Synthesis of Methyl Isobutyl Ketone from Acetone and Hydrogen Catalyzed by Palladium Supported on Zirconium Phosphate

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The one-step synthesis of methylisobutyl ketone from acetone and hydrogen was investigated by using palladium supported on zirconium phosphate, a bifunctional catalyst. Effects of reaction variables on both the conversion of acetone and the selectivity of methylisobutyl ketone were examined. The experiments were carried out with a continuous flow unit at 110—140 °C and 7—25 kg/cm^2 over a range of liquid hourly space velocity of acetone for 2—15 hr^{-1} with a mole ratio of hydrogen to acetone in the range 0.2—1.45. Under these conditions, the conversion of acetone was 20—40%, the selectivity of methylisobutyl ketone being as much 90—97 mol%. It is suggested that the one-step reaction proceeds *via* a consecutive mechanism.

Interest has been shown in the one-step direct synthesis of methylisobutyl ketone from acetone and hydrogen.

$$2CH_3COCH_3 + H_2 \rightarrow (CH_3)_2CHCH_2COCH_3 + H_2O \quad (1)$$

A number of bifunctional catalysts effective for both condensation and hydrogenation have been proposed for direct synthesis.[1,2] However, such catalysts containing basic substances for aldolization of acetone as KOH–Al_2O_3–Pd and SiO_2–MgO–Pd were found to be impractical because of low yield of methylisobutyl ketone.

Most commercial methods for producing methylisobutyl ketone are based on the conventional three-stage process; the aldol condensation of acetone to form diacetone alcohol catalyzed by a base, the dehydration of the alcohol to mesityl oxide with an acid, and the hydrogenation of the unsaturated ketone to methylisobutylketone with nickel or copper chromite catalyst.

Recently, some bifunctional catalysts containing palladium and cation-exchange resins have been reported for the selective one-step synthesis of methylisobutyl ketone.[3–8]

It was found that zirconium phosphate, an inorganic cation-exchanger, shows an excellent catalytic activity for the selective condensation of acetone to mesityl oxide.[9]

Attempts were made to prepare a bifunctional catalyst suitable for the selective one-step conversion of acetone and hydrogen into methylisobutyl ketone by finely dispersing palladium metal onto zirconium phosphate by means of ion-exchange technique.

The present paper is concerned with the general characteristic of the one-step synthesis of methylisobutyl ketone with the new catalyst.

Experimental

Catalyst Preparation. Palladium chloride (0.5 g) was added to an aqueous solution of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$ 97 g/H_2O 3 l) and dissolved by heating. 33 g of phosphoric acid (85 vol%) was diluted with 3 litres of water. The former solution was added to the latter under stirring at room temperature for half an hour. After the reaction, the pH of the reaction mixture was adjusted to 5.0 with ammonia (14%). Stirring was continued for 4 hr, and the reaction mixture was allowed to stand for 24 hr. The resulting precipitate was then filtered, washed with water and dried at 110 °C. The dried gel obtained was crushed into 16—24 mesh particles and calcined at 400 °C for 8 hr in a stream of hydrogen. The palladium content of the resulting catalyst was 0.5 wt.%.

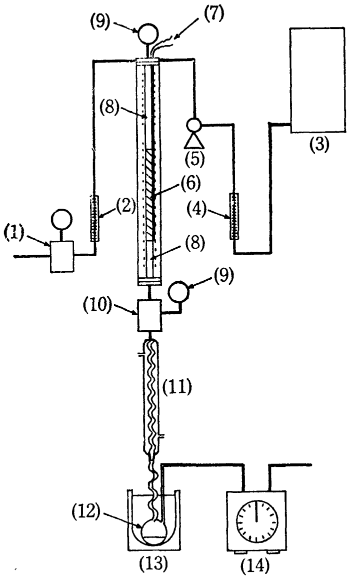

Fig. 1. Reaction apparatus.
(1): Pressure controller, (2): rotor meter, (3): acetone storage tank, (4): rotor meter, (5): plunger pump, (6): catalyst, (7): thermocouple, (8): porcelain chips, (9): pressure gauge, (10): pressure control valve, (11): water condenser, (12): receiver, (13): methanol-dry ice bath, (14): gas meter.

Apparatus and Procedure. Experiments were carried out with a continuous flow unit (Fig. 1). A stainless steel tube, 500 mm in length and 10 mm in inside diameter, was used as a reactor. The reactor was heated electrically with heaters separately controlled. Temperatures at the reaction zone were measured with thermocouples inserted in a thermowell extending longitudinally through the center of the reactor.

