Change in catalytic activity on acetone conversion to aromatic chemicals using H-ZSM-5

Setiadi¹, Slamet¹, Mohammad Nasikin¹, T. Tsutsui², T. Kojima³

¹Jurusan Teknik Kimia, Fakultas Teknik Universitas Indonesia, Kampus UI, Depok-16424
e-mail: setiadi@che.ui.edu
²Department of Applied Chemistry and Chemical Engineering, Kagoshima University,
Kagoshima, Japan
³Department of Applied Chemistry, Faculty of Engineering, Seikei University, Tokyo, Japan,
e-mail: kojima@st.seikei.ac.jp

Abstract

This research is devoted to a catalytic process using H-ZSM-5 catalyst for the reaction of acetone conversion into aromatics chemicals. The reaction was performed in the continuous flow reactor under atmospheric pressure at temperature ranging 573-723 K. This work is intended to examine the change of H-ZSM-5 catalyst in reaction of acetone conversion on the various temperatures and effect of Si/Al atomic ratio. H-ZSM-5 with Si/Al = 25 was more active and stable than the Si/Al ratio 75 or 100, it indicates that the reaction of acetone conversion requires a high acid density of H-ZSM-5 catalyst. The yield of aromatic was obtained higher than 60 wt % during 6 h of reaction. The reaction on 673 K was the most favorable temperature for acetone conversion toward aromatic products. The high selectivity of mono-aromatic product indicates the H-ZSM-5 is shape selective catalyst for the formation of aromatic product and able to suppress the formation the poly-aromatic compound due to the geometrical size of pore. There is no negative effect due to the water addition on acetone conversion and aromatic product selectivities referring to the without the presence of water in the feed, it will simplify the industrial process. It is strongly predicted that the main causes of deactivation process is particularly due to the formation of coke, which was covered or blocked on the surface of H-ZSM-5 catalyst.

Keywords: Acetone, Catalytic conversion, Si/Al ratio, ZSM-5

Introduction

One of the promising route which is expected to be alternative process for producing aromatic compounds coming from a fermentation process which produce acetone, n-butanol or ethanol (Gibbs, 1983, Haggestrom, 1985). If the new route scheme for the production of aromatic compound as fuel or chemicals can be established perfectly, the biomass-based technology will have a greatly contributions to the solving of the energy problem significantly in the future.

Acetone can be transformed into aromatics hydrocarbons through a catalytic process over HZSM-5 (Chang & Silvestri, 1977; Lucas, 2001, Lucas 1997, Setiadi, 2003), but a sufficient study for the acetone aromatization especially on the stability of catalyst during reaction proceed is still lacking. The impressive result of the effect of temperature on the acetone conversion using ZSM-5 has been demonstrated by Chang et al. (1981), Chang and Silvestri (1977). But, the knowledge about the activity and stability on each temperature and the typical ratio of Si/Al of HZSM-5 catalyst were nothing.

The acetone conversion into aromatic hydrocarbons products over HZSM-5 could be described by aldol condensation mechanism (Chang et al., 1981). This reaction mechanism combines both Bronsted-type (proton transfer) acid - base steps and Lewis base (electron transfer) steps. The aldol reaction of acetone begins with the abstraction of the acidic α-proton (Bronsted-Lowry step) to form a resonance-stabilized enolate anion (Xu, et. al., 2002). This reactive anion acting as nucleophilic species attacks the electron poor carbonyl of an free acetone molecule (Lewis step) forming alkoxide intermediate (Xu et al., 1994), which is subsequently protonated to form the aldol molecule product (diacetone alcohol).

At elevated temperatures, this alcohol is dehydrated for releasing of water to form mesityl oxide. Mesityl oxide can undergo subsequent condensation steps to form di-enone, or cyclic isophorone. Theoretically, this reaction could continue with further substitutions on the terminal methyl groups due to its conjugated nature. So, further condensation reaction with another free acetone molecule (unadsorbed state), the conjugated nature of the enone product allows the forming higher molecular weight species that can accumulate in the
pore channel, thus restricting access to the active sites and shutting down the reaction (Stevens, 1999).

