[Regular Paper]

Selective Oxidation of Isobutane to Methacrolein by the Combined Oxide Catalysts, $\text{Ni}_2\text{P}_2\text{O}_7$ for Oxidative Dehydrogenation of Alkanes and Bi–Mo–OxideYoshiaki OBANA^{†1)}, Kazuya ETO^{†1)}, Masami ITO^{†2)}, Qing XIA^{†3)}, Hiroyasu NISHIGUCHI^{†1)}, Tatsumi ISHIHARA^{†1)}, and Yusaku TAKITA^{†1)*}^{†1)} Dept. of Applied Chemistry, Faculty of Engineering, Oita University, Dannoharu 700, Oita 870-1192, JAPAN^{†2)} Research and Development Center, Oita University, Dannoharu 700, Oita 870-1192, JAPAN^{†3)} Venture Business Laboratory, Oita University, Dannoharu 700, Oita 870-1192, JAPAN

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Direct formation of methacrolein from isobutane was investigated using a combination of the catalyst effective for oxidative dehydrogenation of isobutane, $\text{Ni}_2\text{P}_2\text{O}_7$, and the catalyst effective for selective oxidation of olefins, Bi–Mo–Oxide. Methacrolein was formed with the selectivity as high as 65% in a reactor with two catalyst beds in series. A mixed catalyst consisting of a mixture of the powders of both catalysts was effective for isobutene formation, although the conversion was reduced, whereas a mixture of granules was less effective. Addition of water vapor to the reaction system reduced the formation of oxygenates and promoted the formation of isobutene.

Keywords

Catalytic oxidation isobutane, Methacrolein formation, Nickel pyrophosphate catalyst, Bismuth molybdenum oxide, Oxide mixture

1. Introduction

Selective oxidation of alkanes is one of the most challenging chemical processes because of the difficulty in stopping the oxidation at the intermediate stages corresponding to olefin, alcohol, aldehyde, carboxylic acid, or ketone formation. Various studies have investigated the catalytic oxidation of lower alkanes over various oxide catalysts, including Mg–V–O^(1),2), $\text{V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ ³⁾, Pt/Ceramic foam⁴⁾, $\text{Ag}_{0.01}\text{Bi}_{0.85}\text{V}_{0.54}\text{Mo}_{0.45}\text{O}_4$ ^{5),6)}, Bi–Mo–O/TiO₂⁷⁾, B–P–O⁸⁾, $\text{V}_2\text{O}_5/\text{AlNbO}_4$ ⁹⁾, $\text{V}_2\text{O}_5/\text{TiO}_2$ ¹⁰⁾ and ZnFe_2O_4 ¹¹⁾, Sb–Re–O¹²⁾, heteropoly acids^{13)–16)}, K, Ca, and P-doped Ni–Mo–O¹⁷⁾, Pt–Sb–O¹⁸⁾, Bi–Mo–O with Nb_2O_5 ⁵⁾, Mo–V–X–O¹⁹⁾. However, no catalyst exhibiting the high selectivity and other characteristics necessary for practical use has been found so far.

Methacrolein is an important component of methylmethacrylate, the building block of poly-methylmethacrylate as a functional polymer. Methacrolein is produced industrially from isobutene using Bi–Mo based oxide catalysts promoted by Fe, Ni, Cu, and other elements at 300–450°C^{20)–22)}. The formed methacrolein is subsequently oxidized to methacrylic acid

using P–Mo–X heteropoly acid catalysts²³⁾ or is reacted with methanol to form methyl methacrylate using Pd catalysts²⁴⁾.

Our previous investigation of the partial oxidation of isobutane found that the selective oxidative dehydrogenation (ODH) of isobutane proceeds over metal phosphate catalysts such as $\text{Ni}_2\text{P}_2\text{O}_7$, CePO_4 , and LaPO_4 ^{25)–27)}. Introduction of a hydrocarbon rich feed consisting of 75 mol% isobutane, 5 mol% O_2 and 20 mol% N_2 , over these catalysts, obtained isobutene with a selectivity of higher than 80% at 450–550°C. The optimum oxygen concentration for isobutene formation was 5–15 mol%. All oxygen in the feed gas was consumed completely at these reaction temperatures. Therefore, the isobutene formation was promoted under reaction conditions that inhibited the supply of oxygen to catalysts from gaseous oxygen.

