v. %, UNIVAR). The mole ratio of phenol to $H_2O_2$ was 1:3. The mixture solution was magnetically stirred and heated at 70 ℃ for 5 h and sampling was done every hour. The solution was separated from the catalyst, toluene was added as an internal standard and the solution was analyzed by a gas chromatograph (SHIMADZU 14A series) equipped with an ID-BP1 coated capillary column and a flame ionization detector (FID). The quantities of the remaining phenol and products were determined from a calibration curve of each compound.

Phenol conversion was calculated using equation 1, white selectivity to *CAT*, *HQ* and *PBQ* were calculated from equations 2, 3 and 4, respectively.

$$\%\ \text{Phenol conversion} = \left(\frac{\text{Mole phenol}_{inlet} - \text{Mole phenol}_{outlet}}{\text{Mole phenol}_{inlet}}\right)\times 100 \qquad (1)$$

$$\%\ \text{Selectivit y for CAT} = \left(\frac{\text{Mole CAT}}{\text{Mole CAT} + \text{Mole HQ} + \text{Mole PBQ}}\right)\times 100 \qquad (2)$$

$$\%\ \text{Selectivit y for HQ} = \left(\frac{\text{Mole HQ}}{\text{Mole CAT} + \text{Mole HQ} + \text{Mole PBQ}}\right)\times 100 \qquad (3)$$

$$\%\ \text{Selectivit y for PBQ} = \left(\frac{\text{Mole PBQ}}{\text{Mole CAT} + \text{Mole HQ} + \text{Mole PBQ}}\right)\times 100 \qquad (4)$$

# III. RESULTS AND DISCUSSION

## *A. Determination of the Si/Al of NaZSM-5 and NaZSM-5(D)*

The *Si/Al* ratio of the parent *NaZSM-5* obtained from *ICP-MS* was 15. After desilication, the Si/Al ratio changed to 13 confirming that some of the Si atoms were removed. The degree of desilication depended on Si/Al ratio. When *Si/Al* ratio was ≤ 15, formation of mesopores were limited because of Al prevented the Si extraction [10].

## *B. XRD and XANES*

The *XRD* patterns of *NaZSM-5, NaZSM-5(D), 5Fe/ NaZSM-5*, and *5Fe/NaZSM-5(D)* are shown in Fig. 1. All the samples showed typical reflections of the *MFI* structure as the only crystalline phase [14]. The *XRD* patterns did not changed after desilication and loading with Fe. However, the peak intensities were lower in supported Fe catalysts because of the Fe species on the surface can decrease the scattering of *X-rays.* The Fe species were well dispersed on the support because expected peaks corresponding to common Fe compounds such as iron oxide at 33.2 °and 33.5 °, the strongest lines of hematite ($\alpha$-$Fe_2O_3$, *JCPDS PDF* 33-0664) were not observed. Reference [15] reported that when the loading of Fe on *ZSM-5* was less than 5% the peaks of iron oxide were not observed.

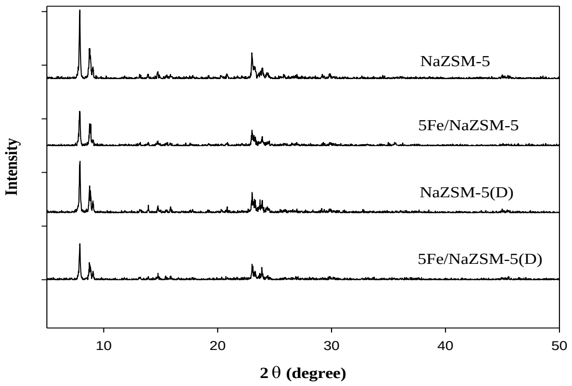


Fig. 1. XRD patterns of NaZSM-5, NaZSM-5(D), 5Fe/NaZSM-5, and 5Fe/NaZSM-5(D).

The *XANES* spectra of Fe standards and Fe catalysts are shown in Fig. 2. The *XANES* spectra of all Fe catalysts were similar indicating the same Fe form on all supports. In addition, the spectrum of the Fe catalyst matched that of the $Fe_2O_3$ standard suggesting that the oxidation number of the Fe supported on all *ZSM-5* zeolites was mainly +3.