In the internal pore channels of ZSM-5, at high temperatures (Zaki et. al., 2000) the decomposition of adsorbed mesitylene oxide or the cracking of diacetone alcohol (Chang, 1981) are susceptible to occur resulting C_3-C_4 hydrocarbons. Subsequently, the formation of the aromatic compounds can proceed through condensation-dehydrocyclization (Chang et. al., 1981), or through dimerization (Marchionna et al., 2001) and alkylation (Albright, 2003) these products such as isobutylene

We have reported in the previous study (Setiadi, 2003) the activity of H-ZSM-5 catalyst with Si/Al ratio=25 is very high with 100 % conversion at 673 K within 2 hrs. Based on these results, this report presents the results of acetone conversion on various temperature and the effect of Si/Al ratio on the longer time of stream.

Materials and Methods

The reaction of acetone conversion was carried out using fixed bed reactor under the atmospheric pressure (Figure 1). The detail of this experimental work has been described elsewhere (Setiadi et al., 2003). The acetone was introduced into the reactor by pumping, and the nitrogen was used as carrier gas. The oil-liquid products is collected by cold trap and the ethanol absorption submerged in the ice-water. And the gaseous product was taken by gas bag. The detail of experimental condition is shown in the Table 1. The weight of catalyst was 1 gram. To fix the catalyst in the reactor, 5 gram of quartz sand was mixed this catalyst weight to avoid excessive increase of pressure drop. Liquid product were analyzed by GC-FID and the gaseous products were detected by TCD.

Table 1 Detail of Experimental condition

<table>
<thead>
<tr>
<th>Item</th>
<th>Data in detail</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>H-ZSM-5</td>
</tr>
<tr>
<td>Origin</td>
<td>N.E. Chemcat</td>
</tr>
<tr>
<td>Si/Al ratio</td>
<td>25, 75, 100</td>
</tr>
<tr>
<td>Particle size (dp)</td>
<td>3 μmeter</td>
</tr>
<tr>
<td>Catalyst weight</td>
<td>1 gram for reaction test</td>
</tr>
<tr>
<td>Quartz sand for blending</td>
<td>5 gram (10-15 mesh)</td>
</tr>
<tr>
<td>Quartz sand for preheating</td>
<td>7 gram (10-15 mesh)</td>
</tr>
<tr>
<td>Aceton (Cica)</td>
<td>min 99.5% purity</td>
</tr>
<tr>
<td>Carrier Gas</td>
<td>N_2</td>
</tr>
</tbody>
</table>

Results and Discussion

Effect of Temperature

The change of catalyst activity is mainly commonly attributed by the extent of acetone conversion obtained from the reaction at the temperature performed. In order to find the optimum temperature for obtaining the high activity and stability of ZSM-5 for Si/Al ratio of 25, the reaction of acetone conversion was done on the various temperature 723 K, 673 K, 623 K and 573 K. As shown at Figure 2, the activity of H-ZSM-5 catalyst on the temperatures lower than 673 K is not good, the acetone conversion was rapid decreases on shorter time on stream of reaction. The temperature condition higher that 673 K, the activity and stability of ZSM-5 shown a little bit higher. However, as shown in Figure 3 the yield or selectivity of aromatic product found were lower than that of reaction temperature done on 673 K. Accordingly, it is can concluded that the temperature reaction of 673 K is a favourable temperature for conversion of acetone toward aromatics formation.
product, but also depends on the surface acidity or acid strength for the acetone reaction. Therefore, the next results present the effect of Si/Al on the activity.

**Figure 2** The change of catalytic activity on various reaction temperature over H-ZSM-5 using Si/Al = 25.

**Figure 3** The change of monoaromatic yields on various reaction temperature over H-ZSM-5 using Si/Al = 25.

**Product Distribution**

**Figure 4** presents the product distribution within 100 min by selectivity of % carbon calculated. It shown that the main monoaromatic product are benzene, toluene, ethyl benzene, m+p-xylene, o-xylene and C9-aromatic, and the small amount of naphthalene derivatives compounds. But, the gaseous products are also formed such as CO, CO\(_2\), CH\(_4\), C\(_2\)H\(_4\), C\(_2\)H\(_6\), C\(_3\)H\(_6\), C\(_3\)H\(_8\). Among the component of gaseous products, the quantity of light alkanes (C\(_3\)-C\(_4\)) was shown in the significant amount.