The catalyst in the form of 16—24 mesh particles (15 ml) was packed in the middle of the reactor. The remainder of the reactor was filled with porcelain chips and served as a preheating section. The chips were previously confirmed to have no appreciable catalytic activity.

After temperature and pressure had reached difinite levels (usually after 2 hr), the liquid products were collected in a receiver held in a methanol-dry ice bath and analyzed by means of gas chromatography.

The operating conditions were so chosen that acetone was always kept in the liquid state in the reactor. The major by-products were isopropyl alcohol, mesityl oxide and diisobutyl ketone. Other by-products such as hexanes and higher ketones were found in trace amount.

The conversion of acetone and the selectivity of each component were defined by the following equations:

$$\%\ \text{conversion} = \frac{y_{\mathrm{IPA}} + 2(y_{\mathrm{MIBK}} + y_{\mathrm{MO}}) + 3y_{\mathrm{DIBK}}}{y_{\mathrm{A}} + y_{\mathrm{IPA}} + 2(y_{\mathrm{MIBK}} + y_{\mathrm{MO}}) + 3y_{\mathrm{DIBK}}}$$

$$\%\ \text{selectivity} = \frac{y_{\mathrm{IPA}},\ 2y_{\mathrm{MIBK}},\ 2y_{\mathrm{MO}}\ \text{or}\ 3y_{\mathrm{DIBK}}}{y_{\mathrm{IPA}} + 2(y_{\mathrm{MIBK}} + y_{\mathrm{MO}}) + 3y_{\mathrm{DIBK}}}$$

where y_{IPA}, y_{MIBK}, y_{MO}, y_{DIBK} and y_{A} denote mole fractions of isopropyl alcohol, methylisobutyl ketone, mesityl oxide, diisobutyl ketone and unconverted acetone, respectively.

Analysis. The product was determined by use of Shimadzu GC-2B gas chromatographic apparatus with the column (3 m in length, 4 mm in diameter) containing 30—60 mesh Shimalite coated with 15% PEG-1,000. Both the column and detector were kept at 95 °C. The flow rate of carrier gas (H_2) was adjusted to 60 ml/min.

Results

Effect of Mass Transfer. Acetone conversion changes with the acetone flow rate at a fixed liquid hourly space velocity (LHSV) and with catalyst particle size (Table 1). The data indicate that the effect of linear velocity on the acetone conversion is insignificant so long as the size of particles remains below 0.5 mm.

Table 1. Effect of mass transfer

Catalyst		Acetone Charge Rate (mol/hr.)	Acetone Conversion (%)
Mesh	Mean Particle Diameter (mm)		
8—12	1.880	0.275	18.3
		0.550	17.9
		0.825	18.1
16—24	0.846	0.550	19.4
		0.825	19.5
24—48	0.491	0.275	20.8
		0.550	20.7
		0.825	20.8
48—100	0.221	0.550	20.7
		0.825	20.5

Data obtained at 122 °C, 19.5 kg/cm^2, 4 hr^{-1}.
Acetone LHSV and 0.4 hydrogen/acetone mole ratio.

Effect of Temperature. The conversion of acetone and the selectivity of each component in the temperature range 110—140 °C are shown in Fig. 2. The conversion of acetone increased monotonously with temperature throughout the range. Although the selectivity gradually decreased with an increase in conversion, it still remained above 90 mol%. The major by-product was diisobutyl ketone, a trimeric condensate of acetone, formation of which being accelerated with a rise in temperature. The amount of another by-product, isopropyl alcohol, was almost unchanged with temperature remaining as low as 2 mol%. No mesityl oxide was detected.

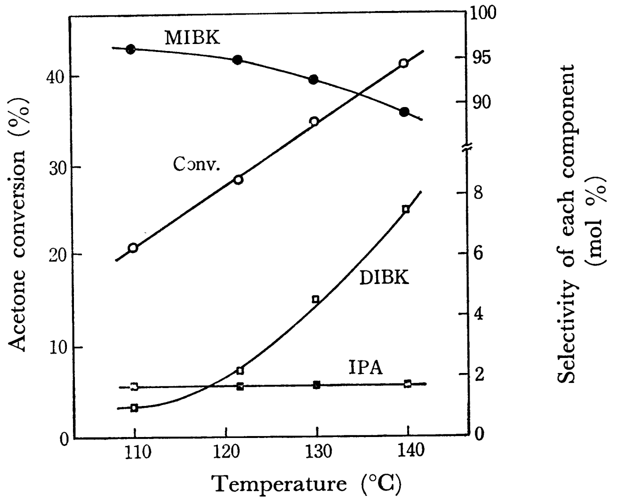

Fig. 2. Effect of temperature.
Data obtained at 20 kg/cm^2, 4 hr^{-1} acetone LHSV, 0.4 hydrogen/acetone mole ratio.

