Methylisobutyl Ketone by Direct Conversion of Acetone and Hydrogen*

by Yasuharu Onoue**, Yukio Mizutani**, Sumio Akiyama**, Yusuke Izumi**, Yoshiaki Watanabe** and Junji Maekawa**

Summary: Tokuyama Soda has recently developed a new process for manufacturing methylisobutyl ketone. This process is based on one-step conversion of acetone and hydrogen in vapor and liquid phases in a trickle reactor using a specially prepared bifunctional catalyst. The catalyst essentially comprises zirconium phosphate containing a small amount of finely and uniformly dispersed palladium metal. High catalytic activity and durability have been confirmed in continuous operations using a pilot plant having a capacity of 300 kg a day.

Besides the excellent durability of the catalyst, high productivity and simplicity of Tokuyama MIBK Process make it far more economical than the conventional process.

1 Introduction

Methylisobutyl ketone (MIBK) has been commercially produced on a large scale by the conventional three-stage process1). This process involves aldolization of acetone to form diacetone alcohol which is then dehydrated to mesityl oxide for final conversion to MIBK:

\[ 2\text{CH}_3\text{COCH}_3 \rightleftharpoons \text{(CH}_3\text{)}_2\text{C(OH)CH}_2\text{COCH}_3 \]
diacetone alcohol

\[ \text{(CH}_3\text{)}_2\text{C(OH)CH}_2\text{COCH}_3 \rightarrow \text{(CH}_3\text{)}_2\text{C=CH COCH}_3 + \text{H}_2\text{O} \]
mesityl oxide

\[ \text{Ni or Cu-Cr} \]

\[ \text{(CH}_3\text{)}_2\text{C=CH COCH}_3 + \text{H}_2 \rightarrow \text{(CH}_3\text{)}_2\text{CHCH}_2\text{COCH}_3 \]
MIBK

This process is plagued not only with low conversion of acetone in the first stage but also with such problems as formation of acetone by the reversible reaction of mesityl oxide with water in the second stage and production of a considerable amount of less useful methylisobutyl carbinol in the final reaction stage.

In recent years, much interest has been shown in one-step synthesis of MIBK from acetone and hydrogen in an attempt to improve the conventional process. Only quite recently, however, some practical one-step processes have been developed.

Recently, Tokuyama Soda has developed an economical process for manufacturing MIBK.

This process is based on the direct conversion of acetone and hydrogen in vapor and liquid phases in a trickle reactor using a highly active bifunctional catalyst. High productivity of the process and excellent durability of the catalyst were confirmed by continuous operations with a pilot plant having a capacity of 300 kg a day.

2 One-step Synthesis of Methylisobutyl Ketone

2.1 Reaction

The direct conversion of acetone and hydrogen to MIBK proceeds catalytically according to the following equation:

\[ 2\text{CH}_3\text{COCH}_3 + \text{H}_2 \rightarrow \text{(CH}_3\text{)}_2\text{CHCH}_2\text{COCH}_3 + \text{H}_2\text{O} \]

The reaction is exothermic, and its heat of reaction calculated from available thermochimical data2) is 21.6 kcal/mol at 400°K in vapor phase.

In one-step synthesis, when the reaction is carried out especially within a short residence time or with an insufficient amount of hydrogen, mesityl oxide is usually detectable in the reaction products. This observation suggests that one-step reaction proceeds via a consecutive mechanism which involves condensation of acetone to form mesityl oxide and its subsequent hydrogenation to MIBK. Mesityl oxide is directly obtainable by condensation of acetone, but its equilibrium conversion is rather low, for example 19.3% at 140°C according to the results reported by Klein et al.3). In one-step reaction, however, it is expected that conversion of acetone is
markedly favored by rapid irreversible hydrogenation of mesityl oxide to yield MIBK. Consequently, the overall reaction probably follows the sequence:

$$2\text{CH}_3\text{COCH}_3 \rightleftharpoons \text{(CH}_3)_2\text{C} = \text{CHCOCH}_3 + \text{H}_2\text{O}$$

$$\text{H}_2 \rightarrow \text{(CH}_3)_2\text{CHCH}_2\text{COCH}_3$$

The major by-products in one-step reaction include isopropanol, mesityl oxide, diisobutyl ketone (DIBK), methylisobutyl carbinol (MIBC) and mesitylene. The alcohols are formed by hydrogenation of the corresponding saturated ketones, DIBK by subsequent condensation of MIBK with acetone, mesitylene by trimeric condensation of acetone. However, it should be noted that the formation of by-products depends significantly on the nature of the catalyst used.

2.2 Catalyst

Most of the previous work on one-step MIBK synthesis have been focused on the development of efficient catalyst systems.

Considering the consecutive nature of one-step reaction, it can be predicted that a combined system of some suitable catalysts for aldolization, dehydration and hydrogenation will be effective for direct synthesis of MIBK. Alternatively, a bifunctional system of an acidic substance combined with a hydrogenation catalyst should likewise be effective, because acetone can directly be converted into mesityl oxide in the presence of an acid without the formation of diacetone alcohol as an intermediate product.

