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One-step synthesis of methyl isobutyl ketone catalyzed by palladium supported on niobic acid

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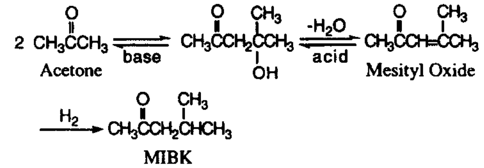
Abstract

The one-step synthesis of methyl isobutyl ketone from acetone and hydrogen was investigated by using $Pd/Nb_2O_5 \cdot nH_2O$ catalyst. $Pd/Nb_2O_5 \cdot nH_2O$ showed much higher catalytic activity and selectivity than $Pd/\gamma\text{-}Al_2O_3$. Palladium metal, supported on niobic acid, seems to inhibit the hydrogenation of C=O double bond. As a result, isopropanol was scarcely formed. Efficiency of the bifunctional catalyst probably depends not only on its acidic character but also on the dispersion state of the palladium metal on the catalyst surface. The catalytic activity of $Pd/Nb_2O_5 \cdot nH_2O$, as was expected, decreased slightly with an increase in the water content. This is one of the excellent properties of niobic acid in comparison with other usual solid acids. $Pd/Nb_2O_5 \cdot nH_2O$ catalyst also showed good durability for methyl isobutyl ketone formation.

Keywords: Methyl isobutyl ketone; Palladium/niobic acid catalyst

1. Introduction

Methyl isobutyl ketone (MIBK) is one of the most important products derived from acetone. This compound is useful not only as an organic solvent but also as a material which can be used in the preparation of paints and chemical compounds, such as stabilizers. MIBK has been commercially produced on a large scale by the conventional three-step process: the aldol condensation of acetone to form diacetone alcohol (DAA) catalyzed by a base followed by the acid catalyzed dehydration of the alcohol to mesityl oxide (MO) and the hydrogenation of the unsaturated ketone to MIBK with nickel or copper chromite catalyst.



These processes are complicated: The condensation equilibrium does not favor aldol formation, the formation of acetone by the reversible reaction of mesityl oxide with water in the second stage, and the production of a considerable amount of less useful methyl isobutyl carbinol in the final stage. In recent years, much interest has been shown in the one-step synthe-

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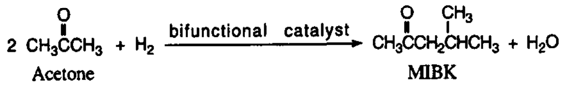
sis of MIBK from acetone and hydrogen in an attempt to improve the conventional process from an economical point of view. Several catalytic systems have been proposed to optimize this process [1–4]. Representative compositions of catalytic system are palladium supported, for example, on cation exchange resins, alumina, zeolite and zirconium phosphate. We believe that palladium can be the best catalyst for the selective hydrogenation of mesityl oxide to MIBK. This one-step process is very advantageous from the viewpoint of equilibrium and leads to an increase in the one-pass conversion of the starting material; it is, thus, economically advantageous over the three-step process.



$$\underset{\text{Acetone}}{2\,CH_3\overset{O}{\overset{\|}{C}}CH_3} + H_2 \xrightarrow{\text{bifunctional catalyst}} \underset{\text{MIBK}}{CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{CH_3}{\overset{|}{C}}HCH_3} + H_2O$$

These methods of the one step process, however, are disadvantageous in that it is not possible to increase the reaction temperature because they use resins, preparation of the catalysts is complicated and the MIBK yield is low. In our own research on catalysis, we have developed an economical process for the manufacturing of MIBK. This process is based on the direct conversion of acetone and hydrogen using a highly active catalyst. The catalyst consists of niobic acid loaded with a small amount of dispersed palladium metal [5]. The present paper describes the general characteristics of the one-step synthesis of MIBK with a palladium supported on niobic acid catalyst.

2. Experimental

2.1. Preparation of catalyst

Niobic acid (produced by CBMM Co.) was soaked in an aqueous solution of palladium chloride, reduced with hydrazine and then calcined at 300°C. The amount of palladium deposited was 0.1%.

2.2. Apparatus and procedure

2.2.1. Batch reactor system for one-step synthesis of MIBK

A 200 ml autoclave equipped with a magnetic stirrer was charged with 50 ml of acetone and then 2 g of niobic acid loaded with palladium metal was introduced in the autoclave. The autoclave was heated to 160°C and hydrogen was introduced in the autoclave. The reaction was carried out while keeping the pressure in the autoclave at 20 kg/cm^2. Hydrogen was continuously supplied for the compensation of consumed hydrogen keeping the total pressure at 20 kg/cm^2. After reacting for 2 h, the autoclave was cooled, and the reaction mixture was taken out of the autoclave and separated from the hydrogen and the catalyst. The reaction mixture was analyzed by gas chromatography.