The process of methacrylic acid production from isobutane could consist of oxidative dehydrogenation of isobutane followed by the known process for selective oxidation of isobutene to methacrylic acid. However, this would be a three-step process, since methacrylic acid production from isobutene requires a two-step process. A very simple and helpful practical would be to perform the oxidative dehydrogenation of isobutane and the selective oxidation of isobutene to

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○: CoMoO₄, △: NiMoO₄, □: MoO₃, ×: Bi₂Mo₃O₁₂.

Fig. 1 XRD Pattern of the NK-1 Catalyst

methacrolein in one reactor.

The present study investigated the formation of methacrolein from isobutane using catalysts effective for the oxidative dehydrogenation of isobutane and Bi₂Mo₃O₁₂ catalyst as a representative of the catalysts for selective isobutene oxidation.

2. Experimental

2.1. Catalysts

Bi-Mo-based multi component oxide was obtained by the procedure described in the patent literature²⁸⁾. A solution containing cobalt(II) nitrate hexahydrate, iron(III) nitrate nonahydrate, nickel(II) nitrate hexahydrate and a HCl solution of bismuth nitrate pentahydrate was added to a solution containing ammonium molybdate tetrahydrate and cesium nitrate with vigorous stirring. Silica gel (5 wt%) was added to the dark brown slurry with stirring and the solvent was distilled off. The resulting powder was dried at 300°C overnight and was calcined at 650°C for 4 h in air. The resulting dark brown solid was pressed and crushed into two different particle sizes; < 250 μm and 1.18-0.45 mm (14-32 mesh). This Bi-Mo-Oxide catalyst has a formula of Bi₁-Mo₁₂-Fe₁-Co₆-Ni₂-Cs_{0.14}-O_x and is denoted as NK-1. The XRD pattern of NK-1 is shown in Fig. 1, and indicates that NK-1 is mainly composed of CoMoO₄, NiMoO₄, MoO₃, and Bi₂Mo₃O₁₂.

Nickel pyrophosphate was prepared by the following procedure. An aqueous solution of sodium pyrophosphate was added to an aqueous solution of nickel nitrate with stirring and the precipitate formed was separated by filtration. The precipitate was adequately washed with pure water and then dried at 130°C overnight. The catalyst powder calcined at 600°C for 5 h in air pressed into pellets and then crushed into 14-32 mesh granules.

Fig. 2 Schematic Diagram of the Reactor with Two Catalyst Beds

2.2. Apparatus and Reaction Procedure

Catalytic reactions were carried out using an ordinary flow-type reaction system with a fixed catalyst bed (i.d. 12 mm), as described elsewhere²⁾. The 14-32 mesh SiC granules were charged in the upper and the lower parts of the reactor (so-called pre- and post-catalytic volume) to avoid homogeneous oxidation of the reactant and the reaction products, respectively. The reactant gas mixture, which consisted of 75 mol% isobutane, 5 mol% oxygen, and 20 mol% nitrogen as an internal standard, was fed into the reactor. The reactant gas and effluent gas were analyzed by gas chromatography with separation columns of molecular sieve 13X, activated alumina, thermon 1000 and PEG 1000.

The reactor with two fixed beds is shown in Fig. 2. Reaction temperatures for each catalyst bed could be controlled separately. Since oxygen in the feed gas is consumed in the first stage catalyst bed, extra oxygen was supplied just before the entrance of the second stage catalyst bed.

3. Results and Discussion

3.1. Oxidation of Isobutene and Isobutane over the Complex Oxide (NK-1)

Bi-Mo-based oxides are effective catalysts for the selective oxidation of propene and isobutene to the corresponding aldehydes: acrolein and methacrolein. Industrial catalysts incorporate many other elements such as Fe, Co, K, and Cs added to the Bi-Mo oxide to improve selectivity and activity. In general, isobutene is more basic than propene, suggesting that isobutene will be strongly adsorbed on the catalyst. To moderate the acidity, an alkaline or alkaline earth element is often added to the Bi-Mo-based oxide catalysts for isobutene oxidation.