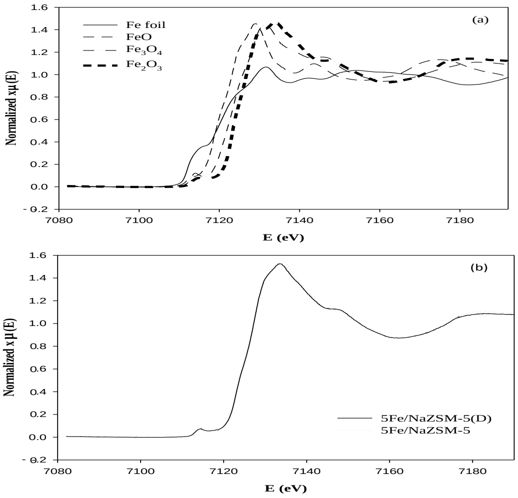


Fig. 2. XANES spectra of (a) Fe standards: Fe metal, *FeO*, $Fe_3O_4$ and $Fe_2O_3$, and (b) Fe catalysts: 5Fe/NaZSM-5, 5Fe/NaZSM-5(D) showing form of Fe as $Fe_2O_3$.

### C. TEM

TEM images of *NaZSM-5, NaZSM-5(D), 5Fe/NaZSM-5*, and *5Fe/NaZSM-5(D)* are shown in Fig. 3 a-d, respectively. The image of *NaZSM-5* (Fig. 3 a) showed a smooth surface indicating that the crystal sizes were very small. After loading with Fe the image of *5Fe/NaZSM-5* (Fig. 3 b) showed some dark spots which could be clusters of Fe oxides outside the zeolite pores. The TEM image of *NaZSM-5(D)* in Fig. 3 c showed light spots of various sizes, which were mesopores generated by partial dissolution of silicon atoms from the zeolite. Similar non-uniform mesopores were also observed in the image of *5Fe/NaZSM-5(D)* in Fig. 3 d along with clusters of oxides. Reference [14] reported the results of generating mesopores to produce properties of hierarchical zeolite in the framework *ZSM-5* by treatment with $NaAlO_2$ followed by leaching with *HCl*. The intracrystalline was observed in TEM images.

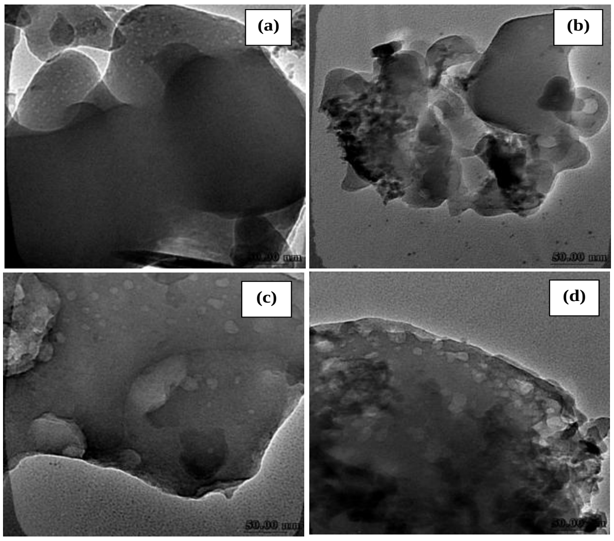


Fig. 3. TEM micrograph of (a) NaZSM-5, (b) NaZSM-5 (D), and (c) 5Fe/NaZSM-5(D).

### D. $N_2$ adsorption-desorption

The $N_2$ adsorption-desorption of *NaZSM-5*, *NaZSM-5(D)*, *5Fe/NaZSM-5*, and 5Fe/NaZSM-5(D) are shown in Fig. 4a. The BET surface area, micropore volume and external surface area of these samples calculated from the $N_2$ adsorption-desorption data are summarized in Table I.

The adsorption isotherms of *NaZSM-5* and *Fe/NaZSM-5* Fig. 4 were type I which is a characteristic of microporous materials. However, there were some areas that deviated from type I. The first one was in the region of $P/P_0$ less than 0.2, where the adsorbed volume increased instead of becoming a plateau. This data indicated multilayer adsorption which could be from defects in the zeolite structure. The second one was in the range 0.4 – 0.7 in which a narrow hysteresis was observed suggesting that the *NaZSM-5* synthesized in one step contained some mesopores. A similar isotherm from similar synthesis was reported in reference [12]. Hysteresis loop was also observed in untreated MFI zeolite, ammonium form reported by reference [10]. After the *NaZSM-5* was loaded with *Fe*, the shape of the isotherm did not change much from that of the *NaZSM-5* except that the volume adsorbed on *Fe/NaZSM-5* decreased in all regions. The result indicated that Fe was dispersed on every part of the zeolite including the

| Samples | Surface area ($m^2.g^{-1}$) | Micropore volume ($cm^3.g^{-1}$) | External surface area ($m^2.g^{-1}$) |
|---|---|---|---|
| NaZSM-5 | 362 | 0.11 | 133 |
| 5Fe/NaZSM-5 | 351 | 0.10 | 137 |
| NaZSM-5 (D) | 380 | 0.11 | 158 |
| 5Fe/NaZSM-5(D) | 348 | 0.10 | 145 |

external surface area, micropores and mesopores.

