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Hydroconversion of Dimethylpentanes from Methylcyclohexane Using Two Consecutive Reactors Packed with Pt-modified Solid Acid Catalyst and Supported Ir Catalyst

Ryuichiro OHNISHI [†1)], Takeshi SUGII [†2)], Hayato DOI [†2)], Yoshinori SAKAMOTO [†1)], and Yuichi KAMIYA [†1)]*

[†1)] Research Faculty of Environmental Earth Science, Hokkaido University, Kita-10 Nishi-5, Kita-ku, Sapporo 060-0810, JAPAN
[†2)] Graduate School of Environmental Earth Science, Hokkaido University, Kita-10 Nishi-5, Kita-ku, Sapporo 060-0810, JAPAN

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Hydroconversion of methylcyclohexane was conducted over various noble metal-loaded catalysts at 493 K and atmospheric pressure. On the bases of the proposed reaction route and the rate of reaction over Ir/H-β zeolite, which was the best catalyst examined, we concluded that the low yield of the desired dimethylpentanes (18%) and high yield of undesired methylhexanes (25%) were due to two reasons: (1) formation of ethylcyclopentane with high selectivity at low conversions and (2) higher ring-opening rate of ethylcyclopentane (a precursor of methylhexanes) than that of dimethylcyclopentanes (a precursor of dimethylpentanes). In order to improve the yield of dimethylpentanes, two catalysts for ring contraction from methylcyclohexane to ethyl- or dimethyl-cyclopentanes (Pt–$H_4SiW_{12}O_{40}/SiO_2$ or Pt/H-β) and for ring opening of the produced cyclopentanes (Ir/Al_2O_3) were used either in one reactor as a physical mixture or in two separate reactors connected in series. When the physical mixture (Pt–$H_4SiW_{12}O_{40}/SiO_2$ and Ir/Al_2O_3) was used, there was only a slight increase in the dimethylpentanes yield (20%) with a large amount of undesired products, such as monobranched heptanes and cracked products. In contrast, when two consecutive reactors packed with Ir/H-β and Ir/Al_2O_3 were used, the yield of dimethylpentanes increased to 30%, which was nearly two times of that of methylhexanes, at a 65% conversion of methylcyclohexane, while the yield of undesired methylhexanes was about 15%.

Keywords
Supported iridium catalyst, Ring contraction, Ring opening, Clean gasoline, Consecutive reactors

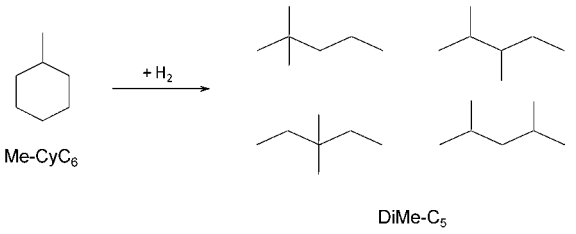
1. Introduction

Although high octane number aromatics are beneficial for motor fuels, aromatics also have shown undesirable properties, such as carcinogenicity, high carbon dioxide emission when are combusted, and possible formation of benzene from alkylbenzenes during engine start-up. For these reasons, the amounts of aromatics in gasoline should be reduced. Highly branched acyclic alkanes are thought to be ideal substitutes for aromatics since they are environmentally friendly compared to aromatics and have comparable octane numbers and clean burning characteristics. Although skeletal isomerization of linear alkanes to branched acyclic alkanes is industrially important, production of highly branched acyclic alkanes from aromatics is a more ideal route[1)].

In this paper, we report the hydroconversion of methylcyclohexane (abbreviated as Me–CyC_6), which could be produced by the hydrogenation of toluene, into multibranched heptanes, especially dimethylpentanes (DiMe–C_5), in the presence of hydrogen (**Scheme 1**). Bifunctional catalysts showing activity for both ring-opening and isomerization, including ring-contraction and/or skeletal isomerization, should be effective toward the hydroconversion of Me–CyC_6 to DiMe–C_5. However, this is a challenge because the catalyst must be capable of promoting C–C bond cleavage on the ring (the ring-opening reaction) without a decrease in the carbon number due to hydrocracking or β-scission of the resulting acyclic alkanes. There have been a few reports concerning the hydroconversion of Me–CyC_6 to DiMe–C_5 using bifunctional catalysts[2)~5)].

Figueras *et al.*[2)] have obtained only trace amounts of ring-opening products along with a large amount of ethylcyclopentane (Et–CyC_5) and dimethylcyclopentanes (DiMe–CyC_5) from the hydroconversion of Me–CyC_6 over Pt-loaded sulfated zirconia at temperatures less than 500 K. Kikuchi *et al.*[3),4)] have found that the product selectivity strongly depends on the Na^+ ion-exchange level of the H-Y zeolite in the case of the reaction over Rh/Na-H-Y. By adjusting the exchange level, they have obtained DiMe–C_5 in a 22% yield with

* To whom correspondence should be addressed.
* E-mail: kamiya@ees.hokudai.ac.jp



Scheme 1 Hydroconversion of Methylcyclohexane into Dimethylpentanes

an 86% conversion using a 3 wt% Rh/Na-H-Y catalyst (Na : H = 34 : 66) at 573 K and 3 MPa with H_2/Me–CyC_6 = 5.

McVicker *et al.*[6),7)] have reported that the ring-opening of Me–CyC_6 in the presence of hydrogen proceeds selectively over 0.9 wt% Ir/Al_2O_3 (87% selectivity at 15% conversion at 578 K). They have further reported that the Ir/Al_2O_3 catalyst shows extremely high selectivity (99%) for the ring-opening reaction of three DiMe–CyC_5 (1,1-, 1,2-, and 1,3-dimethylcyclopentane) and Et–CyC_5 and that a cyclopentane ring can be opened more easily than a cyclohexane ring. On the basis of these results, they have proposed that a combination of a solid acid, which is effective for ring-contraction, and a supported Ir catalyst is active toward the selective hydroconversion of Me–CyC_6 to the corresponding acyclic alkanes. However, since their aim was to synthesize linear alkanes for use in diesel fuel, they did not investigate the synthesis of DiMe–C_5 from Me–CyC_6 by hydroconversion. Resasco and coworkers[5)] have reported the hydroconversion of Me–CyC_6 into DiMe–C_5 by using two catalysts: Me–CyC_6 is converted to DiMe–CyC_5 over Pt/H-Y, and then the resulting DiMe–CyC_5 is converted to DiMe–C_5 over Ir/SiO_2. At 553 and 533 K, respectively, and 2 MPa with H_2/Me–CyC_6 = 40, the yield of DiMe–C_5 is reported to be 24.5%, and the yields of the undesired methylhexanes and cracked products are 12.6 and 3.1%, respectively. In addition, they have calculated the research octane number (RON) and motor octane number (MON) and show that the reaction products give higher RON and MON than Me–CyC_6 does.