We selected the multi-component Bi-Mo-X-Oxide

Table 1 Oxidation of Isobutene over NK-1 Catalyst

Temp. [°C]	Conversion [%]		Rate of formation [μmol/min]		Selectivity [%]	
	<i>i</i> -C ₄ H ₈	O ₂	MAL + MAA	CO _x	MAL + MAA	CO _x
300	8.6	8.1	4.4	1.1	76.1	17.0
350	40.2	31.6	19.3	5.7	71.1	22.3
400	57.0	55.5	21.7	15.7	56.4	40.8
450	80.4	79.1	25.2	28.4	46.1	51.9
500	66.1	85.7	12.9	30.7	28.7	68.1

Catalyst: 0.83 g; Feed gas concentration (mol%): *i*-C₄H₈ 5, O₂ 20, N₂ 75, at 30 cm³/min.

Table 2 Oxidation of Isobutane over NK-1 Catalyst

Temp. [°C]	Conversion [%]		Rate of formation [μmol/min]			Selectivity [%]		
	<i>i</i> -C ₄ H ₁₀	O ₂	<i>i</i> -C ₄ H ₈	MAL + MAA	CO _x	<i>i</i> -C ₄ H ₈	MAL + MAA	CO _x
400	0.9	85.4	0.2	2.2	5.4	2.4	27.0	65.3
450	1.5	84.6	1.7	4.2	6.8	12.1	29.9	48.2
500	2.3	96.7	4.5	4.2 + 7.8	7.7	20.9	19.1	35.8

Catalyst: 1.69 g; Feed gas concentration (mol%): *i*-C₄H₁₀ 75, O₂ 5, N₂ 20, at 30 cm³/min.

catalyst (NK-1) as a selective oxidation catalyst for isobutene. The results of isobutene oxidation over this catalyst are shown in **Table 1**. The products of isobutene oxidation over NK-1 were mainly CH₂=C(CH₃)CHO, CO₂, CO and a trace amount of CH₂=C(CH₃)COOH. The conversion of isobutene was 8.6% at 300°C and increased at higher reaction temperature to 80% at around 500°C. The selectivity for CH₂=C(CH₃)CHO was as high as 70% at 400°C and decreased with higher reaction temperature to 29% at 550°C. The selectivity for CO_x (CO₂ and CO) increased with higher reaction temperature. The maximum formation of CH₂=C(CH₃)CHO was about 30.4 μmol/min·g at 450°C but less at 500°C. Although the rate of isobutene formation increased with higher reaction temperature, CO_x formation was also significantly promoted, so the selectivity for isobutene decreased. That the optimum temperature range of the prepared catalyst (NK-1) for selective isobutene oxidation is around 350-400°C.

The oxidation of isobutane was studied over NK-1 catalyst. The catalytic performance is shown in **Table 2**. The major products were CH₂=C(CH₃)CHO, isobutene, CO₂ and CO. Isobutane conversion over NK-1 catalyst was slow below 350°C and isobutane began to react at 400°C. At 400°C, the conversion of isobutane was 0.9% and the selectivities for CH₂=C(CH₃)CHO, isobutene and CO_x were 27%, 2.4% and 65%, respectively. The rate of CH₂=C(CH₃)CHO formation, 2.5 μmol/min·g, was slightly increased at 450°C. The formation of isobutene and CO_x increased appreciably. Comparison of the reactivity of isobutane (**Table 2**) and isobutene (**Table 1**) over NK-1

catalyst, shows that the reactivity of isobutene is much higher than that of isobutane. Therefore, combining NK-1 with catalysts effective for oxidative dehydrogenation of isobutane may allow the one-step formation of CH₂=C(CH₃)CHO from isobutane.

The oxidation of isobutane is less selective over NK-1 catalyst, possibly due to the direct formation of CO_x from isobutane.