2.2.2. Continuous flow reactor system for the one-step synthesis of MIBK

100 ml of catalyst was packed in a vertically aligned reactor having an inner diameter of 28 mm. While keeping the temperature at 160°C and the pressure at 20 kg/cm^2, the reaction is initiated by introducing acetone and hydrogen in the reactor at rates of 158 g/h (LHSV = 2 h^{-1}) and 265 Nml/min, respectively.

3. Results and discussion

Niobic acid is known to show a high acidic strength and high catalytic activity, selectivity, and stability for various types of reactions, such as esterification, hydrolysis, hydration, dehydration, Prins reaction, etc., in which water molecules participate or are liberated [6–8]. Usually acidic metal oxides show acidity on calcination at about 500°C and the acidity is lost or decreased by absorbing water. However, niobic acid shows a high acidic strength on the surface in spite of its water content. We thus expected that niobic acid, unusual solid acid,

Table 1
Dehydration of diacetone alcohol

Catalyst	Conc. in the reaction mixture (wt.-%)		
	Diacetone alcohol	Mesityl oxide	Acetone
$Nb_2O_5 \cdot nH_2O$	71.9	22.8	4.4
HY Zeolite	78.7	17.6	2.6
$SiO_2-Al_2O_3$	87.5	4.4	6.6
γ-Al_2O_3	23.7	5.2	68.9
ZrO_2	65.5	2.3	31.0

Reactant: 50 g, catalyst amount: 1.0 g., temperature: 90°C, reaction time: 4.0 h.

Table 2
Reaction mechanism for the one-step synthesis of MIBK over $Pd/Nb_2O_5 \cdot nH_2O$

Reactant	Conc. in the reaction mixture (wt.-%)			
	Acetone	DAA	MO	MIBK
Acetone	72.6	N.D.	0.1	25.4
Diacetone alcohol	33.6	N.D.	N.D.	64.6
Mesityl oxide	1.2	N.D.	N.D.	96.0

Reactant: 50 g, catalyst $Pd/Nb_2O_5 \cdot nH_2O$: 2.0 g, temperature: 160°C, H_2 pressure: 20 kg/cm^2, reaction time: 0.5 h.

may show stable catalytic activity for the one-step synthesis of MIBK in which water molecules are liberated.

3.1. Dehydration of diacetone alcohol

Table 1 shows the results of the dehydration activities of several solid acid catalysts. We found that niobic acid had the highest activity for the dehydration of diacetone alcohol. Its dehydration activity was higher than HY zeolite and SiO_2–Al_2O_3. On the other hand, in the case of γ-Al_2O_3 and ZrO_2, retro-aldol reaction predominantly occurred and a large amount of acetone was formed. This result seems to be attributed to the function of basic sites on the surface of these catalysts.

3.2. Investigation of the reaction mechanism for the one-step process

Three different reactants were used under the same reaction conditions, with $Pd/Nb_2O_5 \cdot nH_2O$ catalyst for these reactions. Table 2 shows the distribution of the products for different reactants. The hydrogenation of mesityl oxide was very rapid and MIBK was obtained quantitatively. It is interesting to note that the conversion of diacetone alcohol was much higher than the conversion of acetone. Furthermore, diacetone alcohol was not detected in these two reaction mixtures. These results indicate that the reaction proceeds via a consecutive mechanism in which mesityl oxide is firstly formed directly by condensation of acetone, without the formation of diacetone alcohol as an intermediate product, on the acid sites of the catalyst and then converted to MIBK by subsequent hydrogenation over palladium metal dispersed on the support.

3.3. Direct conversion of acetone to MIBK

3.3.1. Bifunctional catalysts for the one-step synthesis of MIBK

Table 3 shows the results of catalytic activities of several bifunctional catalysts for the one step synthesis of MIBK.

As shown in Table 3, $Pd/Nb_2O_5 \cdot n$H2O catalyst showed high activity and excellent selectivity for the formation of methyl isobutyl ketone. It should be noted that the formation of alcohols depends significantly on the nature of the catalyst used. Palladium metal supported on γ-Al_2O_3 had strong hydrogenation activity for

Table 3
Catalytic activities for the one-step synthesis of MIBK

Catalyst	Acetone Conv. (%)	MIBK	Selectivity (%)		
			IPA	MO	DIBK
0.1% Pd/ $Nb_2O_5 \cdot nH_2O$	45.6	92.5	0.6	N.D.	3.6
0.3% Pd/γ-Al_2O_3 (A)	30.1	69.2	26.8	N.D.	1.4
0.1% Pd/γ-Al_2O_3 (B)	26.3	82.5	10.8	N.D.	1.9
0.5% Pd/ $SiO_2 \cdot Al_2O_3$	7.5	81.6	10.2	0.1	0.5

Reactant: acetone 50 g, catalyst amount: 2.0 g, temperature: 160°C, H_2 pressure: 20 kg/cm^2, reaction time: 2 h.

