Catalytic Conversion of Acetone to Monoaromatic Chemicals using HZSM-5

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Abstract - The effects of process variables (temperature, space velocity, water addition and Si/Al ratio) on the conversion of acetone to aromatic chemicals have been investigated. The reaction is carried out by fixed bed reactor at an atmospheric pressure to examine the activity and selectivity of HZSM-5. The results show that HZSM-5 exhibited a high active and a shape-selective catalyst for the formation of monoaromatic chemicals. The favourable condition for aceton anatometazation is found i.e. at 673 K with space velocity of 4 h⁻¹, the acetone conversion is close to 100 % and monoaromatic selectivity is approximately 71 %. There is no effect of water existence in the acetone feed on the aromatization reaction process, making the process will be simplified. A significant effect of Si/Al ratio on the activity of HZSM-5 on the durability reaction test for 10 h reaction in a fixed bed reactor at 673 K, space velocity of 4 h⁻¹. The acetone conversions with Si/Al ratio of 25 were much better than those of other ratios during 10 h of reaction. Over HZSM-5 with Si/Al ratio of 75 or 100, the acetone conversion and the monoaromatic selectivity were gradually decreased after 10 h of reaction. It can be concluded that the acetone conversion to monoaromatic chemicals requires a high acid density.

Index Term- acetone conversion, monoaromatic, HZSM-5, Si/Al ratio

I. INTRODUCTION

A new process based on renewable feedstocks and the efforts to diminish the dependency on the fossil resource has recently become an important issue for establishing a sustainable system of chemical/petrochemical industries in the future [1]. Monoaromatic compounds are important chemicals as raw material for many petrochemical industries.

Conventionally, these compounds are obtained from crude-oil by petroleum refining processes. A new route with the utilization of renewable compounds from a fermentation product such as acetone or ethanol [2],[3] could be considered for the production aromatic chemicals. HZSM-5 zeolite is crystalline aluminosilicate and to posses a pore channel structure built by ten-membered oxygen ring system. One pore type has straight but slightly elliptical openings (0.51 x 0.55 nm); the other zig-zags and has essentially circular openings (0.54 x 0.56 nm). ZSM-5 and similar medium structure pore zeolites are sometimes termed pentasil because the framework structure (not the pore openings) consists of chains of 5-membered oxygen rings as secondary building units [4],[5]. Its activity is due to Bronsted acidic site called bridging hydroxyl groups interposed between a silicon and an aluminium atom. The largest dimension offered by the pore apertures is 0.56 nm. Shape selectivity can be manifested in terms of size constrains in the reactants, the complex in transition states and products. HZSM-5 is supposed to be a shape-selective catalyst for the formation of aromatic products [6].

The shape selective catalysis remains as one the attractive topics in heterogeneous catalysis since the work reported by Weisz and Frilette and their patent [7],[8]. During the earlier decade, the extensive studies of HZSM-5 as shape selective catalyst led to the improvement of this catalyst for transforming hydrocarbons to aromatic chemicals : from aliphatic or olefinic compounds [9]-[18] and methane [18]-[22]. Moreover, the ability of HZSM-5 is not only used for the aromatization reaction, but several reactions are also catalyzed by this type of zeolite structure such as alkylation [23],[24], isomerization (25), and catalytic cracking [26]-[28]. Commonly, those studies were contributing steadily to our knowledge concerning the transformation petroleum hydrocarbons originated non-renewable crude oil. Currently, a progress study of converting some simple organic compound methanol since the first paper of Chang-Silvestri [29] has attracted a great attention [30]-[33]. Even the industrial scale for methanol to gasoline (MTG) process have been established. But, the other study related to the reaction of acetone aromatization was not so rapid. Many researchers [34]-[39] have reported the acetone conversion, but the reaction proceeded toward the aldol condensation of acetone and the mixture of acetone have been used as reactant feed. A sufficient study for the acetone aromatization for developing a process is still lacking. In this research, the effect of process variables on catalytic acetone conversion over HZSM-5 by changing the reaction temperature, space velocity, reaction temperature, water presence in acetone feed and effect of Si/Al molar ratio of zeolite on the reaction stability is reported.

