# Structure and catalytic stability of zeolites in sub- and supercritical water

## -Abstract-

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## Introduction

Sub- and supercritical water exhibits properties that are quite different from water at room temperature such as high diffusion rates due to low viscosity in supercritical water had an excellent medium for homogeneous reaction, without limiting of mass transfer. Even though sub- and supercritical water has high dissociation of water and act as acid/base catalytic properties, catalysts are frequently used to promote and control the reaction. However, finding stable catalysts which can operate in severe condition is one of major challenges for the development of economical processes[1]. Currently, $TiO_2$ and $ZrO_2$ are the most general catalyst support that usually use in sub- and supercritical water due to low solubility in water and hydrothermal stablility[2]. However, this type of catalysts has problems that limiting property such as absent shape selectivity, lower surface area, and little acidity site comparing with current conventional catalyst such as zeolites.

Zeolites are crystalline aluminosilicate based compounds with open 3D framework structures composed of $SiO_4$ and $AlO_4$ tetrahedra. They have been widely used as catalyst in many industrial processes because of their selective nature due to their specific pore size, large surface area and high acid density[3]. Zeolites have shown great conversion and selectivity in vapor phase reaction with high stability during severe condition (400-550°C)[4]. However, the thermal stability of zeolites in liquid water is interestingly different from vapor phase. While zeolites can sustain long treatments under steam at a temperature around 500 °C, they may collapse and lose their crystallinity after only a couple hours in hot liquid water (100-200°C). In recent study of zeolites in hot liquid water by Ravenelle et al.[5], they found that one zeolite framework, H-ZSM-5, provided highly stability unlike other zeolite frameworks. H-ZSM-5 showed no appreciable change of XRD intensity under steam 6 hours at autogenic pressure, temperature 200 °C.

In sub- and supercritical water, most researchers believed that zeolites would completely lose their crystallinity by dissolving of Si and Al due to the extremely high temperature and pressure. Moreover, liquid water at elevated temperature (>200°C) is much more corrosive due to the high-water dissociation. However, operating in this temperature range also provide the advantage in gasification of biomass (supercritical water) and hydration reaction (sub-critical water) because it can eliminate the surface boundary between organic and water phase. Mo and Savage[6], applied using H-ZSM-5 in supercritical water for hydrothermal catalytic cracking of fatty acids. The result indicated that the XRD result between fresh and regenerated ones were indistinguishable. However, further investigation such as remaining crystallinity change and solubility of silica was unpublished in the report.

The main objective of our research is to investigate the stability of zeolites in sub- and supercritical water in terms of structure stability and catalytic stability which is defined as an infinitesimal change of conversion and selectivity to find the opportunity to be applied to practical reaction process.

## Experiment section

**Materials.** Beta-zeolites with $SiO_2/Al_2O_3$ = 40, and ZSM-5 zeolites with three different $SiO_2/Al_2O_3$ = 24, 40, 1500 (H-ZSM-5(x); x= 24,40,1500) were obtained from Tosoh to investigate the structure stability, In the case of overall stability**,** ZSM-5 zeolites were provided in pellet forms mixed with 20% alumina binder($Al_2O_3$). Afterward, all pellet samples were ground and sieved to 0.50-0.70 mm.

**Reaction experiment.** 1) The structure stability experiment was conducted in 10 mL stainless steel batch reactors. 0.2 mg of zeolites and the desired amount of water or Si/Al solution were loaded. The sealed reactors were placed into a fluidized sand bath for 6 hours (except 1 hour for Beta-zeolites at 400 °C), and then submerged into a water bath to stop reaction. 2) Catalytic stability experiment was

conducted using a dehydration of cyclohexanol in supercritical condition as model reaction in the fixed bed systems with various size of micro-reactor filing with 0.2, 1 and 3 grams of zeolites. The experimental conditions were at temperature of 400 °C, pressure 25 MPa, and feed ratio of water to 3% by weight of cyclohexanol in water solution (Vol/Vol): 10/1. The reactants were collected every 0.5 hours and the effluent of the reactor including both the organic phase and water phase was extracted with methyl acetate to collect all the organics into single liquid phase.

 **Product Analysis.** XRD pattern were scanned from $2\theta = 4°$ to $50°$. The relative crystallinity was determined based on comparing the area of five strong peaks in the 22.5 to $25°$ (ASTM method). The morphology of zeolites was observed by SEM and TEM. EDX was also performed to evaluate the $SiO_2/Al_2O_3$ ratio of zeolites. The amount of Si and Al content in water residual was investigated by ICP-AES. The liquid phase extraction in cyclohexanol dehydration was analyzed by GC-FID. The qualitative analysis of unknown compound mixtures was performed on GC-MS. The acidity of zeolites in both before and after reaction were investigated by $NH_3$-TPD.