3. 2. Selective Oxidation of Isobutane Using One Reactor with Separate Ni₂P₂O₇ and NK-1 Catalyst Beds

Isobutane is less active over NK-1 at 400-500°C and the selective oxidation of isobutene proceeds at 300-350°C, so the oxidation of isobutane was examined using two catalysts; NK-1 and Ni₂P₂O₇, which is effective for the oxidative dehydrogenation of isobutane, in the reactor with two catalyst beds depicted in **Fig. 2**. Ni₂P₂O₇ was located at the upper part of the reactor and NK-1 in the lower part, and extra oxygen was fed between the beds because the oxygen in the feed gas was controlled to the low concentration of 5 mol% to be consumed completely in the first catalyst bed to avoid the deep oxidation of isobutane. The first catalyst bed was kept at the optimal temperature of 550°C. The results are shown in **Table 3**.

When no oxygen was supplied between the catalyst beds, the major product was isobutene (65.4-68.0% selectivity) at every reaction temperature of the 2nd bed and the selectivity for CO_x was 20.7-21.2%. Only a small amount of CH₂=C(CH₃)CHO was formed. The formation rates of CH₂=CHCH₃, CH₃CHO, and CH₂=CC₃COOH were also very small. Therefore, the activity of the NK-1 catalyst is very low in the absence

Table 3 Oxidation of Isobutane over NK-1 Catalyst

Temp. [°C]	O ₂ feed rate [μmol/min]		Conversion [%]		Selectivity [%]								
	1st	2nd	<i>i</i> -C ₄ H ₁₀	O ₂ 2nd	<i>i</i> -C ₄ H ₈	MAL	MAA	CO _x	C ₃ H ₆	AcH	ATN	ALN	AcOH
330	57	0	3.8		67.8	2.8	0.0	21.2	5.7	1.6	0.0	0.0	0.0
330	57	61	3.6	85.1	31.0	36.9	0.5	11.4	3.6	1.1	2.2	0.68	1.4
360	53	0	4.0		68.0	4.0	0.0	19.7	5.5	2.4	0.0	0.43	0.0
360	53	61	4.1	98.5	11.7	52.7	0.7	24.3	3.6	1.4	1.5	1.21	0.91
390	52	0	3.7		65.4	3.9	0.0	20.7	6.1	2.2	0.0	0.28	0.0
390	52	60	3.9	99.0	4.7	63.4	0.3	19.0	3.7	1.6	1.3	2.5	0.86

Catalyst: 1.69 g; Feed gas concentration (mol%): *i*-C₄H₁₀ 75, O₂ 5, N₂ 20, at 30 cm³/min; Catalyst bed: 1st Ni₂P₂O₇ 0.80 g, 550°C, 2nd NK-1 3.55 g; Products: MAL CH₃C(CH₃)CHO, MAA CH₃C(CH₃)COOH, AcH CH₃CHO, ATN CH₃COCH₃, ALN CH₂CHCHO, AcOH CH₃COOH.

of gaseous oxygen. When oxygen was fed between the catalyst beds at 60–61 μmol/min, no significant influence was observed on the isobutane conversion but the product distribution was drastically changed: The selectivity for isobutene was decreased and that for CH₂=C(CH₃)CHO was increased. The selectivity for CH₂=C(CH₃)CHO was 36.5% at 330°C and increased to 65.4% at 390°C. The selectivity for CO_x was almost unchanged except at 330°C. The selectivity for C₃H₆ was slightly decreased showing that a portion of produced C₃H₆ was oxidized to CH₂=CHCHO over NK-1 in the presence of molecular oxygen. The selectivity for CH₃CHO was also decreased by the addition of oxygen, probably because some CH₃CHO produced was successively oxidized to CH₃COOH. Only a small amount of CH₃COCH₃ was obtained by the addition of oxygen before the 2nd catalyst bed. CH₃COCH₃ is formed from C₃H₈ via C₃H₇O intermediate, but no C₃H₈ formation is observed in the oxidation of isobutane over Ni₂P₂O₇^{25),26)}. The path of CH₃COCH₃ formation remains unclear.