II. MATERIALS AND METHODS

Fine crystal powder of HZSM-5 (Si/Al=25) was used as catalyst for the acetone aromatization. One gram of this HZSM-5 (3μmeter particle size) was mixed with quartz sand (10-15 mesh) to avoid the excessive increase of pressure drop. This mixture was packed in a SUS 316 reactor tube with 6 mm i.d and 700 mm length. Some amount of quartz sand (ca. 7 g) was added at the upper part of the catalyst bed for preheating and vaporizing the acetone loaded into reactor. A stainless steel rod was inserted at the lower part of the reactor to strengthen the catalyst bed against the pressure due to the flow of gas going through. To fix completely the catalyst bed in its position, a quartz wool was filled on each side of catalyst layer to keep the possible entrainment of powder during the experiment. The experimental set-up is shown in Figure 1.
Prior to the reaction, the catalyst was pretreated at 673K under nitrogen flowing at 30 ml/min for 1 hour to remove the possibly adsorbed water. Subsequently, the reaction of acetone aromatisation was started by pumping the acetone into the reactor with this nitrogen as carrier gas. The pumping rate of acetone was adjusted in such a way the acetone space velocity (SV) on the range of 2–8 h⁻¹ with the total pressure between 0.13 – 0.25 MPa. Reaction temperature was operated at 673 K and 623 K. The liquid product was collected with a cold trap and an ethanol absorption-trap submerged in the ice-water bath. The gaseous product was taken by a gas-bag. The liquid and gaseous products were analyzed by GC-FID (Hewlett Packard GC-5890) with DB-1 capillary column and GC-TCD (Shimadzu GC-14A), respectively.

The characterization of HZSM-5 catalyst has been completely described elsewhere [40]. The XRD measurement was carried out using an X-ray diffractometer (Cu-Kα radiation) especially for estimation of the crystallite size of the HZSM-5 catalyst. The crystallite size was determined by the method of line broadening based on the Scherrer equation.

The BET surface area of the HZSM-5 catalyst was examined by means of nitrogen adsorption. The adsorption was carried at the liquid nitrogen temperature. The external surface area of catalyst was calculated by t plot method [41] in where the adsorbed film thickness t was calculated by Halsey equation. The Si/Al atomic ratio was measured using inductively-coupled plasma analysis (ICP) for bulk of the solid and electron spectroscopy for chemical analysis (ESCA) was used to measure the Si/Al ratio of the surface.

### III. RESULTS AND DISCUSSION

**HZSM-5 catalyst used for the reaction**

Fine crystal powder of HZSM-5 used in this experiment was obtained from NE Chemcat corp. The properties of this HZSM-5 are shown in Table 1.

The high enough of BET surface area (426 m²/g) comparing to the result measurement of external surface area calculated by t-plot method (19 m²/g) suggests that HZSM-5 must have a internal surface area in form of pore channel structure[42]. About 95 % of BET surface area should be provided by pore channel and consequently, almost of surface acid sites will be distributed on the walls of all pore channels. It should be noted that the parameter of Si/Al ratio is a indicator for acidity of HZSM-5. Mostly, the location of acetone conversion should take place in the pore, even though the acidity of external surface is slight higher than the acidity in the bulk (result of ICP and ESCA in table 1).

![Fig. 1. Schematic diagram of experimental set-up for acetone conversion](image)

![Fig. 2. XRD spectrum for HZSM-5 catalyst used for the reaction](image)

<table>
<thead>
<tr>
<th>Property</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area</td>
<td>426 m²/g</td>
</tr>
<tr>
<td>External surface area</td>
<td>19 m²/g</td>
</tr>
<tr>
<td>Si/Al ratio (bulk)</td>
<td>28.2</td>
</tr>
<tr>
<td>Si/Al ratio (surface)</td>
<td>20</td>
</tr>
<tr>
<td>Crystal size</td>
<td>43 nm</td>
</tr>
</tbody>
</table>

The result of XRD measurement for the HZSM-5 is shown in Fig. 2. It shows a high crystallinity of HZSM-5 and crystal size in approximately 43 nm from the based on the appearance peak at position 23.3 degree (FWHM-full width at half maximum=0.00351 radian and the wavelength for Cu K-α radiation = 1.54056 Å). The photograph taken by FE-SEM with various magnification (5000x, 10,000x, 50,000x and 100,000x) as shown in Figure 3, HZSM-5 has a narrow crystal size distribution. The microcrystal structure of HZSM-5 in such that should be able to give a high accessibility of acetone molecules.
toward surface acid sites and also a high mobility of reaction products with acceleration to move out from internal channel structure. It is hoped that the pore diffusion regime is not controlling step on the global reaction mechanism. Hence, those features possessed by HZSM-5 are expected to be highly reactive for acetone conversion.