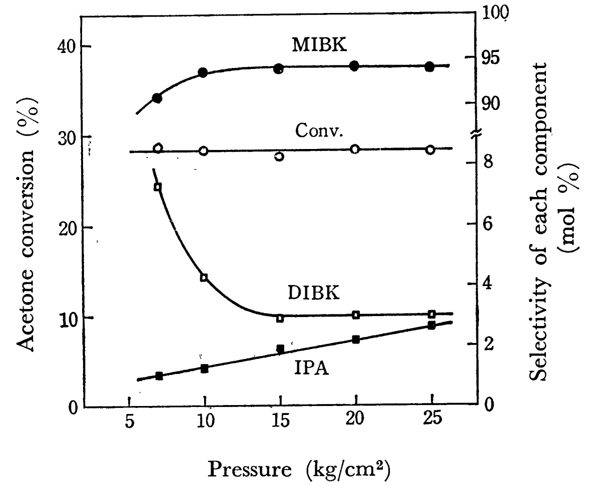

Fig. 3. Effect of pressure.
Data obtained at 120 °C, 4 hr^{-1} acetone LHSV, 0.3 hydrogen/acetone mole ratio.

Effect of Pressure. Figure 3 shows the effect of total pressure on the conversion of acetone and the selectivity to each component in the range 7—25 kg/cm^2. No appreciable change in acetone conversion with pressure was observed. However, the amount of isopropyl alcohol increased gradually with increase in pressure, the change being approximately linear. In contrast, the selectivity to diisobutyl ketone decreased with increase in pressure. The increase in the formation of diisobutyl ketone at a lower pressure or higher temperature suggests that the formation of diisobutyl ketone became dominant in vapour-phase reaction.

Thus, it is always necessary to keep acetone at the liquid phase by high pressure operation in order to obtain a good yield of methylisobutyl ketone.

Effect of Acetone Space Velocity. Figure 4 shows the effect of acetone space velocity on its conversion at 120 °C. Although the conversion decreased with increase in the space velocity, the change was less pro-

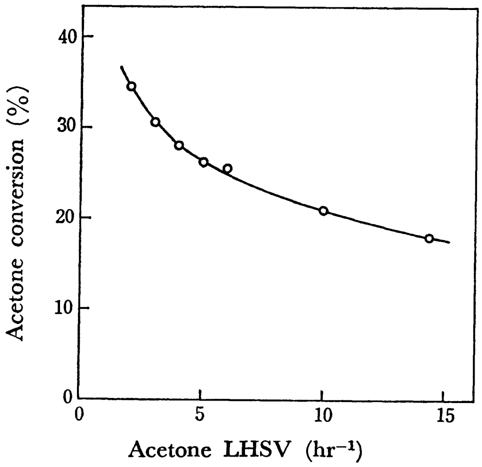

Fig. 4. Effect of acetone LHSV on acetone conversion. Data obtained at 20 kg/cm^2, 0.3—0.4 hydrogen/acetone mole ratio.

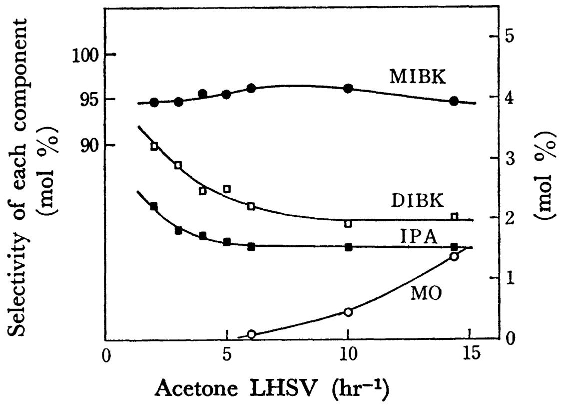

Fig. 5. Effect of acetone LHSV on selectivities. Data obtained at 20 kg/cm^2, 120 °C, 0.3—0.4 hydrogen/acetone mole ratio.

nounced in the LHSV range 5.0—15.0.

The formation of both isopropyl alcohol and diisobutyl ketone decreased with increase in space velocity (Fig. 5). These changes became slight for LHSV above 6. Mesityl oxide was detectable in the reaction products at an LHSV higher than 5.0. The change in the selectivity of methylisobutyl ketone was small under the conditions given.

Effect of Mole Ratio of Hydrogen/Acetone. The conversion of acetone remained almost unchanged, whereas the selectivity to isopropyl alcohol and diisobutyl ketone increased with an increase in mole ratio (Fig. 6). The change of selectivity to diisobutyl ketone was noticeable as compared with a slight linear change of isopropyl alcohol. No mesityl oxide was detected under these reaction conditions.