## Results and discussion

1. The structure stability

Crystallinity, $SiO_2/Al_2O_3$, morphology, and the presence of amorphous phase determined by XRD are summarized in Table 1. The effect of structure and temperature are discussed as following.

1.1. Effect of zeolites structures

In supercritical water, Beta-zeolites structure (No.2) completely destructed and changed to amorphous structure due to high pressure and temperature of supercritical water. However, this phenomenon did not present in the case of H-ZSM-5 (No.7, 13 and 18). According to thermodynamic analysis, the structure strength of H-ZSM-5 is higher than Beta-zeolites due to lower energy of formation, and lower steric effect, which H-ZSM-5 has $SiO_4$ angle close to perfect tetrahedral angle $(109.47°)$.

In sub-critical water, the remaining crystallinity of Beta-zeolites (No.1) was lower than H-ZSM-5 (No.3, 9 and 15). Silanol defect is believed to be the main reason of crystallinity deceasing, and normally Beta-zeolite has higher Silanol defect due to limitation of synthesis process (the defect density of Beta-zeolites, and H-ZSM-5 are 0.22 and 0.04 mmol/g, respectively).

Table 1 summarize various evaluating parameters of stability of zeolites

| No. | Samples | Temperature (°C) | Crystallinity (%) | SiO₂/Al₂O₃ (EDX) | Amorphous phase (Y/N) | Morphology change (Y/N) |
|---|---|---|---|---|---|---|
| 1 | Beta-zeolite | 200 | 82.5 | 39.3 | N | N |
| 2 | | 400 | 0.0 | 42.0 | Y | N |
| 3 | | 200 | 100.3 | 24.3 | N | N |
| 4 | H-ZSM-5 | 250 | 102.5 | 25 | N | N |
| 5 | with | 300 | 101.1 | 25.5 | N | N |
| 6 | SiO₂/Al₂O₃ | 350 | 93.4 | 24.8 | N | N |
| 7 | =24 | 400 | 60.3 | 20.7 | Y | Y |
| 8 | | 450 | 34.5 | 20.1 | Y | Y |
| 9 | | 200 | 97.4 | 40.2 | N | N |
| 10 | H-ZSM-5 | 250 | 97.2 | 40.2 | N | N |
| 11 | with | 300 | 95.0 | 39.2 | N | N |
| 12 | SiO₂/Al₂O₃ | 350 | 99.5 | 46.2 | N | N |
| 13 | =40 | 400 | 85.6 | 24.8 | N | Y |
| 14 | | 450 | 81.0 | 35.7 | N | Y |
| 15 | H-ZSM-5 | 250 | 105.0 | - | N | N |
| 16 | with | 300 | 105.2 | - | N | N |
| 17 | SiO₂/Al₂O₃ | 350 | 103.3 | - | N | N |
| 18 | =1500 | 400 | 100.4 | - | N | N |

1.2. Effect of $SiO_2/Al_2O_3$ ratio and temperature on H-ZSM-5

The remaining crystallinities of H-ZSM-5 are strongly affected by $SiO_2/Al_2O_3$ ratio since the water attack degradation is believed to start on alumina in framework by dealumination. In details, H-ZSM-5(23) (No.6-8) have lower crystallinity than H-ZSM-5(40) (No.12-14) at the same temperatures due to lower content of alumina in the structure. Moreover, H-ZSM-5(1500) (No.17-18) with alumina slightly in framework does not change the crystallinity. The crystallinity over 100% in H-ZSM-5(1500) (No.13-16) was explained by peak split in XRD result at $2\theta = 23$ to $25°$ from doublet to triplet cause integration area increasing. It also indicated that minor structure change from orthorhombic to monoclinic structure.

EDX analysis in all samples are found to be lower comparing with fresh zeolites, and ICP-AES analysis found high silica in water residual (Si content at temperature 250 °C are 115, 90.2 and 84.4 ppm for H-ZSM-5 $SiO_2/Al_2O_3$ = 24, 40, 1500, respectively). This result supported the hypothesis that desilication which is a chain reaction to destroy zeolites structure occurred, but this reaction does not affect the remaining crystallinity due to the dissolution of Si reaches equilibrium.

Since desilication and dealumination are directly related with the dissociation of water. The remaining crystallinity are lower at higher temperature (see Table1).