The formation rates of CH₂=C(CH₃)CHO from CH₂=C(CH₃)CH₃ and CH₃C(CH₃)CH₃ were compared. Oxidation of CH₂=C(CH₃)CH₃ with a feed rate of 60.9 μmol/min resulted in CH₂=C(CH₃)CHO formation rates of 19.7 and 21.0 μmol/min at 330°C and 360°C, respectively, from **Table 1**. On the other hand, oxidation in the two bed reactor resulted in CH₂=C(CH₃)CHO formation rates of 22.7 and 25.1 μmol/min, whereas the formation rate of CH₂=C(CH₃)CH₃ in the first catalyst bed was estimated at 34.7 μmol/min which is much smaller than 60.9 μmol/min in the oxidation of CH₂=C(CH₃)CH₃. What is the cause of this difference? Oxygen was present in the reaction system in the oxidation of CH₂=C(CH₃)CH₃, but most of the oxygen introduced was consumed in the oxidation by the reactor with two catalyst beds at 360°C and 390°C. This may account for the increase in the formation rate of CH₂=C(CH₃)CHO by the reactor with two catalyst beds. The formation rate of CO_x was not

so much enhanced at 360°C and 390°C, which supports this hypothesis.

Selective CH₂=C(CH₃)CHO formation from isobutane was achieved using a single reactor with two catalyst beds. Optimization of the reaction conditions may further improve the CH₂=C(CH₃)CHO yields.

3.3. Isobutane Oxidation Using Mixed Catalysts of NK-1 and Ni₂P₂O₇

The reactor with two catalyst beds allowed the selective partial oxidation of isobutane, but a reactor with one catalyst bed would be more useful in practical applications. Therefore, we studied the mixing of the catalysts in one catalyst bed. The oxidation of isobutane was investigated using the mixed oxide catalyst (Ni₂P₂O₇ : NK-1 = 2 : 1 by volume) prepared by two different mixing methods and the results are shown in **Fig. 3** together with the results using NK-1 and Ni₂P₂O₇ catalysts at 450°C. The mixed oxide catalyst was first prepared by thorough mixing of the component powders in an agate mortar and pestle, followed by pressing, crushing and sieving between 14–32 meshes. The catalytic performances of Ni₂P₂O₇ and NK-1 are shown in **Fig. 3** (a) and (d). The reaction rate over the mixed powder catalyst (b) is significantly smaller than (e) that is the simple summation of (a) and (d). However, reduction in the formation rate of CO_x is responsible for most of the fall in product formation. In other words, only CO_x formation was suppressed. The close proximity of the active sites of both catalysts might inhibit the deep oxidation of isobutene over Ni₂P₂O₇. In contrast, preparation of mixed catalyst by mixing of the components as 14–32 mesh granules caused a significant reduction in activity, as shown in **Fig. 3** (c). Comparison of (b) and (c) in **Fig. 3** shows the consumption rate of isobutane was smaller than that over the mixed powder catalyst. The catalytic activity and product distribution of the mixed powder catalyst (c) were very similar to those of the NK-1 catalyst (d), suggesting that the activity of the NK-1 was dominant. The catalytic activity of NK-1 is stronger than that of

Catalyst: Ni₂P₂O₇ 1.68 g; mixtures: Ni₂P₂O₇ 1.68 g + NK-1 0.98 g, NK-1 0.98 g; simulation: (a) + (d), 450°C, granule 14-32 mesh.

Isobutene, CH₂=C(CH₃)CHO + CH₂=C(CH₃)COOH, CH₂=C(CH₃)CHO + CH₂=C(CH₃)COOH, CO_x.