**Effect of temperature**

Main result of reaction is shown in table II. At 627 K (350 °C), acetone conversion is not more than 10 %, and the composition of aromatic product (benzene, toluene, xylene, ethyl benzene and C9,10 aromatics) is low. Presumably, the acetone aromatization was going with a low reaction rate at this temperature. However, the dramatically increasing in acetone conversion up to more than 95% as well as selectivity of the aromatic compounds at 723 K (400 °C) is observed. Whereas at higher temperature (450 °C), the selectivity of monoaromatics or total aromatics was decreased, even though the acetone conversion was also high. These results suggests that at 400 °C was the optimum temperature condition and the reaction of acetone aromatization by HZSM-5 catalyst could proceed in an accelerated way.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>400</th>
<th>400</th>
<th>400</th>
<th>350</th>
<th>450</th>
</tr>
</thead>
<tbody>
<tr>
<td>SV acetone [h⁻¹]</td>
<td>2.18</td>
<td>4.74</td>
<td>7.13</td>
<td>8.67</td>
<td>4</td>
</tr>
<tr>
<td>Acetone conversion [%]</td>
<td>98.9</td>
<td>98.4</td>
<td>95.8</td>
<td>7.8</td>
<td>98.6</td>
</tr>
</tbody>
</table>

Table II: Summary result of acetone conversion over HZSM-5

![Fig. 3. FE-SEM photograph of HZSM-5 used for the reaction](image)
As shown in Fig. 5 and Table 2, at the reaction temperature of 673 K (400 °C) the selectivity of liquid products are 70 - 80 % and that of gaseous products are 20-30 %. Particularly, selectivity of monoaromatic product is 60 - 70 %. The trace amount of CO and CO₂ in the gaseous products was formed with selectivity lower than 5 %.

**Effect of space velocity**

Space velocity is an important variable in a full-size reactor at 673 K by reproducing from the laboratory setting. The space velocity was changed in the range of 2-8 h⁻¹. Fig. 4 shows the effect of space velocity on the acetone conversion. It looks like that the change of space velocity did not influence the acetone conversions. Acetone conversion were close to 100 %, slightly decreased with the increasing of acetone space velocity.

The effects of acetone space velocity on some products are also shown in Fig. 4. The selectivity of propane + propylene were obviously decreased due to the increasing of space velocity. However, in case of the non-aromatics containing the oil product (majoring C₅-C₆ aliphatic), the amount increased with the higher space velocity. So the formation of monoaromatic products is not favourable, if the reaction is performed under the condition in either too high space velocity or too low space velocity region. It is clear that the aromatic selectivity seems to be a maximum value at space velocity around at 4 h⁻¹. The selectivity of monoaromatic was as high as 71 % and the total aromatic selectivity naphthalene ring compounds is 75 %. From the results described above, it could be concluded that the experimental condition at 673 K (400 °C) with acetone space velocity of 4 h⁻¹ was most suitable in our experimental conditions.

**Product selectivity**

Fig. 5 presents the product selectivity of acetone conversion observed under space velocity 4 h⁻¹ and at 400 °C within 100 minutes. It is shown that the wide spectrum of product distribution was obtained from acetone conversion with HZSM-5. The monoaromatics detected are the compounds with benzene-single ring structure (C₆-C₁₀ monoaromatics), e.g. 1,2,4,5-tetramethylbenzene (durene) for C₁₀ aromatic. The compounds with double ring structure (diaromatics) i.e. naphthalene and polyalkynaphthalene were also detected. Likely, the HZSM-5 employed in this reaction has a high ability to catalyze the aromatization reaction. However, the formation oxygenated products such as diacetone, isophorone, phorone, mesityl oxide were not detected. Most probably, those species are not stable on the reaction condition as high as 400 °C.