Here we report our studies to improve the yield of DiMe–C_5 obtained from the hydroconversion of Me–CyC_6. First, we conducted the reaction over various noble metal-loaded catalysts and investigated the reasons for the low yield of DiMe–C_5 over iridium-loaded H-β catalyst, which was the best among the single component catalysts examined. After gaining insight into the reasons for the low yield by examining the reaction pathways and comparing the reaction rates of the individual steps, we were able to improve the yield of DiMe–C_5 by using two reactors connected in series and packed with different catalysts. The first reactor was used to convert Me–CyC_6 to DiMe–CyC_5 up to the thermodynamic equilibrium level, and the second one was used for the ring-opening reaction of DiMe–CyC_5 to DiMe–C_5. We carried out the reactions at atmospheric pressure. In order to avoid the formation of toluene by dehydrogenation of Me–CyC_6, the reaction was conducted at 493 K. Under the reaction conditions, the yield of toluene was less than 1.5% due to chemical equilibrium. In addition, we further discuss the roles of the iridium metal sites and acidic sites in the hydroconversion of Me–CyC_6 on the basis of the catalytic performances over various iridium-loaded catalysts in relation to analysis of X-ray diffraction (XRD) patterns, IR spectra of CO adsorbed on catalysts, and CO adsorption measurements.

2. Experimental

2. 1. Catalysts

Five noble metals, including Ir, Rh, Ru, Pd, and Pt, were loaded on various solid acids, including H-β zeolite (Süd-Chemie, Si/Al = 75), H-ZSM-5 zeolite (Tosoh Corp., Si/Al = 36), 15 wt% $H_4SiW_{12}O_{40}/SiO_2$ (abbreviated as H4SiW), an acidic Cs salt of $H_3PW_{12}O_{40}$ ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$, abbreviated as Cs2.5PW), sulfated zirconia (abbreviated as S–Zr), and tungsten zirconia (abbreviated as W–Zr), by using an impregnation method with an aqueous solution of the corresponding metal chlorides. Similarly, these noble metals were loaded on non-acidic or weakly-acidic supports, such as a fully neutralized Cs salt of a heteropolyacid ($Cs_3PW_{12}O_{40}$, abbreviated as Cs3.0PW), SiO_2 (Aerosil 300, 274 $m^2 \cdot g^{-1}$), and γ-Al_2O_3 (Reference Catalyst of the Catalysis Society of Japan, JRC-ALO-4). The amount of the metals loaded was adjusted to 2.0 wt%.

H4SiW was prepared by using an incipient wetness method with SiO_2 (Aerosil 300) and an aqueous solution of $H_4SiW_{12}O_{40}$ (Nippon Inorganic Colour & Chemical Co., Ltd.), as reported previously[8)]. S–Zr was obtained by reacting sulfuric acid (Wako Pure Chem. Ind., Ltd.) and zirconium hydroxide (Daiichi Kigenso Kagaku Kogyo Co., Ltd.), followed by calcination at 893 K for 5 h, as reported in the literature[9)]. W–Zr was prepared by using an incipient wetness method with zirconium hydroxide and an aqueous solution of ammonium tungstate (Wako Pure Chem. Ind., Ltd.), followed by calcination at 1073 K for 3 h, as previously reported[10)]. Cs2.5PW and Cs3.0PW were prepared by using a titration method, in which an aqueous solution of cesium carbonate (Aldrich) was added dropwise with vigorous stirring at ambient temperature to an aqueous solution of $H_3PW_{12}O_{40}$ (Nippon Inorganic Colour & Chemical Co., Ltd.), as described previously[11),12)]. Water was removed from the resulting colloidal solution after aging overnight on a rotary evaporator.

2. 2. Catalytic Reaction

Hydroconversion (hydrogenolysis and skeletal isomerization in the presence of hydrogen) of Me–CyC_6 was conducted in a fixed-bed flow reactor (Pyrex, 10 mm inner diameter) at atmospheric pressure. The catalyst (0.1-2 g) diluted with a three-fold volume of silica was treated in a flow of oxygen (50 ml·min^{-1}) for 2 h at 573 K and in a flow of hydrogen (50 ml·min^{-1}) for 1 h at 573 K. Then, the reactant gas (Me–CyC_6 : H_2 = 1.6 : 98.4 vol%, 5-50 ml·min^{-1}) was fed over the catalyst at 493 K. The composition of the gas at the outlet of the reactor was analyzed using a gas chromatograph (Shimadzu Corp., GC-14B) equipped with a flame ionization detector and a capillary column (CHROMPACK; WCOT fused silica squalane, 0.25 mm × 100 m). In some cases, the reaction was conducted using two reactors filled with different catalysts and connected in series. In the first reactor, Pt/H-β or Pt/H4SiW was used to convert Me–CyC_6 to DiMe–CyC_5 and Et–CyC_5, and in the second one, Ir/Al_2O_3 or Ir/H-β was used to perform the ring-opening reaction.

Products were separated into five classes: (1) cyclic molecules with a cyclopentane ring, including 1,1-, 1,2- and 1,3-dimethylcyclopentane (DiMe–CyC_5) and Et–CyC_5, (2) DiMe–C_5, including 2,2-, 2,3-, 2,4- and 3,3-dimethylpentane, (3) methylhexanes (abbreviated as Me–C_6), including 2- and 3-methylhexane, *n*-heptane, and 3-ethylpentane, (4) cracking products (abbreviated as C_{6-}) with carbon numbers less than seven, and (5) toluene (abbreviated as TOL). Hereafter, products in class (1) are referred to as CyC_5.

Similarly, hydroconversion of methylcyclopentane (Me–CyC_5) was conducted over Ir/SiO_2 in the presence of hydrogen at 493 K, where the gas composition was 5.4 vol% Me–CyC_5 and 94.6 vol% H_2.

2. 3. Other Measurements and Calculations

For all measurements, the catalyst was pretreated under the same conditions as the catalytic reaction described in section **2. 2.**

XRD patterns of the catalysts were obtained in a 2θ range of 20-60° on an XRD diffractometer (MiniFlex, Rigaku Corp.) using Cu Kα radiation (λ = 0.154 nm, 30 kV and 15 mA).