Palladium is probably the best catalyst for selective hydrogenation of mesityl oxide to MIBK with the least formation of methylisobutyl carbinol by further reduction of MIBK.

A number of polyfunctional catalyst systems for one-step synthesis of MIBK have been proposed for these twenty years. Such systems containing basic substances as KOH-Al$_2$O$_3$-Pd and SiO$_2$-MgO-Pd for aldolization of acetone are apparently impractical because of the low yields of MIBK they produce. On the other hand, some preferable catalyst systems which comprise metallic palladium and ion exchangers such as cation exchange resin and zeolite in their hydrogen forms have been developed by Rheinpreussen A.G. and Showa Denko Co. According to their recent patents and literature, these systems enable a conversion of acetone and hydrogen into MIBK in good yields, for example, the selectivity of MIBK on converted acetone is as high as 95 mol% at an acetone conversion rate of about 30%.

Efficiency of bifunctional catalyst probably depends not only on its acidic character but also on the state of dispersion of the palladium metal on the catalyst surface. It is, therefore, expected that more effective catalyst systems can be developed for selective condensation of acetone to MIBK by combining metallic palladium in a finely dispersed state with a certain solid acid having an appropriate acid-strength.

Tokuyama Soda has found that, through its extensive studies on the catalysis of several kinds of inorganic ion exchangers, zirconium phosphate in the hydrogen form possesses the desirable acidic characteristics to catalyze the liquid-phase selective condensation of acetone to form mesityl oxide. On the basis of this finding, Tokuyama Soda has further attempted to develop a bifunctional catalyst for one-step synthesis of MIBK by introducing palladium ions finely dispersed and uniformly into zirconium phosphate employing the ion exchange technique, and the company has developed an excellent catalyst.

Ion-exchange resin catalysts in which metallic palladium is introduced by a similar technique have been recently developed by Scholven-Chemie A.G. and Showa Denko Co.

### 3 Tokuyama MIBK Process

3.1 Efficiency of Catalyst

The catalyst employed in the Tokuyama trickle process essentially comprises zirconium phosphate containing a small amount of palladium metal uniformly dispersed in almost atomic order. The catalyst is highly active and selective for one-step conversion of acetone and hydrogen to MIBK in vapor and liquid phases. Some examples of the data obtained with the Tokuyama catalyst using a continuous flow unit are illustrated in Figs. 1, 2 and 3.

Table 1 summarizes the data obtained with some typical ion-exchange resin catalysts reported in the recent patents.

Besides the excellent selectivity at high conversion rates, remarkably high space-time yields of MIBK can be obtained with the Tokuyama catalyst in comparison with the usual resin catalysts. In addition to its mechanical toughness and chemical resistance to the impurities in the feed, the catalyst has also an excellent thermal...
Methylisobutyl Ketone by Direct Conversion of Acetone and Hydrogen

Table 1 Reaction Activity of Ion-Exchange Resin Catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature (°C)</th>
<th>Pressure (atm)</th>
<th>H₂/Acetone Mole Ratio</th>
<th>Acetone Conversion (at 150°C)</th>
<th>MIBK Selectivity (mol%)</th>
<th>MIBK STY (g/l-cat-hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dowex 50WX8-Pd(1) (3.09)</td>
<td>137~140</td>
<td>30</td>
<td>0.246</td>
<td>2.4</td>
<td>44.6</td>
<td>91.0</td>
</tr>
<tr>
<td>Lerviat SP 120-Pd(2) (0.05)</td>
<td>80~135</td>
<td>50</td>
<td>1.64~2.05</td>
<td>1.0</td>
<td>34.4</td>
<td>96.5</td>
</tr>
<tr>
<td>Amberlite 200-Pd(3) (0.08)</td>
<td>135</td>
<td>100</td>
<td>—</td>
<td>4.0</td>
<td>24.2</td>
<td>97.4</td>
</tr>
</tbody>
</table>

* Selectivity of MIBK based on converted acetone.

stability owing to its inorganic nature. Consequently, it is well applicable even under such severe reaction conditions that probably would decompose resin catalysts.

Results obtained on lifetime of the catalyst from the pilot plant test runs proved that conversion rate of acetone and selectivity of MIBK were almost completely maintained at their stable levels during 1,500 hours' operation except for a slight decrease in conversion in the initial 100 hours period.

Furthermore, the Tokuyama catalyst can be
regenerated, if necessary, with air at a high temperature (about 400°C).