The isotherm of *NaZSM-5(D*) was type IV (also in Fig. 4). The adsorbed volume at low pressure was similar to the parent *NaZSM-5* with a higher degree of multilayer. A wide hysteresis loop was observed in the $P/P_0$ region of 0.45 – 0.95 caused by filling and emptying the mesopores. The loop can be classified to the H3-type which is a characteristic of slit-shaped pores. After the *NaZSM-5(D)* was loaded with Fe, the adsorbed volume in the all-region decreased. The adsorption line of the *Fe/NaZSM-5* was nearly parallel to that of the bare *NaZSM-5(D)* and the hysteresis loop was slightly narrower. The results suggested that Fe was well dispersed on all areas of *NaZSM-5(D).*

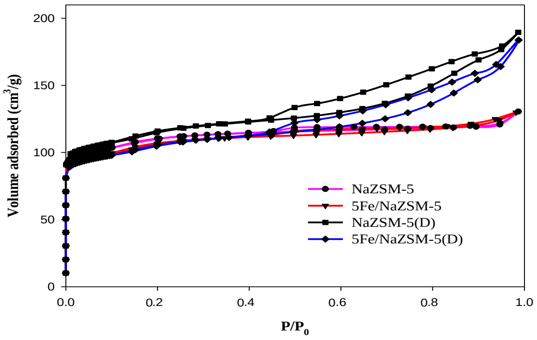


Fig. 4. $N_2$ *a*dsorption-desorption isotherms of parent *NaZSM-5* and modified of catalysts.

The pore size distributions of *NaZSM-5*, *NaZSM-5(D)*, *5Fe/NaZSM-5* and *5Fe/NaZSM-5(D)* calculated by the BJH method are shown in Fig. 5. The pore size distribution of *NaZSM-5* confirms the presence of microporosity centered around 2 nm. When loaded with Fe, the *5Fe/NaZSM-5* showed a slightly narrower pore size distribution. The pore size distribution of *NaZSM-5(D)* and *Fe/NaZSM-5(D)* showed similar micropore size with their parent zeolites. In addition, broad range of mesopores were observed in these samples as a result of desilication with *NaOH* solution, showing the development of a broad pore size distribution centered around 8 nm Fig. 5. This result was similar to the results reported by reference [10] and [6] that the formation of uniform pores of 10 nm was obtained on *ZSM-5* after desilication with 0.2 M of *NaOH.* Reference [9] reported that *HZSM-5* desilicated with 0.2 M of *NaOH* generated ink-bottle type mesopores which increased with the treatment time. Moreover, reference [10] stated that the counter-cation in the starting zeolite ($H^+$, $Na^+$, $NH_4^+$) had a minor influence on the mesoporous surface area by silicon extraction with NaOH solution.

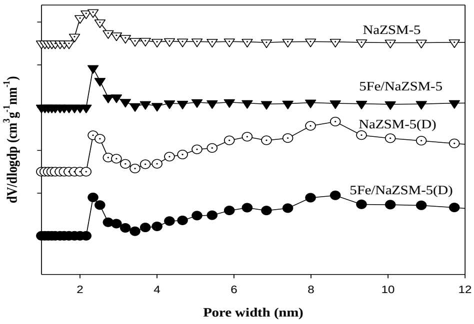


Fig. 5. BJH pore size distribution of samples NaZSM-5, 5Fe/NaZSM-5, NaZSM-5(D), and 5Fe/NaZSM-5(D) at 65˚C 0.2 M NaOH for 30 min.

. TABLE I: RESULTS FROM $N_2$ ADSORPTION-DESORPTION ANALYSIS

| Samples | Surface area (m$^2$.g$^{-1}$) | Micropore volume (cm$^3$.g$^{-1}$) | External surface area (m$^2$.g$^{-1}$) |
|---|---|---|---|
| NaZSM-5 | 362 | 0.11 | 133 |
| 5Fe/NaZSM-5 | 351 | 0.10 | 137 |
| NaZSM-5 (D) | 380 | 0.11 | 158 |
| 5Fe/NaZSM-5(D) | 348 | 0.10 | 145 |

### *D. Phenol Hydroxylation*

Both 5Fe/NaZSM-5 and 5Fe/NaZSM-5(D) catalysts were tested for phenol hydroxylation. The phenol conversions at various hours are shown in Fig. 6 and product selectivities are summarized in Table II.