It is obviously shown that monoaromatic compounds are the dominant products and their selectivity surpassed the selectivity of other compounds with a significant amount. This means that HZSM-5 is shape selective catalyst for the formation of aromatic product compound and stable during these reaction time periods with the acetone conversion was constant at 100%. These results is enough consistent with the results presented by Chang and Silvestri [29].

Table 2 shows the formation of CO and CO₂ in mol from the conversion of one mole acetone at the reaction temperature at 400 °C. A chemical transformation of the oxygenated compound like acetone into hydrocarbon product over HZSM-5 could produce stoichiometrically a product in the form of H₂O and CO₂. The reaction of these oxygenated compounds can be most generally characterized as dehydration and de-carboxylation. Due to the formation of CO in the gaseous product, it should be considered that not only CO but also CO₂ is as part of stoichiometric products for the balance of oxygen atom. It is clearly shown that the extent of (CO+CO₂)/acetone conversion is not more than 0.02 mole/mole. Considering the oxygen-balance for this reaction, oxygen atoms from converted acetone are included in these undesired products with not more than 2 %. It could be supposed that the most oxygen contained in acetone will chemically transform to form H₂O.

In respect to gaseous products, it seems that propane and propylene are produced with a significance amount with ca. 10 % of total selectivity of those compounds. These compounds should come initially from acetone molecules and there is no cleavage within skeletal carbon atoms in the acetone molecule. Probably, it could be explained by the reaction of de-oxygenating reaction or hydrogen transfer reaction [26].
surface complex structure will be enhanced. When a proton in the bronsted site is completely transferred, the site will be a framework oxygen atom with Lewis base character. So, this study will report the activity and stability of ZSM-5 with various Si/Al ratios in the acetone conversion to obtain a suitable ratio.

The acetone conversion

The activity of catalyst is measured by the extent of acetone conversion can be achieved and the stability is considered with how long the activity and selectivity is able to be kept. Firstly, we evaluated the activity and stability of ZSM-5 in the reaction of acetone conversion during 10 h using various Si/Al ratio of 25, 75 and 100. The result is shown in Fig. 6 which is a plot of acetone conversion as a function of time on stream. The reaction condition were T=673 K and acetone space velocity 4 h⁻¹. By the experiment tested with the absence of HZSM-5 catalyst, it was confirmed that there was no significant products formation either in the liquid phase or gaseous phase. As shown in the figure, it is clearly seen that in the initial stage of reaction (within 2h), the acetone conversion for each ratio was very similar, i.e. nearly 100 %. Surprisingly, if the reaction was brought in the longer time on stream, it shows that a big difference in result was found. Especially for HZSM-5 with Si/Al ratio of 25, the acetone conversion was nearly constant (ca. 100 %) during 10 h of reaction. However, the both line-curves for Si/Al ratio 75 and 100 obviously exhibit the same trend; the acetone conversion decreases monotonously along with time on stream. The losses of acetone conversion are in the order of 40 % after 10 h of reaction from the initial conversion. These findings reflect that the activity and stability for HZSM-5 with Si/Al =25 was superior than the Si/Al of 75 or 100 for acetone conversion. It seems that the HZSM-5 for Si/Al ratio of 75 and 100 were susceptible to undergo a deactivation after 3 h reaction. Probably, the behavior of this acetone conversion is strongly correlated to the acid site amount HZSM-5 and require the high acid density.