Fourier transform infrared spectroscopy (FT-IR) spectra of the CO adsorbed on the catalyst were recorded on an FT-IR spectrometer (FT/IR-230, JASCO Corp.). The catalyst wafer was exposed to CO for 30 min and then placed under vacuum for 30 min at room temperature.

The amount of CO adsorbed on the catalyst was determined by using a CO pulse measurement system (BEL-CAT, BEL Japan, Inc.) at 323 K.

Equilibrium concentrations of the reactants and products were calculated using compiled and estimated thermodynamic data of $\Delta_f H^0_{gas}$, S^o_{gas} and $C_{p,gas}$ for each molecule at various temperatures[13].

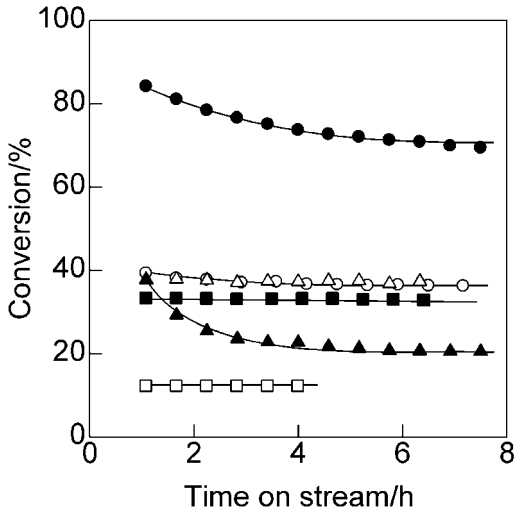


Fig. 1 Time Courses of Conversion in Hydroconversion of Me–CyC_6 over Ir (●), Rh (○), Ru (▲), Pt (△), Pd (■) and Non-metal (□) Loaded H-β Catalysts at 493 K with a Catalyst Weight of 0.1 g and a Total Flow Rate of 10 ml·min^{-1} (W/F = 0.6 g·s·ml^{-1})

3. Results

3. 1. Hydroconversion of Me–CyC_6 over Noble Metal-loaded H-β, H4SiW, and SiO_2 Catalysts

Figure 1 shows time courses for the conversion of Me–CyC_6 over noble metal-loaded H-β catalysts at 493 K with a catalyst weight of 0.1 g and a total flow rate of 10 ml·min^{-1}. The conversions were stable from the beginning of the reaction to 6-8 h of time on stream, except over Ir/H-β and Ru/H-β. The conversions over Ir/H-β and Ru/H-β decreased in the initial stage and then became stable after 5-6 h of time on stream. On the other hand, the reaction proceeded smoothly without appreciable deactivation over all noble metal-loaded H4SiW and SiO_2 catalysts (data not shown).

Table 1 summarizes conversions and selectivities for the five classes of compounds (see Experimental section) when the conversion was stable under the same reaction conditions. The SiO_2-supported noble metal catalysts were the least active, and the activities of Rh/SiO_2, Pt/SiO_2, and Pd/SiO_2 were very low. C–C bond cleavage of Me–CyC_6 proceeded only over Ir/SiO_2 and Ru/SiO_2. No CyC_5 was obtained for all of the SiO_2-supported catalysts, showing that no ring-contraction (isomerization) occurred over these catalysts under the reaction conditions. These catalysts were classified as Group 1 catalysts. On the other hand, CyC_5 was exclusively produced over noble metal-loaded H4SiW catalysts, Pd/H-β, and Pt/H-β, indicating that ring contraction from C6 ring to C5 ring occurred selectively. These catalysts were classified as Group 2 catalysts. Over other catalysts, including Ir-, Rh-, and Ru-loaded H-β, a relatively large amount of acyclic alkanes

Table 1 Catalytic Performances of Noble Metal-loaded H-β, 15 wt% $H_4SiW_{12}O_{40}/SiO_2$, and SiO_2 Catalysts in the Hydroconversion of Methylcyclohexane (Me–CyC_6)

Support[a]	Metal[b]	Conversion [%]	Selectivity to each class of products [%]					Classification of catalyst
			CyC_5[c]	DiMe–C_5[c]	Me–C_6[c]	C_{6-}[c]	TOL[c]	
H-β	Ir	70	29	17	33	20	1	Group 3
	Rh	36	76	4	8	10	2	
	Ru	20	24	1	3	72	0	
	Pd	33	98	0	0	0	2	Group 2
	Pt	37	100	0	0	0	0	
	none	12	100	0	0	0	0	
H4SiW	Ir	42	92	2	0	4	2	
	Rh	42	97	0	0	0	3	
	Pt	41	97	0	0	0	3	
	Ru	30	100	0	0	0	0	
	Pd	32	98	0	0	0	2	
	none	18	100	0	0	0	0	
SiO_2	Ir	10	0	0	59	32	9	Group 1
	Ru	20	0	0	0	100	0	
	Rh	2	0	0	0	0	100	
	Pt	2	0	0	0	0	100	
	Pd	1	0	0	0	0	100	

Reaction conditions: reaction temperature, 493 K; catalyst weight, 0.1 g; total flow rate, 10 m$l\cdot min^{-1}$; Me–CyC_6 : H_2 = 1.6 : 98.4, W/F = 0.6 g·s·ml^{-1}.
a) H4SiW = 15 wt% $H_4SiW_{12}O_{40}/SiO_2$.
b) metal loading = 2 wt%.
c) See experimental section (**2. 2.**).

Table 2 Catalytic Data of Iridium-loaded Catalysts in Hydroconversion of Me–CyC_6

Support[a]	Conversion [%]	Selectivity to each class of products [%]					Classification of catalyst
		CyC_5[b]	DiMe–C_5[b]	Me–C_6[b]	C_{6-}[b]	TOL[b]	
H-β (Si/Al = 75)	70	29	17	33	20	1	Group 3
H-ZSM-5(Si/Al = 36)	67	15	15	24	45	0	
H4SiW	42	92	2	0	4	2	Group 2
Cs2.5PW	42	93	2	0	4	1	
W–Zr	39	95	0	4	0	1	
S–Zr	38	100	0	0	0	0	
Al_2O_3	23	0	0	48	47	5	Group 1
SiO_2	10	0	0	59	32	9	
Cs3.0PW	7	0	0	55	29	16	

Reaction conditions: reaction temperature = 493 K; catalyst weight = 0.1 g; total flow rate = 10 m$l\cdot min^{-1}$; Me–CyC_6 : H_2 = 1.6 : 98.4, W/F = 0.6 g·s·ml^{-1}.
a) H4SiW = 15 wt% $H_4SiW_{12}O_{40}/SiO_2$, Cs2.5PW = $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, W–Zr = tungsten zirconia, S–Zr = sulfated zirconia, and Cs3.0PW = $Cs_3PW_{12}O_{40}$.
b) See experimental section (**2. 2.**).