3.2 Kinetics

Fig. 4 shows a typical aspect of the reaction examined at 160°C and 30 kg/cm²-G in a

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It is clearly indicated that one-step reaction proceeds via a consecutive mechanism. Thus, the data represented in Fig. 4 can well be interpreted in terms of the following rate expressions:

\[
\begin{align*}
dy_a/df &= 5.52y_a^2/(1 + 187(1 - y_a))^2 \\
dy_m/df &= (1/2) (dy_a/df) - 212.5y_m/(1 + 2.35ya) \\
dy_b/df &= 212.5y_m/(1 + 2.35ya)
\end{align*}
\]

where, \(y_a\), \(y_m\) and \(y_b\) denote the mole fractions of acetone, mesityl oxide and MIBK, respectively, and \(B\) the reciprocal of acetone LHSV.

At LHVs over 10 hr\(^{-1}\), the rate of condensation, as well as that of hydrogenation, is generally influenced by the change in the reaction pressure, whereas little change is observed at a moderate LHSV. The amounts of isopropanol and diisobutyl ketone, however, remain almost unchanged with reaction pressure.

An excess amount of hydrogen has no significant effect on both the conversion rate of acetone and selectivity of MIBK.

### 3.3 Process Description

Fig. 5 shows a flow diagram of Tokuyama MIBK Process.

Acetone and hydrogen within a range of H\(_2\)/acetone mole ratio of from 0.2 to 0.4 are preheated and fed to a fixed-bed catalytic reactor at 20~50 kg/cm\(^2\)-G and 120~160\(^\circ\)C. The actual LHSV of the acetone feed is in a range of 6~12 hr\(^{-1}\). Conversion of acetone takes place at a rate of about 30~40\(^\circ\), per pass. The heat of reaction is removed by indirect heat exchange with an appropriate heat-transfer medium. The reaction products are cooled by heat exchange with the acetone feed and then sent to a gas separator where unreacted hydrogen is separated and recycled. The liquid product from the gas separator is sent to an acetone recovery column where unreacted acetone is removed and recycled to the feed stock. The crude MIBK discharged at the bottom of the recovery column is separated from water and purified by further distillation.

Under certain combination of reaction conditions, selectivity of MIBK is between 95 and 97 mol\%. The main by-products are isopropanol and diisobutyl ketone.

### 3.4 Features of Process

Tokuyama MIBK Process has a number of advantages inherent to its proprietary catalyst and process design. Features of the process confirmed in the pilot plant operations are as follows:

1. The process is so simple that it is decisively more economical than the conventional process.
2. Due to the high reactivity and selectivity of the liquid phase reaction with the catalyst, the yield of MIBK is high, and the size of the reactor can be considerably reduced.
3. The catalyst has a long operating life without requiring regeneration owing to its thermal and mechanical stability, and to the mild reaction conditions of the process.
4. The catalyst is highly resistant to the impurities present in the feed, so no special purification of acetone or hydrogen is required.
Table 2 Typical Properties of MIBK

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color (APHA)</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Specific Gravity (20°/20°C)</td>
<td>0.802</td>
</tr>
<tr>
<td>Distillation Test</td>
<td></td>
</tr>
<tr>
<td>Initial Boiling Point</td>
<td>114.5 °C</td>
</tr>
<tr>
<td>Dry Point</td>
<td>116.2 °C</td>
</tr>
<tr>
<td>Purity</td>
<td>&gt; 99.9 wt%</td>
</tr>
<tr>
<td>Water Content</td>
<td>&lt; 0.02 wt%</td>
</tr>
<tr>
<td>Free Acid</td>
<td>&lt; 0.0002 wt%</td>
</tr>
</tbody>
</table>

Table 3 Economics of Tokuyama MIBK Process

<table>
<thead>
<tr>
<th>Plant Capacity</th>
<th>20,000 metric tons of MIBK per annum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investments, Battery Limits</td>
<td>1,800,000 U.S. dollars (1973 rate)</td>
</tr>
</tbody>
</table>

Consumption per metric ton of MIBK

<table>
<thead>
<tr>
<th>Material</th>
<th>Consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>1.24 t</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>240 Nm³</td>
</tr>
<tr>
<td>Catalyst &amp; Chemicals</td>
<td>1.8 dollars</td>
</tr>
<tr>
<td>Steam (2.5 kg/cm²-G)</td>
<td>4 t</td>
</tr>
<tr>
<td>Electric Power</td>
<td>80 kW·hr</td>
</tr>
<tr>
<td>Cooling Water</td>
<td>250 m³</td>
</tr>
</tbody>
</table>

(5) The process is sufficiently flexible to produce either MIBK exclusively or MIBK and mesityl oxide in a certain given ratio by controlling the reaction conditions.

(6) Equipment requires no special construction materials since no corrosive chemicals are used nor produced.

3.5 Quality of Product

Typical data of MIBK obtained in a pilot-plant test run are given in Table 2.

3.6 Economics

The results of economic studies on exclusive production by Tokuyama Process of 99.9 wt% pure MIBK are shown in Table 3.

4 Conclusion

In addition to the excellent durability of the catalyst, high productivity and simplicity of Tokuyama MIBK Process make it far more economical than the conventional process.

Tokuyama Soda plans to use the new MIBK Process for future commercial plants and expansion.

References