The conversion on 5Fe/NaZSM-5(D) increased and reached equilibrium faster than that on 5Fe/NaZSM-5. The presence of mesopores in NaZSM-5(D) generated by desilication could facilitate the diffusion of the starting reagents to active sites of the Fe catalysts. Besides, NaZSM-5(D) had a lower Si/Al ratio suggesting that the Lewis acid sites, which are Al atoms, were more accessible for adsorption of reactants prior to the reactions. Thus, the reaction depended on the structure and properties of supports. The Fe catalyst on ZSM-5 without mesopores and with low Si/Al atomic ratio [8] showed faster reaction rate than that supported on silica [16]. At the fifth hour, the conversion of 5Fe/NaZSM-5 was 68%. In other previous work, the catalyst supported on mesoporous modified by leaching with acid and base 5Fe/ABMOR [5], showed a faster reaction than that supported on Fe/MOR [4]. For zeolites with uniform of mesopores, Fe/MCM-41 [17] gave a higher phenol conversion than 5Fe0.5Pt/RH-MCM-41 [13]. The rates of the reaction depend on the factor of phenol hydroxylation of phenol: $H_2O_2$ mole ratio, metal loading, temperature, time, and types of support.

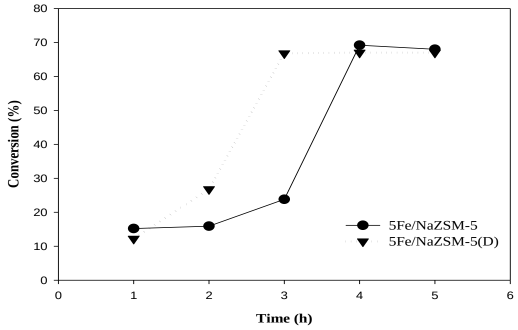


Fig. 6. Phenol conversions of 5Fe/NaZSM-5 and 5Fe/NaZSM-5 (D).

Table II shows the product selectivity in phenol hydroxylation on 5Fe/NaZSM-5 and 5Fe/NaZSM-5(D) catalysts. The PBQ was first observed in both catalysts and disappeared in the next hours. Thus, PBQ was a kinetic product generated from the excess concentration of $H_2O_2$. After reaching equilibrium, the ratio of CAT: HQ was about 2:1 in both catalysts. This was not surprising because there are two *ortho-* positions (producing CAT) and one *para-*

position (producing HQ) on phenol. These selectivities could be the result of the locations of Fe oxide which are on the external surface. In general, the selectivity of the product depended on the reaction conditions and the type of supports. Reference [8] and [17] showed that the product ratio was close to 2:1. Catechol to hydroquinone ratio in the product was close to 1:1 as proposed in references [13] and [5].

TABLE II: PRODUCT SELECTIVITY OF 5Fe/NaZSM-5 AND 5Fe/NaZSM-5 (D)

| Catalysts | Time | % Selectivity | | |
|---|---|---|---|---|
| | (h) | CAT | HQ | PBQ |
| 5Fe/NaZSM-5 | 1 | 0.0 | 0.0 | 0.0 |
| | 2 | 0.0 | 0.0 | 0.0 |
| | 3 | 0.0 | 0.0 | 100.0 |
| | 4 | 67.5 | 32.5 | 0.0 |
| | 5 | 67.9 | 32.1 | 0.0 |
| 5Fe/NaZSM-5(D) | 1 | 0.0 | 0.0 | 0.0 |
| | 2 | 0.0 | 0.0 | 100.0 |
| | 3 | 66.6 | 33.4 | 0.0 |
| | 4 | 67.2 | 32.8 | 0.0 |
| | 5 | 66.9 | 33.1 | 0.0 |

## IV. CONCLUSION

The parent zeolite *NaZSM-5* was synthesized by using *RHS* as a silica source and modified by desilication to remove silicon from the framework. After desilication, mesopores were generated in the framework of *ZSM-5*, *Si/*Al molar ratio was decreased and surface areas were increased. Fe was loaded on sample *NaZSM-5(D)*. All the supported catalysts were tested in phenol hydroxylation. The catalyst *5Fe/NaZSM-5(D)* showed the faster reaction and higher phenol conversion indicating that mesoporous *ZSM-5* could improve the diffusion of the reactants. However, the selectivity was not much improved and the main products obtained are catechol and hydroquinone.

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