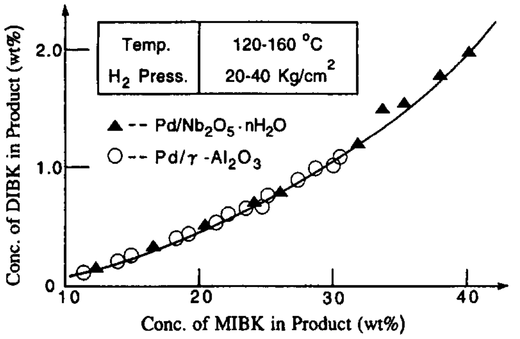


Fig. 1. Relationship between acetone conversion and DIBK selectivity.

carbonyl group, which resulted in the formation of a large amount of isopropanol. On the other hand, palladium metal supported on niobic acid seems to inhibit the hydrogenation of the C=O double bond, as a result isopropanol was scarcely formed. We are not able to explain the reason for the difference of hydrogenation activity between palladium metal supported on γ-Al_2O_3 and palladium metal supported on niobic acid clearly but it might be suggested that the dispersion state of palladium metal, deposited on the catalyst surface, strongly affects the hydrogenation activity and selectivity of the catalyst. Efficiency of the bifunctional catalyst probably depends not only on its acidic character but also on the state of dispersion of palladium metal on the catalyst surface.

3.3.2. Acetone conversion vs. diisobutyl ketone selectivity

Fig. 1 shows the relationship between the conversion of acetone and the selectivity of diisobutyl ketone (DIBK).

The experiments were carried out at 120–160°C and 20–40 kg/cm^2 over Pd/γ-Al_2O_3 and $Pd/Nb_2O_5 \cdot nH_2O$ catalysts. Under these conditions, the concentration of DIBK in the reaction mixtures are plotted against the concentration of MIBK for all reaction conditions which include temperature, hydrogen pressure and catalyst. The mechanism of DIBK formation involves the same series of reactions as the one of MIBK formation. Thus, these results suggest that the active sites for DIBK formation is the same for the MIBK formation sites.

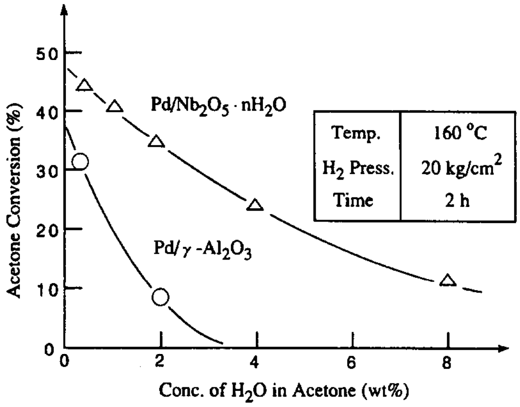


Fig. 2. Effect of water in acetone for acetone conversion.

3.3.3. Effect of water in acetone

Fig. 2 shows the effect of the water content on the conversion of acetone. In the case of Pd/γ-Al_2O_3 catalyst, the conversion of acetone decreased rapidly with an increase in the water content. In contrast, as we expected, the catalytic activity of $Pd/Nb_2O_5 \cdot nH_2O$ decreased slightly with an increase in the water content. This is the excellent property of niobic acid in comparison with other used solid acids.

3.3.4. Examination of catalyst durability

Examination of the catalyst life of $Pd/Nb_2O_5 \cdot nH_2O$ catalyst was carried out with a continuous flow reactor system. As shown in Fig. 3, both conversion of acetone and selectivity of MIBK were maintained at stationary levels for 1500 on-stream hours.

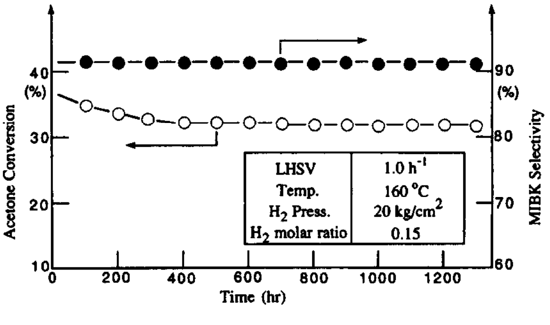


Fig. 3. Life test of $Pd/Nb_2O_5 \cdot nH_2O$ catalyst.

4. Conclusions

$Pd/Nb_2O_5 \cdot nH_2O$ catalyst showed high activity and selectivity for MIBK formation and also showed good durability for the one-step synthesis of MIBK. Furthermore, this catalyst is highly resistant to water in acetone. This catalyst is bifunctional: the acid site on niobic acid catalyzes condensation of acetone to mesityl oxide and the palladium metal, deposited on the catalyst surface, selectively hydrogenates mesityl oxide to MIBK.

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