Fig. 3 Oxidation of Isobutane over Mixed Oxide Catalysts

Ni₂P₂O₇ for isobutane oxidation, so that CO_x formation requires much more oxygen than the formation of the other products. In the oxidation of isobutane over the mixture of granules of two catalysts, the oxygen supply would be rapidly consumed over NK-1, so the concentration of oxygen in the reaction system would be lower than that required for the reaction catalyzed by the single Ni₂P₂O₇ catalyst. At lower oxygen concentrations, the isobutane oxidation will not proceed over the Ni₂P₂O₇ catalyst. This mechanism may account for the product distribution over the mechanical mixture of granules. It is concluded that the powder mixing is better than the granule mixing for the preparation of the mixed catalyst. Optimization of the reaction conditions may improve the yields of CH₂=C(CH₃)CHO and CH₂=C(CH₃)COOH, but seems to be difficult the performance of the reactor with separate catalyst beds.

3. 4. Effect of the Composition of the Catalyst

The effects of the weight percentage of NK-1 in the mixed catalyst (Ni₂P₂O₇ and NK-1) on the isobutane oxidation at 450°C are shown in Fig. 4. Isobutane conversion over Ni₂P₂O₇ was 1.8% and increased with NK-1 concentration up to 3.6% at 80% NK-1. The conversion over pure NK-1 was smaller than over pure

Conversion: ● O₂, ○ isobutane; Yield: △ isobutene, ▽ CH₂=C(CH₃)CHO + CH₂=C(CH₃)COOH, □ CO_x; Reaction temperature 450°C.

Fig. 4 Effects of NK-1 Concentration on the Reaction

Ni₂P₂O₇. Oxygen conversion reached nearly 100% at 50-75% NK-1. The yield of isobutene was as high as 1.36% over the Ni₂P₂O₇ catalyst and decreased in proportion to the NK-1 concentration, whereas the sum of the yields of CH₂=C(CH₃)CHO and CH₂=C(CH₃)COOH increased with NK-1 content to a maximum of 75% and then decreased to as low as 0.19% over pure NK-1 catalyst. The yield of CO_x over the pure Ni₂P₂O₇ catalyst was as small as 0.44% but was almost independent of the composition of the catalysts above 33% NK-1. The optimum concentration of NK-1 for CH₂=C(CH₃)CHO and CH₂=C(CH₃)COOH formation is between 75% and 100%.

The catalytic activities of the two catalysts were almost the same for isobutane consumption. Therefore, if isobutane oxidation takes place separately on the surface of both catalysts, the isobutane conversion should be independent of the composition of the catalysts. However, the promotion observed by mixing the catalysts indicates that isobutene molecules formed on the Ni₂P₂O₇ catalyst moved to the surface of the NK-1 catalyst. Re-adsorption of formed isobutene onto the Ni₂P₂O₇ surface may be reduced due to the presence of NK-1. This will account for the synergy

Table 4 Effect of Water Vapor on the Isobutane Oxidation over the Granule Mixed Catalyst

Concentration of water vapor		0 mol%			10 mol%		
Temperature [°C]		400	425	450	400	425	450
Conversion [%]	<i>i</i> -C ₄ H ₁₀	1.9	2.3	3.6	1.8	2.0	3.9
	O ₂	98.1	98.5	99.5	96.0	98.8	98.7
Yield [%]	CH ₄			0.130		0.022	0.285
	C ₃ H ₆		0.055	0.454		0.056	0.542
	C ₄ H ₈	0.201	0.324	0.889	0.194	0.248	1.070
	CO	0.251	0.294	0.403	0.211	0.142	0.417
	CO ₂	0.473	0.446	0.310	0.470	0.442	0.339
	CH ₃ CHO	0.025	0.071	0.072	0.040	0.062	0.059
	CH ₃ C(CH ₃)CHO	0.027	0.053	0.083			0.059
	CH ₃ COCH ₃	0.049	0.055	0.058	0.061	0.076	0.062
	CH ₂ =CHCHO	0.021	0.035	0.050	0.025	0.036	0.035
	CH ₂ =C(CH ₃)CHO	0.749	0.869	0.972	0.707	0.846	0.991
	CH ₂ =C(CH ₃)COOH	0.015			0.031	0.026	
	CH ₃ OH	0.032	0.062	0.011			
	C ₂ H ₅ OH	0.011	0.012				
	CH ₃ COOH		0.030	0.022		0.044	0.035

Catalyst: 0.375 g Ni₂P₂O₇, 1.125 g NK-1; Feed gas: 75 mol% C₄H₁₀, 5 mol% O₂, balance N₂, at 30 cm³/min.

effect of the mixing of the catalysts. The specific surface areas of the Ni₂P₂O₇ and NK-1 catalysts were 27 m²/g and 19 m²/g, respectively. This difference in specific surface areas may account for the shift of the maxima of the isobutane conversion and the selectivity for CH₂=C(CH₃)CH₃ from the expected 50% to the NK-1 rich region.