(DiMe–C_5, Me–C_6 and C_{6-}) were produced along with CyC_5. These were classified as Group 3 catalysts.

3. 2. Hydroconversion of Me–CyC_6 over Various Iridium-loaded Catalysts and Characterization of These Catalysts

Table 2 summarizes the catalytic data for the hydroconversion of Me–CyC_6 over the Ir-loaded catalysts. Similar to the catalysts in **Table 1**, the iridium-loaded catalysts could be classified into three groups depending on supports: (Group 1) Ir loaded on weakly acidic or non-acidic Al_2O_3, SiO_2, and Cs3.0PW, which promoted simple C–C bond cleavage and dehydrogenation, (Group 2) Ir loaded on acidic supports, including H4SiW, Cs2.5PW, W–Zr, and S–Zr, which catalyzed ring-contraction of Me–CyC_6 to CyC_5 but scarcely afforded the products derived from C–C bond cleavage, including ring-opening, and (Group 3) Ir loaded on zelolites, including H-β and H-ZSM-5, which promoted both ring-contraction and ring-opening.

In order to discuss the catalytic properties in con-

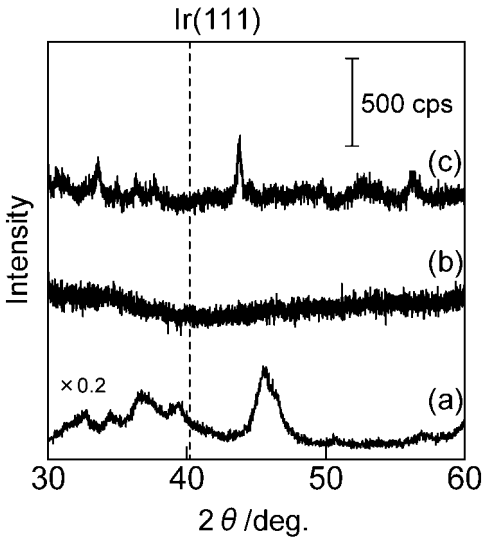


Fig. 2 XRD Patterns of (a) Ir/Al_2O_3, (b) Ir/H4SiW, and (c) Ir/H-β

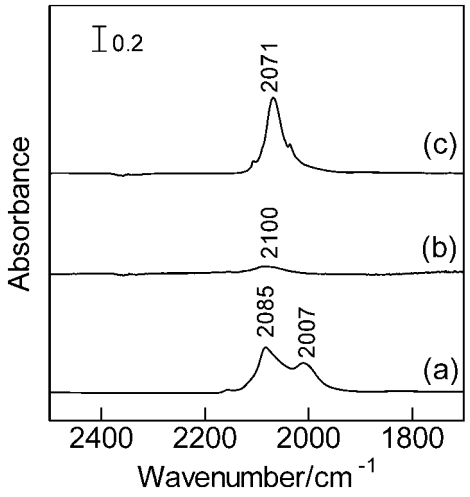


Fig. 3 IR Spectra of the CO Adsorbed on (a) Ir/Al_2O_3, (b) Ir/H4SiW, and (c) Ir/H-β

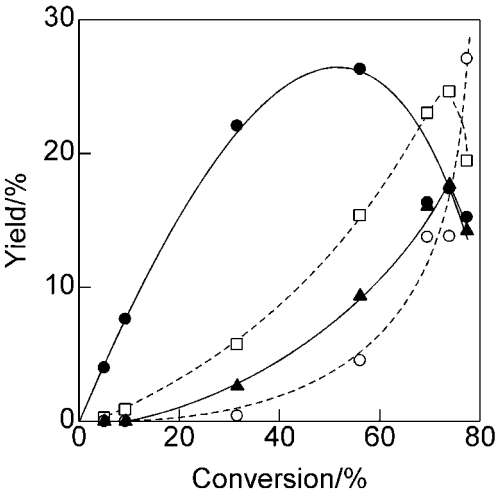
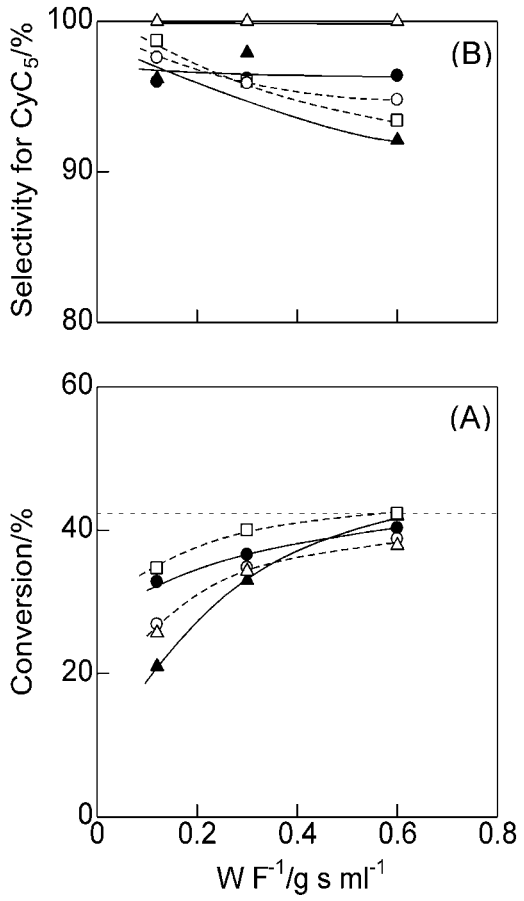


Fig. 4 Plot of the Yields of CyC_5 (●), DiMe–C_5 (▲), Me–C_6 (□) and C_{6-} (○) against Me–CyC_6 Conversion over Ir/H-β at 493 K with *W/F* in the Range of 0.03-1.05 g·s·ml^{-1}

junction with their chemical and physical properties, we will focus on Ir/Al_2O_3, Ir/H4SiW, and Ir/H-β as typical catalysts from Groups 1, 2, and 3, respectively. **Figure 2** shows the XRD patterns of Ir/Al_2O_3, Ir/H4SiW, and Ir/H-β. There was no diffraction line corresponding to metallic iridium crystallites in the XRD patterns of the three catalysts, suggesting that the iridium was highly dispersed. In **Fig. 3**, IR spectra of the CO adsorbed on Ir/Al_2O_3 showed two sharp at 2085 and 2007 cm^{-1}, which we assigned to linear CO, whereas only one sharp band was observed at 2071 cm^{-1} (linear CO) in the spectrum of Ir/H-β. In the spectrum of Ir/H4SiW, one weak band was observed at *ca.* 2100 cm^{-1}. The amounts of adsorbed CO, which were measured by using a CO pulse chemisorption method at 323 K, on Ir/Al_2O_3, Ir/H4SiW, and Ir/H-β were 101, 3, and 61 μmol·g^{-1}, respectively. Although a large amount of CO was adsorbed on Ir/Al_2O_3, only a small amount (less than 10% of Ir/Al_2O_3) of CO was adsorbed on Ir/H4SiW. This is consistent with the IR results. The amount of CO adsorbed on Ir/H-β was *ca.* 50% of that of Ir/Al_2O_3.