Effect of Si/Al ratio

The abilities of HZSM-5 to accelerate many reactions are mostly related to their acid strength or acid site amount and this important parameter might be controlled by Si/Al ratio. The variation in the Si/Al ratio in the zeolite does not affect the structure but causes a change in the acidity and acid strength distribution and consequently a change in catalytic properties (Bhatia, 1990). However, a less study have been tried to explore the effect of Si/Al ratio on the catalytic performance of HZSM-5 in the acetone conversion. In case of HZSM-5 with lower Si/Al ratio (high acid density), the proton mobility is supposed to be higher than that with higher Si/Al ratio and hence the acidic proton transfer from bronsted acid site to molecule acetone in the
The targeted product from this reaction is monoaromatic compounds, which comprise benzene, toluene, xylene, ethyl benzene or their derivatives such as ethyl benzene or C₅ aromatic group (trimethyl benzene, n-propyl benzene, methyl ethyl benzene, mesitylene). These aromatic compounds are very important feedstocks in the chemical or petrochemical industries. One reason of the choice of HZSM-5 for acetone conversion is due to its pore channel dimension which is very close to molecular size of aromatic compound in such a way that enable monoaromatic product to be generated selectively. The result is shown in Fig. 7 that is a plot of aromatic selectivity during 10 h of stream for each Si/Al ratio. It is clearly shown that during 10 h of reaction, HZSM-5 with Si/Al ratio of 25 which is very active catalyst as described before is also more selective for aromatic formation than that with other ratios. The aromatic selectivity obtained was above 70 % during 10 h of time on stream observed.

The yield of a desired product is also an important variable output from a result of reaction test especially for comparing a catalytic performance and evaluating an importance of the economic-added value. Here, the aromatic yields were calculated from the result of multiplication of conversion and selectivity. Fig. 8 shows the effect of Si/Al ratio on the yield of monoaromatic compound. It is obviously shown that the catalytic performance of HZSM-5 with Si/Al =25 is much better than of the others ratio. During 10 h of reaction tested, with HZSM-5 with Si/Al=25 the yields of monoaromatic compound was obtained over 70 %. Comparing to the result obtained by Lucas [38], these yields are much better by twice. However, the yields of monoaromatic with the others of Si/Al ratios exhibited a sharp decrease initially from 5 h of reaction. This evaluation confirms a significance effect of Si/Al ratio on the catalytic performance of HZSM-5.

**The effect of water addition**

The addition of water into the acetone feed was also carried out to find the its effect on the activity and selectivity of HZSM-5. This work is done due to the much water in the mixture of acetone in real product from biomass conversion by fermentation or pyrolysis. It is noted that there was a positive effect of water addition in the feed have been found. The result of reaction under the presence of water as much as 50 wt % in the feed is shown in table III (in column 4).

**Table III**

<table>
<thead>
<tr>
<th>Reactant feed</th>
<th>Acetone</th>
<th>Acetone</th>
<th>Acetone + H₂O (50 %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>673</td>
<td>673</td>
<td>673</td>
</tr>
<tr>
<td>Pressure (MPa)</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>SV acetone (h⁻¹)</td>
<td>2.18</td>
<td>4.74</td>
<td>4.32</td>
</tr>
<tr>
<td>Conversion (%)</td>
<td>98.1</td>
<td>98.4</td>
<td>99.1</td>
</tr>
</tbody>
</table>

Selected Products (%mol Carbon)

| Total aromatics | 69.0 | 75.0 | 68.0 |
| Monoaromatics   | 63.3 | 71.2 | 64.0 |
| Benzene         | 6.34 | 4.69 | 4.6  |
| Toluene         | 23.8 | 21.4 | 19.6 |
| Xylene          | 22.5 | 24.2 | 22.5 |

Interestingly, the acetone conversion and product selectivity of selected product (aromatic compound) in the presence and without water in the acetone feed is quite similar. This result indicates that the aromatization of acetone over HZSM-5 can proceed even in the existence of water and the aromatisation process can be simplified.

**IV. CONCLUSION**

Acetone aromatization over HZSM-5 proceeded effectively at the 400 ⁰C and acetone space velocity of 4 h⁻¹. Acetone conversion was close to 100 % with monoaromatic selectivity 71 %. HZSM-5 is a high shape selective catalyst to inhibit the formation of aromatic product molecules more than 10 carbon atoms and stable during the reaction time periods (100 min). The effect of Si/Al ratio containing HZSM-5 on the acetone conversion showed that with ratio of Si/Al = 25 was more active and stable than that with Si/Al ratio 75 or 100, which indicates that the reaction of acetone conversion to monoaromatic compounds requires a
high acid density. The acetic acid conversion was nearly 100% while the selectivity and the yield of monoaromatics were obtained in more than 70% during 10 h of reaction. The aromatization of acetic over HZSM-5 can be carried out in the existence of water and therefore the aromatisation process can be simplified. The further work should be studied concerning the catalyst deactivation under various condition of acetone conversion.

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REFRENCES