1.3. Si and Al solution

Instead of pure water, Si and Al solution were used to prove that the destructive structure was suppressed by the saturation of Si and Al in closed system (see Fig.2). As a result (see Table 2), after treatment with Si and Al at concentrations 125 and 0.1 ppm, the crystallinity of H-ZSM-5 remained higher than the treaded in pure water, especially H-ZSM-5(24) with Si and Al solution(No.19). It has remained crystallinity 87.7% after operating in supercritical condition comparing with only 60.3% of crystallinity in pure water. Moreover, the morphology of this sample(No.19) observed by SEM also appear undistinguishably with H-ZSM-5(24) before treatment. For H-ZSM-5(1500), the crystallinity treated in pure water and Si and Al solution are nearly identical due to low Al content.

2. Catalytic stability in dehydration of cyclohexanol

In preliminary experiment without catalyst, cyclohexanol hydration has the relatively low conversion around 1-2 %, and dicyclohexylether, which is by-product from side reaction, is also detected. However, in case of operating with H-ZSM-5 (1500) (see Fig. 3a), conversion is close to 100%, and highly stable over 5 hours operation with 98% selectivity to derivative methyl-cyclopentene, without dicyclohexylether. It means that the porous structure of zeolites can prevent the side reaction to product large molecules such as dimer which was normally generated in non-porous catalyst. Other H-ZSM-5 (24,40) also provide the same result without significant difference of conversion and selectivity. XRD pattern also maintained the characteristic peak of ZSM-5. In addition, the morphology observed by SEM also shown the identical result in both before and

Table 2 The effect of Si and Al solution on stability of zeolites

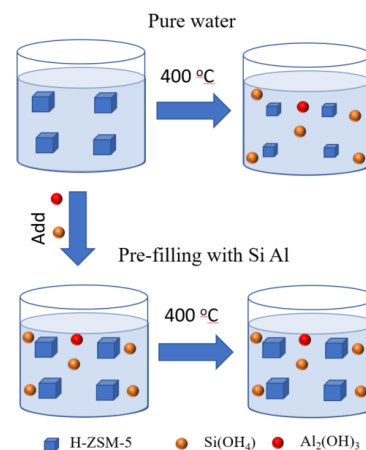| No. | Samples | Temp (°C) | Si solution (ppm) | Al solution (ppm) | Crystallinity (%) | Morphology change (Y/N) |
|---|---|---|---|---|---|---|
| 19 | H-ZSM-5(24) | 400 | 125 | 0.1 | 87.7 | N |
| 7 | | 400 | 0 | 0 | 60.3 | Y |
| 20 | H-ZSM-5(1500) | 400 | 125 | 0.1 | 104.3 | N |
| 18 | | 400 | 0 | 0 | 106.2 | N |



Fig.2 schematic diagram of stability of zeolites in batch rector with filling with pure water and Si Al solution



Cyclohexanone
Cyclopentanol, 1-methyl-
3-Pentanone, 2-methyl-
Cyclopentene, 1-methyl-
Cyclopentanone, 3-methyl-
Pentanone, 3-methyl-
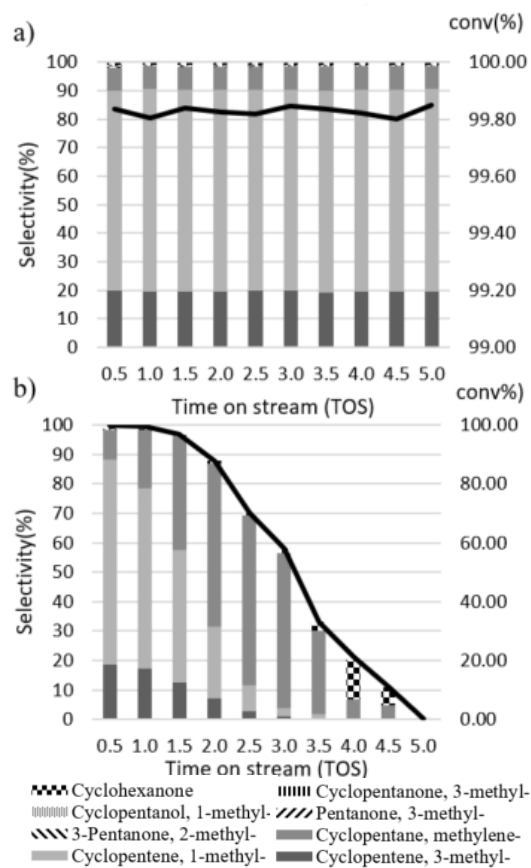Cyclopentane, methylene-
Cyclopentene, 3-methyl-