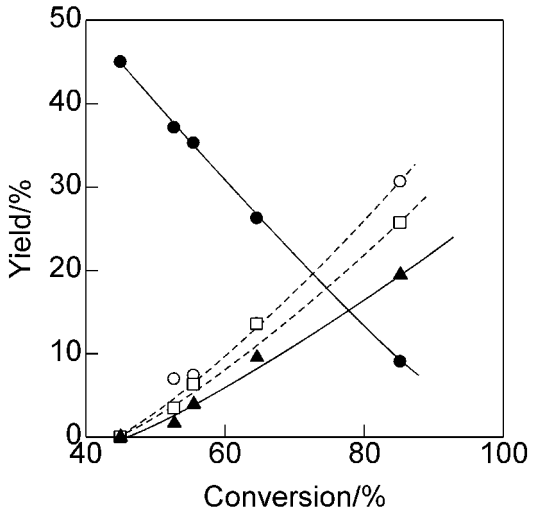
3. 3. Optimization of the Yield of DiMe–C_5 from a Single Reactor Process

As shown by the data in **Table 2**, Ir/H-β is a potential catalyst for the hydroconversion of Me–CyC_6 to DiMe–C_5 because both ring-contraction and ring opening proceeded over the catalyst. However, decomposition of DiMe–C_5 to C_{6-} is thermodynamically favorable, meaning that DiMe–C_5 decomposes to C_{6-} by hydrogenolysis. In order to maximize the one-pass yield of DiMe–C_5 over Ir/H-β, which was the best catalyst examined in this study, the weight per flow rate ratio (*W/F*) was optimized. In **Fig. 4**, the yield of each product is plotted against the conversion of Me–CyC_6. The maximum yield of DiMe–C_5 was 18% at 74% conversion, which was far lower than that of Me–C_6 (25%) and that of C_{6-} (27%). As will be discussed later (section **4. 1.**) in detail, reasons for the low yield of DiMe–C_5 for Ir/H-β were formation of Et–CyC_5 with high selectivity at low conversions and higher ring-opening rate of Et–CyC_5 (a precursor of Me–C_6) than that of DiMe–CyC_5 (a precursor of DiMe–C_5). That is to say, the formation of Et–CyC_5 should be avoided to improve the yield of DiMe–C_5. However, this cannot be prevented, because ring-contraction and ring-opening occurred simultaneously on Ir/H-β. Thus, in order to further improve the yield of DiMe–C_5, we used one catalyst for ring-contraction from Me–CyC_6 to CyC_5 and another for ring opening of the resulting CyC_5 to DiMe–C_5 packed in one reactor as a physical mixture or in two separate reactors.



Dotted line represents the equilibrium values.

Fig. 5 *W/F* Dependence of (A) Conversion and (B) Selectivity for CyC_5 over Pd/H-β (●), Ir/H4SiW (▲), Ir/Cs2.5PW (□), Ir/W–Zr (○) and Ir/S–Zr (△) at 493 K



The total mass of the catalyst was fixed to 0.5 g.

Fig. 6 Change in Yields of CyC_5 (●), $DiMe–C_5$ (▲), $Me–C_6$ (□), and C_{6-} (○) *vs.* $Me–CyC_6$ Conversion over a Physical Mixture of Pt/H4SiW (0.5-0.1 g) and Ir/Al_2O_3 (0-0.4 g) at 493 K of Reaction Temperature with a Total Flow Rate of 5 $ml \cdot min^{-1}$ ($W/F = 6\ g \cdot s \cdot ml^{-1}$)

3. 4. Hydroconversion of Me–CyC_6 over Group 2 Catalysts

Figure 5(A) shows the changes in the conversion *versus W/F* over five Group 2 catalysts. The conversions nearly reached 42% with an increase in *W/F* over all catalysts examined, and the selectivity for CyC_5 remained over 90% (see **Fig. 5(B)**). The equilibrium conversion of $Me–CyC_6$ was calculated to be 42.3% at 493.15 K, excluding reactions other than isomerization, and this value agreed well with the experimental data, as shown by the dotted line.

3. 5. Attempts to Improve the Yield of $DiMe–C_5$ by Using Physically Mixed Catalysts in a Single Reactor

We conducted the hydroconversion of $Me–CyC_6$ in the presence of a physical mixture of two catalysts (Group 1 and Group 2). As mentioned above, the formation of $Et–CyC_5$ is disadvantageous to obtain a high yield of $DiMe–C_5$, we first searched for a Group 2 catalyst having a high selectivity towards $DiMe–CyC_5$, *i.e.*, low selectivity towards $Et–CyC_5$, even at low conversion in the $Me–CyC_6$ isomerization reaction. According to McVicker *et al.*[6], formation of $Et–CyC_5$ at 10-20% $Me–CyC_6$ conversion is suppressed over zeolitic materials with higher acid strength, such as ZSM-5, USY with low Si/Al, mordenite, EU-1, and H-β. After investigating various solid acids, we found that noble metal-loaded H4SiW had a selectivity of 10% toward $Et–CyC_5$ among the various CyC_5 at 10% $Me–CyC_6$ conversion under the reaction conditions (data is not shown) and, thus, were good candidates. Since the heteropolyacid $H4SiW_{12}O_{40}$ has strong acid sites, our results are consistent with the findings of McVicker *et al.*[6]. Noble metal-loaded H4SiW must be combined with Group 1 or Group 3 type catalysts because they are inactive towards ring-opening. Thus, we attempted to improve the yield of $DiMe–C_5$ by physically mixing Pt–H4SiW (Group 2) and Ir/Al_2O_3 (Group 1).