The preferable range of the mole ratio of hydrogen/acetone was deduced to be 0.2—0.4.

Effect of Water in Acetone Feed. The conversion of acetone decreased rapidly with an increase in the water content, the change being approximately linear (Fig. 7).

Since the water content of commercial acetone is usually as low as under 500 ppm, the commercial grade of acetone has no adverse effect upon the conversion of acetone to methylisobutyl ketone.

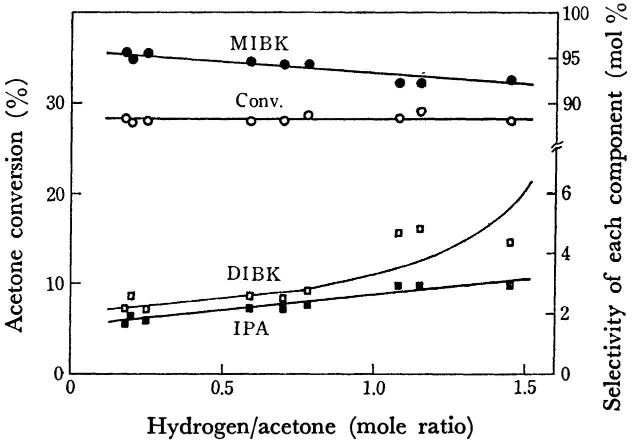

Fig. 6. Effect of mole ratio of hydrogen/acetone. Data obtained at 120 °C, 20 kg/cm^2, 4 hr^{-1} acetone LHSV.

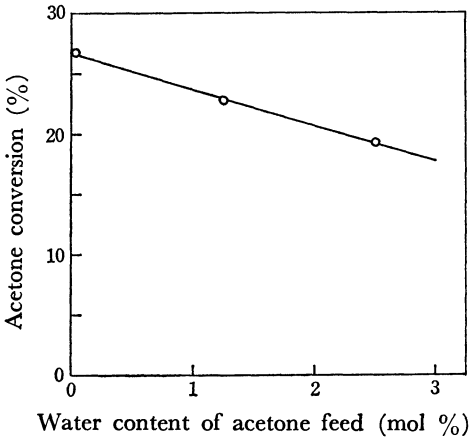

Fig. 7. Effect of water content of acetone feed on acetone conversion.
Data obtained at 120 °C, 20 kg/cm^2, 4 hr^{-1} acetone LHSV, 0.3—0.4 hydrogen/acetone mole ratio.

Discussion

Formation of mesityl oxide as an intermediate product under higher LHSV conditions suggests that the one-step reaction probably proceeds *via* a consecutive reaction mechanism:

$$2CH_3COCH_3 \rightleftharpoons (CH_3)_2C{=}CHCOCH_3 + H_2O \qquad (2)$$

$$(CH_3)_2C{=}CHCOCH_3 + H_2 \rightarrow (CH_3)_2CHCH_2COCH_3 \qquad (3)$$

The retardation of the acetone conversion into methylisobutyl ketone by the presence of water in the acetone feed is explained in terms of the reversibility of (2).

The conversion of acetone is much higher in the one-step synthesis of methylisobutyl ketone than in the synthesis of mesityl oxide under similar reaction conditions. This can be confirmed by direct comparison with the data.[9] This indicates that, in the direct conversion of acetone and hydrogen into methylisobutyl ketone, the conversion of acetone in (2) is enhanced by a rapid change of mesityl oxide into methylisobutyl ketone by (3).

Formation of isopropyl alcohol is due to the hydro-

Table 2. Results of vapor-phase reaction

Pressure (kg/cm^2)	Conversion (%)	Selectivity (mol %)			
		MIBK	IPA	DIBK	Higher ketone[a)]
2.1	40.7	66.6	3.8	26.3	3.3
1.2	38.7	65.6	2.9	28.5	3.0
0.5	38.9	62.4	3.0	31.8	2.8
0.2	34.3	64.0	1.6	31.7	2.7

a) 4,6-Dimethyl heptanone-2

Data obtained at 130 °C, 4 hr^{-1} acetone LHSV and 0.8—1.1 hydrogen/acetone mole ratio.

genation of acetone, and another by-product, diisobutyl ketone, is probably formed by further condensation of methylisobutyl ketone with acetone. Formation of diisobutyl ketone is considered to be dominant in vapour-phase reaction. For the sake of confirmation, one-step reaction in vapor-phase was examined. The results indicate that the presumption is reasonable (Table 2).

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