The high selectivity of mono-aromatic product indicate that H-ZSM-5 is very selective for the formation of this product. It can be considered that the pore opening of ZSM-5 is very close to the geometrical molecular size of the aromatic compounds, so that the very high probability of aromatization of acetone occur in the internal surface of channel pore structure. But the activity of H-ZSM-5 is not only on its abilities to shape the product selectivity toward benzene-ring hydrocarbons

**Effect of Si/Al Ratio**

The result of reaction test is presented by acetone conversion as the indicator performance of catalytic activity of H-ZSM-5 catalyst during the time on stream of reaction up to 10 h. As seen at **Figure 5**, there was a big difference between

**Figure 4** The product distribution as the result of acetone conversion at 673 K after 40 min using H-ZSM-5 (Si/Al=25).

**Figure 5** The change of acetone conversion during 10 hours of reaction for the each Si/Al ratio of H-ZSM-5 at 673 K. Symbol : Si/Al=25 (●), Si/Al=75 (■) dan Si/Al=100 (△)
Si/Al ratio of 25 and the others ratio (75 or 100). The activity and as well as stability of Si/Al ratio of 25 exhibited the stability during 10 hours of reaction. The activity of H-ZSM-5 with this Si/Al ratio was stable at 100 % conversion. However, the both line-curves for Si/Al ratio 75 and 100 showed the same trend, acetone conversion decreases monotonously along with reaction proceeded. Commonly, the higher Si/Al ratio containing H-ZSM-5 the tendency of acid amount of this zeolite is lower. This result suggested that the activity and stability of H-ZSM-5 catalyst for the acetone conversion is strong correlation with surface acid density of ZSM-5.

The yield for hydrocarbon mono-aromatic for each Si/Al ratio is seen at Figure 6. It is obviously shown that yields of aromatic hydrocarbons from acetone conversion using Si/Al=25 were obtained more than 60 %.

**Figure 6** The change of yield of monoaromatic hydrocarbons during 10 hours of reaction for the each Si/Al ratio of H-ZSM-5 at 673 K. Symbol : Si/Al=25 (●), Si/Al=75 (■) dan Si/Al=100 (▲)

Apparently, The high selectivity of mono-aromatic product indicates the H-ZSM-5 is shape selective catalyst due to its pore structure with pore opening 0.56 nm and able to suppress the formation the poly-aromatic compound due to the geometrical size of pore. In such pore dimension, the mono-aromatic molecule may have a capability to wriggle out from the pore channel of ZSM-5. But, it is likely that the progress of acetone conversion is paralleled with the progress of deactivation. Currently, the main causes of deactivation is convinced of the formation of coke, which was covered or blocked on the surface of H-ZSM-5 catalyst. This is due to the change of physical state between fresh and used catalysts. The study on the confirmation of deactivation is still under progressing such as the change of surface area measurements, the change coke identification, SEM, the change of acidity of used and fresh catalysts.

**The presence of water in the reactant feed**

One more interesting result is the reaction of acetone conversion due to the presence of water in the reactant feed. 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 and MEK in real product from biomass conversion particularly the liquid product resulted from fermentation process (Lucas et al., 2001. The other effect is if the reaction of acetone conversion can be carried out in the existence of water, the high input energy for separation process of acetone fermented product can be reduced significantly.

**Table 2** Acetone conversion using H-ZSM-5 catalyst under presence and absence of water in the feed

<table>
<thead>
<tr>
<th>Reactant feed</th>
<th>Acetone</th>
<th>Acetone</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (K)</td>
<td>Pressure (MPa)</td>
<td>SV acetone (h⁻¹)</td>
</tr>
<tr>
<td></td>
<td>673</td>
<td>0.13</td>
<td>2.18</td>
</tr>
</tbody>
</table>

It is clearly shown in the Table 2, the result of reaction under the presence of water as much as 50 wt % in the feed is shown in in column 4. 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.

**Conclusions**

The change of catalytic activity of H-ZSM-5 catalyst on acetone conversion has been performed by the reaction test on same condition during the time on stream.

- The time on stream reaction test, 673 K is a favorable temperature for acetone conversion toward aromatic products. The lower temperatures of reaction lead to rapid deactivation, and the higher
temperatures tend to decline the yield/selectivity of aromatics products

And the time on stream reaction test within 10 h was also found that H-ZSM-5 with Si/Al = 25 is the high active and stable than the Si/Al ratio, it indicates that the reaction of acetone conversion required the high acid density.

The presence of water in reactant feed, the no significance changes of activity of H-ZSM-5 on acetone conversion and aromatic product selectivity.

References