Figure 6 shows plots of the yields of the five classes of products against $Me–CyC_6$ conversion over a physical mixture of Pt–H4SiW and Ir/Al_2O_3. In these experiments, the total amount of the catalysts and total flow rate were fixed at 0.5 g and 5 $ml \cdot min^{-1}$, respectively. The conversion increased with an increase in the concentration of Ir/Al_2O_3 in the catalyst mixture. The yield of CyC_5 linearly decreased with an increase in the conversion, indicating that ring-opening occurred. The yield of all classes of acyclic products ($DiMe–C_5$, $Me–C_6$ and C_{6-}) linearly increased. The yield of $DiMe–C_5$ was 20% at 85% conversion with catalyst masses of Pt–H4SiW and Ir/Al_2O_3 of 0.1 and 0.4 g, respectively. If there is a linear relationship between

DiMe–C_5 yield and the conversion, the yield of DiMe–C_5 should reach a maximum of about 27% at 100% conversion. This yield of DiMe–C_5 over a physical mixture of Pt–H4SiW and Ir/Al_2O_3 is far higher than that of 18% over Ir/H-β and that of 22% yield over a 3 wt% Rh/Na-H-Y catalyst (Na : H = 34 : 66)[3),4)] but is lower than that (34%) over a physical mixture of Pt/H-Y and Ir/SiO_2[5)]. Our results are still unacceptable because the undesired products Me–C_6 and C_{6-} were produced in a higher yield than DiMe–C_5 was.

3. 5. Two-step Process for Increasing the Yield of DiMe–C_5 from the Hydroconversion of Me–CyC_6

We used two consecutive reactors to increase the yield of DiMe–C_5. In the first reactor, Me–CyC_6 and CyC_5 were equilibrated over a Group 2 catalyst, and in the second, a mixture of equilibrated CyC_5 and Me–CyC_6 was reacted under hydrogenolysis conditions over a Group 1 or Group 3 catalyst. Among the Group 2 catalysts, Pt/H-β showed the highest activity and gave negligible amount of undesired toluene as shown in **Table 1**, we applied Pt/H-β as a catalyst for the first reactor. **Figure 7** shows plots of the yields of the five classes of products *versus* the Me–CyC_6 conversion using two consecutive reactors packed with Pt/H-β (Group 2) and Ir/Al_2O_3 (Group 1) in the first and second reactors, respectively. At the outlet of first reactor, the concentrations of Me–CyC_6, DiMe–CyC_5, and Et–CyC_5 were 58%, 37%, and 5%, respectively (first line of **Table 3**), which are close to the equilibrium concentrations. The mixture was passed through the second reactor in order to perform the C–C bond cleavage reaction over Ir/Al_2O_3. It should be noted that, at low conversions of Me–CyC_6 of 42-47%, C_{6-} was scarcely produced, whereas half of the CyC_5 was transformed to DiMe–C_5 and Me–C_6. During this period, the yields of DiMe–CyC_5 and Et–CyC_5 decreased by 18% and 5%, respectively, and the yields of DiMe–C_5 and Me–C_6 increased by 19% and 6%, respectively (top half of **Table 3**), suggesting that DiMe–CyC_5 and Et–CyC_5 converted mainly to DiMe–C_5 and Me–C_6, respectively, as shown in the bottom half of **Table 3**. In addition, a minor increase in the yield of Me–C_6 and C_{6-} occurred due to direct C–C bond cleavage of Me–CyC_6. Me–CyC_6 and the remaining DiMe–CyC_5 further reacted when the mass of the Ir/Al_2O_3 catalyst packed in the second reactor was higher. This is first time in our experiments that the yield of DiMe–C_5 was greater than that of Me–C_6. In fact, it was almost two times higher than that of Me–C_6. The maximum yield of DiMe–C_5 was 30%, although 35% of Me–CyC_6 remained, while the yield of Me–C_6 was 16%, which corresponded to only 30% of the equilibrium composition (55%).

In order to further improve the yield of DiMe–C_5, Ir/Al_2O_3 was replaced with a Group 3 catalyst in the second reactor to convert unreacted Me–CyC_6 to DiMe–C_5. **Figure 8** shows that the yield of DiMe–C_5 increased to 32% at 81% conversion when Pt/H4SiW and Ir/H-β were packed in the first and the second reactors, respec-

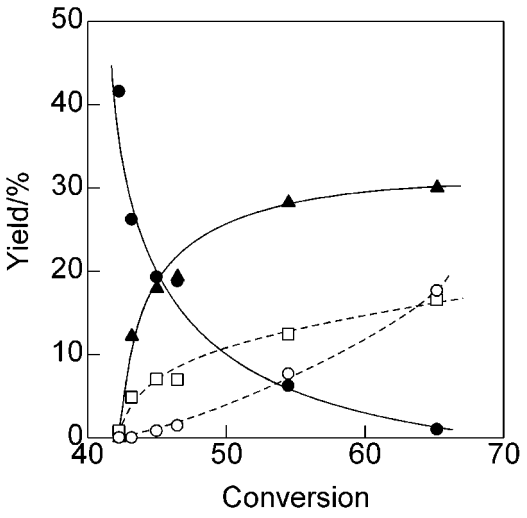


Fig. 7 Change in Yields of CyC_5 (●), DiMe–C_5 (▲), Me–C_6 (□) and C_{6-} (○) *vs.* Me–CyC_6 Conversion Using Two Consecutive Reactors Packed with Pt/H-β (0.5 g) in the First Reactor and Ir/Al_2O_3 (0.1-1 g) in the Second Reactor at 493 K with a Total Flow Rate of 10 m*l*·min^{-1}

Table 3 Concentration of the Products and Reactants at the Inlet and Outlet of the Second Reactor and the Differences between the Inlet and Outlet of the Second Reactor

	Concentration [%]					
	Me–CyC_6	DiMe–CyC_5	Et–CyC_5	DiMe–C_5	Me–C_6	C_{6-}
Inlet of the second reactor	58	37	5	0	1	0
Outlet of the second reactor (0.3 g of Ir/Al_2O_3)	54	19	0	19	7	1
Difference between inlet and outlet of the second reactor[a)]	−4	−18	−5	+19	+6	+1
Outlet of the second reactor (1.0 g of Ir/Al_2O_3)	35	1	0	30	17	18
Difference between inlet and outlet of the second reactor[a)]	−24	−36	−5	+30	+16	+18

a) Values with minus and plus refer to amounts consumed and formed, respectively.