3. 5. Effect of Water Vapor Addition into the Feed Gas on Isobutane Oxidation

The effect of water vapor on isobutane oxidation was studied over the mechanical (granule) mixture of 25 wt% of Ni₂P₂O₇ and 75 wt% of NK-1 as shown in Table 4.

The formation rates of the products were similar at 400°C and 425°C, but those of oxygen containing products were decreased and those of hydrocarbons were increased in the presence of water vapor at 450°C. The presence of water vapor had no effect on the formation rates of CO and CO₂. The formation rates of all hydrocarbon products, methane, propylene, and isobutene, were increased. Isobutene is thought to be formed from an isobutyl intermediate. Propene and methane are also formed from an intermediate derived from adsorbed species on the acidic sites²⁹. Water vapor is always present in the reaction system in the oxidation of hydrocarbons since the reactants contain hydrogen atoms. The addition of 10 mol% water vapor in the feed may increase the concentration of Brönsted acid sites on the catalyst surface, and thus promote the formation of surface intermediates derived from isobutane. The increase in the formation rates of methane and propylene, and isobutene may reflect such a situation on the catalyst.

4. Conclusions

The following conclusions were obtained:

- (1) Selective oxidation of isobutane to CH₂=C(CH₃)CHO can be achieved by the use of the two catalysts effective for oxidative dehydrogenation (Ni₂P₂O₇) and allylic oxidation of olefins (NK-1, complex Bi-Mo oxide) in separate beds in one reactor.
- (2) Catalyst composed of a mixture of Ni₂P₂O₇ and NK-1 powders showed a better performance in the oxidation of isobutane than a mechanical mixture of granules of the catalyst.
- (3) NK-1 catalyst dominated the oxidation over the mechanical mixture of granules.
- (4) Optimum concentration of NK-1 for CH₂=C(CH₃)CHO and CH₂=C(CH₃)COOH formation is between 75% and 100%.
- (5) Presence of water vapor reduced the formation of oxygen containing products and enhanced the formation of hydrocarbons without changing the formation of CO and CO₂, possibly due to the increase in the concentration of Brönsted acid sites on the catalyst surface.

References

- 1) Sam, D. S. H., Soenen, V., Volta, J. C., *J. Catal.*, **123**, 417 (1990).
- 2) Kung, M. C., Kung, H. H., *J. Catal.*, **134**, 668 (1992).
- 3) Eon, J. G., Olier, R., Volta, J. C., *J. Catal.*, **145**, 318 (1994).
- 4) Erdohelyi, A., Solymosi, F., *J. Catal.*, **123**, 31 (1990).
- 5) Kim, Y. C., Ueda, W., Moro-oka, Y., *Chem. Lett.*, **1988**, 531.
- 6) Kim, Y. C., Ueda, W., Moro-oka, Y., *J. Chem. Soc., Chem. Commun.*, **1989**, 652.
- 7) Barraut, J., Magaud, L., Ganne, M., Journoux, M., *Stud. Surf. Sci. Catal.*, **82**, 305 (1994).
- 8) Otsuka, K., Urugami, Y., Komatsu, T., Hatano, M., *Stud. Surf. Sci. Catal.*, **61**, 15 (1991).