Fig.3 GC results of Cyclohexanol dehydration at 400 °C, P= 25 MPa, pellet H-ZSM-5 (1500) a) 1g b) 0.2 g

after reaction. However, dissolving of Si in all collected effluences are relatively high without decreasing tendency over the time at 80 ppm. To evaluate Si loss from the structure, operating at lower number of zeolites filling in reactor was performed (see Fig 3b). It was found that conversion shapely dropped, and the decreasing of conversion begun at 1 hours of time on stream(TOS), and conversion remain only 1 % after 5 hours. Furthermore, no zeolites remained in the reactor after pack bed was disassembled. This result indicated that the zeolite structure was destructed by dealumination and desilication. Undetected destructive tendency of activity (GC-FID) and structure (XRD, BET, and crystallinity) operating with 1 g of zeolites (Fig.3a) was explained by the equilibrium between the disassociation and zeolite structure corresponding to section 1.3. The destruction should begin at the entrance zone of pack bed reactor and the concentration of Si and Al reach equilibrium, which protect the exit zone from destruction. (see Fig 4).
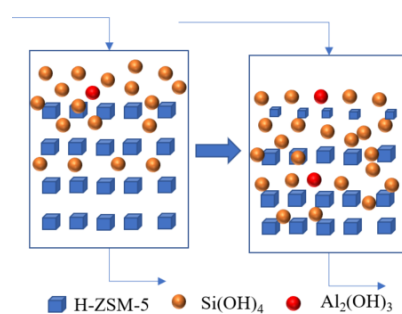


H-ZSM-5 ▪   Si(OH)$_4$ ●   Al$_2$(OH)$_3$ ●

Fig.4 schematic diagram of zeolite destruction in pack bed reactor.

### 3. Acidity of zeolites investigated by NH$_3$-TPD

Acidity investigated by NH$_3$-TPD was deceased in all H-ZSM-5 samples comparing with before treatment with water (see Table 3). This result supports the hypothesis that water begin to attack and remove alumina framework since Al atoms are the source of negative change of zeolites. In the case of H-ZSM-5(1500) (No.18, 24), the acidity deceased to nearly zero since it has already low alumina content at the beginning. However, pellet H-ZSM-5(1500) provided surprisingly higher acidity than powder form. It was explained that mixing alumina binder (Al$_2$O$_3$) cause the saturation of alumina ion which decreased water attack on alumina framework.

Table 3 NH$_3$-TPD of H-ZSM-5 after water attack at different condition

| No. | Type | Temp (°C) | Pressure (MPa) | NH3-TPD(mmol/g) | Note** |
|---|---|---|---|---|---|
| A | H-ZSM-5(24) | RT* | Atm. | 1.949 | 1.8 |
| 7 | | 400 | 24.1 | 0.351 | |
| B | H-ZSM-5(40) | RT* | Atm. | 1.551 | 1.3 |
| 13 | | 400 | 24.1 | 0.627 | |
| C | H-ZSM-5(1500) | RT* | Atm. | 0.372 | |
| 15 | | 250 | saturated | 0.015 | |
| 18 | | 400 | 24.1 | 0.000 | |
| 24 | | 400 | 26.9 | 0.003 | |
| 21 | Pellet H-ZSM-5(1500) | RT* | Atm. | 0.244 | |
| 22 | | 200 | 25 | 0.167 | |
| 23 | | 400 | 25 | 0.029 | |

*Room temperature(RT),  ** Measurement by Tosoh co., Ltd

### Conclusion

The structure stability of zeolites strongly depended on their framework and SiO$_2$/Al$_2$O$_3$ ratio. It was found that Beta-zeolites completely transform to amorphous phase. However, H-ZSM-5 maintain mostly their structure in supercritical water, especially H-ZSM-5 with higher SiO$_2$/Al$_2$O$_3$ ratio providing infinitesimal change of crystallinity. Nevertheless, dissolving of Si and Al was observed by ICP-AES, and decreasing of acidity was found by NH$_3$-TPD in both sub- and supercritical water, which indicated that desilication and dealumination occurred. The reason why structure of zeolites remained in sub- and supercritical water was explained by the saturation of Si and Al in the effluence which stop destructive reaction to proceed. To improve the structure stability, pre-filling with Si and Al in water was found to increase the remaining crystallinity.

### Future plans

Improving the stability of zeolites by pre-adding Si and Al in water before operating in flow reactor and modification the end-chain of structure (fluoride or silane treatment) was planned to perform to further applied it as the catalyst in bio-mass process in sub- and supercritical water.

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