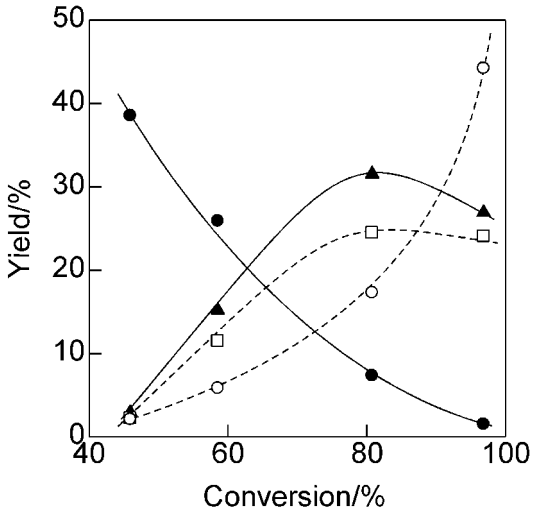
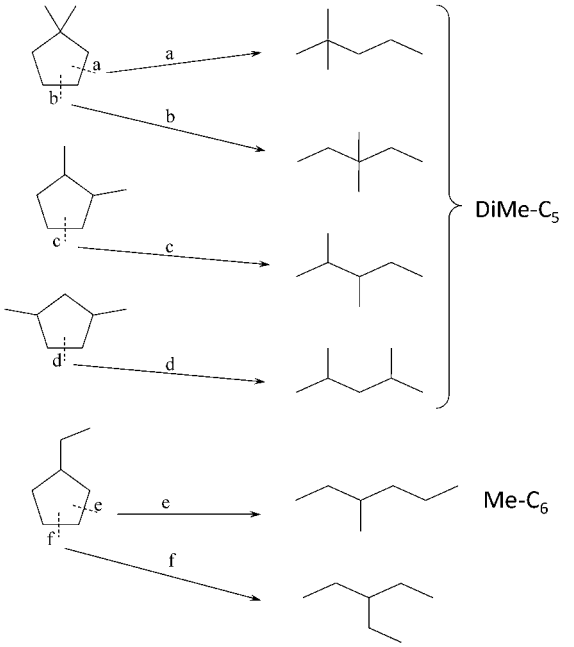


Fig. 8 Change in Yields of CyC_5 (●), DiMe–C_5 (▲), Me–C_6 (□) and C_{6-} (○) *vs.* Me–CyC_6 Conversion Using Two Consecutive Reactors with Pt/H4SiW (0.5 g) in the First Reactor and Ir/H-β (0.1-0.75 g) in the Second Reactor at 493 K with a Total Flow Rate of 10 ml·min^{-1}



Scheme 2 Products Formed by Hydrogenolysis of Methylcyclopentane and Methylcyclohexane

tively. The same yield of DiMe–C_5 was obtained when Pt/H-β and Ir/H-β were packed in the first and the second reactors, respectively. Under the reaction conditions, the equilibrium composition of DiMe–C_5 was calculated to be 43.1%, excluding the cracking reaction to form C_{6-}. The maximum yield (32%) of DiMe–C_5 corresponded to 74% of the equilibrium composition. At that time, the yield of undesired Me–C_6 was 26%, which corresponded to 47% of the equilibrium composition.

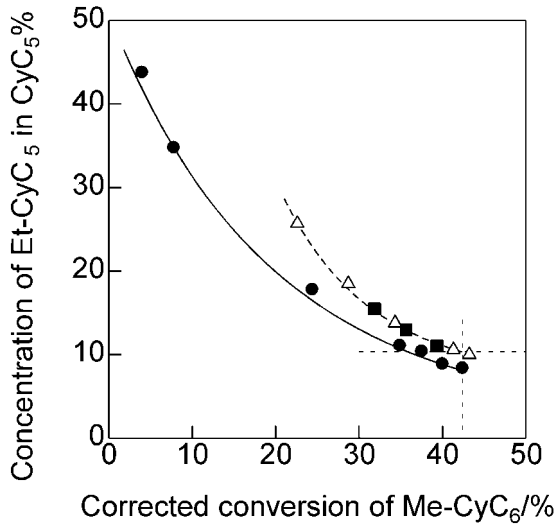
4. Discussion

4. 1. Reasons for the Low Yield of DiMe–C_5 from the Hydroconversion of Me–CyC_6 over Ir/H-β in a Single Reactor

As **Fig. 4** shows, CyC_5 forms even at low conversions, whereas the yields of the acyclic products Me–C_6 and DiMe–C_5 and cracking products C_{6-} were almost zero at low conversions and these formed with an induction period. In other words, CyC_5 was the primary product, and the acyclic products were secondary ones, which were derived from the primary products. This result implies that C–C bond in the C_6 ring is far less reactive than that in the C_5 ring in the ring-opening reaction. In fact, the reaction rate for the hydrocracking of the C_5 ring in Me–CyC_5 was 10 times faster than that of the C_6 ring in Me–CyC_6 over Ir/SiO_2: 91% and 9% conversions of Me–CyC_5 and Me–CyC_6 with *W*/*F* ratios of 0.03 and 0.61 g·s·ml^{-1}, respectively, at 493 K. McVicker *et al.* have also reported that the reaction rate for the ring-opening of the C_6 ring is one to two orders of magnitude slower than that of the C_5 ring over 0.9 wt% Ir/Al_2O_3 at 548 K and 3.54 MPa[6].

In the hydrocracking of Me–CyC_5 and Me–CyC_6 over Ir/SiO_2, monobranched acyclic alkanes including Me–C_5 and Me–C_6 were mainly produced from the hydrocracking of Me–CyC_5 and Me–CyC_6 over Ir/SiO_2, respectively, suggesting that the ring-opening predominantly occurs at an unsubstituted C–C bond of the C_5 and C_6 rings. We have reported that the reaction rate of the skeletal isomerization of Me–C_6 to DiMe–C_5 is very low over Ir/H-β at 493 K[14]. However, the methyl group rapidly shifts from the 2-position to 3-position. On the basis of these findings, we believe that DiMe–C_5 is preferentially produced from DiMe–CyC_5 and that Me–C_6 is formed from Et–CyC_5 (**Scheme 2**). A small amount of Me–C_6 may also be produced *via* a minor ring-opening reaction of CyC_5 at the substituted C–C bond of the cyclopentane ring and Me–CyC_6. Resasco and coworkers have reported that C–C bond opening at unsubstituted positions occurs on Ir/SiO_2 in the hydrocracking of 1,3-dimethylcyclohexane[15]. Our results from the hydrocracking of Me–CyC_5 and Me–CyC_6 over Ir/SiO_2 are consistent with theirs, though the reaction temperature and pressure and the loading amount of Ir were different.