- 9) Pries de Oliveira, P. G., Lefbvre, F., Orimet, M., Eon, J. G., Volta, J. C., *J. Catal.*, **130**, 293 (1991).
- 10) Grzybowska, G., Mekess, P., Grabowski, R., Wcislo, K., Barbaux, Y., Gengembre, L., *Stud. Surf. Sci. Catal.*, **82**, 151 (1994).
- 11) Aemendariz, H., Agurilar-Rios, G., Salas, P., Sachifter, M., Arriola, H., Nava, N., *Appl. Catal. A*, **167**, 49 (1998).
- 12) Liu, H., Gaigneaux, E. M., Imoto, H., Shido, T., Iwasawa, Y., *Appl. Catal. A*, **202**, (2), 251 (2000).
- 13) Ueda, W., Suzuki, Y., *Chem. Lett.*, **1995**, 541.
- 14) Mizuno, N., Tateishi, M., Iwamoto, M., *J. Chem. Soc., Chem. Commun.*, **1994**, 1411.
- 15) Cavani, F., Commuzi, C., Dolcetti, G., Giuliano, E., Etinne, E., Finke, R.-G., Sella, G., Trifiro, F., Trovarelli, A., *J. Catal.*, **160**, 317 (1996).
- 16) Kaddouri, A., Mazzocchia, C., Tempsesti, E., *Appl. Catal. A*, **169**, L3 (1998).
- 17) Inoue, T., Oyama, S. T., Imoto, H., Asakura, K., Iwasawa, Y., *Appl. Catal. A*, **191**, (1, 2), 131 (2000).
- 18) Matsuura, I., Oda, H., Oshida, K., *Catal. Today*, **16**, 547 (1993).
- 19) For example, Jpn. Kokai Tokkyo Koho JP06-279351 (1994), JP07-10801 (1995).
- 20) Artz, D., *Catal. Today*, **18**, 173 (1993).
- 21) Misono, M., Nojiri, N., *Appl. Catal.*, **64**, 1 (1990).
- 22) For example, Jpn. Kokai Tokkyo Koho JP50-105606 (1975); JP51-63112 (1976); JP55-057533 (1980); JP55-085535 (1980); JP56-012331 (1981); JP56-095135 (1981); JP56-161341 (1981).
- 23) For example, Jpn. Kokai Tokkyo Koho JP54-022319 (1979); JP 54-106419 (1979); JP 55-105641 (1980); JP 55-122734 (1980); JP 56-037050 (1981); U.S. Pat. 4321160; Jpn. Kokai Tokkyo Koho JP 57-012830 (1982); JP 57-045130 (1982); JP 57-072937 (1982).
- 24) For example, Jpn. Kokai Tokkyo Koho JP 09-057101 (1997); EP972759.
- 25) Takita, Y., Kurosaki, K., Mizuhara, Y., Ishihara, T., *Chem. Lett.*, **1993**, 335.
- 26) Takita, Y., Sano, K., Kurosaki, K., Kawata, N., Nishiguchi, H., Ito, M., Ishihara, T., *Appl. Catal. A*, **167**, 49 (1998).
- 27) Takita, Y., Sano, K., Muraya, T., Nishiguchi, H., Kawata, N., Ito, M., Akbay, T., Ishihara, T., *Appl. Catal. A*, **170**, 23 (1998).
- 28) Jpn. Kokai Tokkyo Koho JP50-105606 (1975).
- 29) Kotrel, S., Knözinger, H., Gates, B. C., *Microporous microporous mater.*, **35-36**, 11 (2000).

要 旨

アルカンの酸化的脱水素触媒の $\text{Ni}_2\text{P}_2\text{O}_7$ と Bi-Mo-酸化物の組合せによるイソブタンのメタクロレインへの選択的酸化反応

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アルカンの酸化的脱水素反応に有効なピロリン酸ニッケル触媒とオレフィンのアリル型酸化反応に有効な Bi-Mo₁₂-Fe₁-Co₆-Ni₂-Cs_{0.14}-O_x 触媒の組合せによるイソブタンのメタクロレインへの直接合成について検討した。二つの触媒層を持つ一つの反応器での酸化ではメタクロレインが 65% もの高い選択率で生

成した。両触媒を粉末混合した触媒では CO_x への酸化分解は抑制され、イソブテン合成に活性であったが、粒体混合した触媒の活性は低かった。反応系への水蒸気の添加は含酸素化合物の生成を抑制し、イソブテンの生成を促進した。