The equilibrium concentration of Et–CyC_5 was calculated to be 10.3% of the CyC_5 species at 493.15 K. The maximum selectivity for Me–C_6 of the acyclic heptanes should be as low as 10% if the reactivities of DiMe–CyC_5 and Et–CyC_5 in the ring-opening reaction are similar and equilibrium is established between different CyC_5. However, on the bases of **Fig. 4** and **Tables 1** and **2**, the yield of Me–C_6 was higher than that



Dotted lines represent the equilibrium values. See text for calculation of the *x* and *y* values.

Fig. 9 Change in the Concentration of the Cyclic Isomers *vs.* Me–CyC_6 Conversion over Ir (●), Pt (△) and Pd (■) Loaded H-β Catalysts at 493 K with *W*/*F* in the Range of 0.03-4.29 g·s·ml^{-1}

of DiMe–C_5. In **Fig. 9**, the concentration of Et–CyC_5 in CyC_5 (= Et–CyC_5/(DiMe–CyC_5 + Et–CyC_5)) is plotted against the corrected Me–CyC_6 conversion (= CyC_5/(Me–CyC_6 + CyC_5)), which is the conversion of the reactions other than the ring-contraction of Me–CyC_6 to CyC_5, in the hydroconversion of Me–CyC_6 over Group 2 catalysts (Pd/H-β and Pt/H-β) and a Group 3 catalyst (Ir/H-β). The concentration of Et–CyC_5 changed from ~ 50% at low conversion to almost the equilibrium value (10.3%) at high conversion (~40%). The high concentration of Et–CyC_5 at low conversion is most likely one reason for the low yield of DiMe–C_5 from the hydroconversion of Me–CyC_6 over Ir/H-β for a single reactor process, because Me–C_6 was formed from Et–CyC_5. That is to say, at low Me–CyC_6 conversion, the ring-opening of Et–CyC_5 proceeded more than expected from the equilibrium Et–CyC_5 concentration. Furthermore, as shown in **Fig. 9**, the reactivity of Et–CyC_5 was higher than that of DiMe–CyC_5 in ring-opening because the concentration of Et–CyC_5 over Ir/H-β, which promotes C–C bond cleavage, was lower than that over Pt/H-β and Pd/H-β, which do not promote C–C bond cleavage, at the same conversion level. Accordingly, we concluded that both the high Et–CyC_5 concentration at low conversion and higher reactivity of Et–CyC_5 than that of DiMe–CyC_5 predominantly contributed to the formation of Me–C_6 as compared with DiMe–C_5 over Ir/H-β using a single reactor.

4. 2. Roles of the Iridium Metal Sites and Acidic Sites in the Hydroconversion of Me–CyC_6

As shown in **Fig. 2**, there were no diffraction lines due to metallic iridium crystallites in the XRD patterns of Ir/SiO_2 (Group 1), Ir/H4SiW (Group 2), and Ir/H-β (Group 3). Since a large amount of CO (107 μmol·g^{-1}) was adsorbed on Ir/SiO_2, metallic iridium crystallites and/or small particles were present on Ir/SiO_2. However, Ir was present mainly as ionic iridium on Ir/H4SiW because only a tiny amount of CO (3 μmol·g^{-1}) was adsorbed on it. On the other hand, the state of iridium on H-β was intermediate between that on SiO_2 and H4SiW. Since Ir/SiO_2 and Ir/H-β promoted ring-opening, we concluded that metallic iridium was responsible for C–C bond cleavage.

It has been well-documented that a catalyst with acidic and metallic characteristics effectively promotes the skeletal isomerization of saturated hydrocarbons[1),14),16)]. Isomerization has been reported to occur in four steps: (1) formation of an alkene from the corresponding alkane by dehydrogenation, (2) formation of a carbenium ion by the addition of H^+ to the alkene, (3) intramolecular rearrangement of the carbenium ion, and (4) formation of the isomerized alkane *via* intermolecular hydride transfer. Metals accelerate step 1 due to their dehydrogenation ability from alkanes to alkenes, which is easily protonated to form a carbenium ion. As **Table 1** shows, loading of Ir on H4SiW significantly enhanced the catalytic activity for the ring-contraction from Me–CyC_6 to CyC_5. Thus, ionic iridium sites as well as metallic ones promote the dehydrogenation of alkanes to alkenes.

5. Conclusions

The maximum one pass yield of the desired product DiMe–C_5 over Ir/H-β, which was the best among single component catalysts, was only 18% and much lower than those of the undesired products Me–C_6 (25%) and C_{6-} (27%). We found that the low yield of DiMe–C_5 was due to the formation of Et–CyC_5 with high selectivity at low conversion and a higher ring-opening rate of Et–CyC_5 than that of DiMe–CyC_5.

The yield of DiMe–C_5 was only 20% at 85% conversion over a physical mixture of Pt/H4SiW (Group 2) and Ir/Al_2O_3 (Group 1). By using two consecutive reactors, where Me–CyC_6 and CyC_5 were equilibrated over Pt/H-β catalyst in the first reactor and equilibrated CyC_5 was reacted under hydrogenolysis conditions over Ir/Al_2O_3 in the second reactor, the yield of DiMe–C_5 reached 30%, which was around two times that of Me–C_6, at 65% conversion. In addition, a further increase in the yield of DiMe–C_5 (32%) was obtained using two consecutive reactors packed with Pt/H4SiW or Pt/H-β in the first reactor and Ir/H-β in the second reactor.

Noble metal-loaded catalysts for the hydroconversion of Me–CyC_6 were classified into three groups depending on catalyzed reactions: Group 1 involves simple

C–C bond cleavage and dehydrogenation, Group 2 involves ring-contraction isomerization of Me–CyC_6 to CyC_5 but not C–C bond cleavage in the ring (ring-opening), and Group 3 involves both ring-contraction isomerization of Me–CyC_6 to CyC_5 and ring-opening to DiMe–C_5 and Me–C_6. On the bases of the XRD patterns, FT-IR spectra of adsorbed CO, and the amount of CO adsorbed on iridium-loaded catalysts, we concluded that metallic iridium was responsible for C–C bond cleavage and ionic iridium as well as metallic Ir promoted the dehydrogenation of the alkanes to alkenes, which can easily be protonated to form a carbenium ion.

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要　　旨

白金修飾固体酸触媒と担持イリジウム触媒を充填した連続二段反応器による水素共存下でのメチルシクロヘキサン転換反応によるジメチルペンタン類合成

大西　隆一郎[†1)]，杉井　　武[†2)]，土居　隼人[†2)]，坂本　啓典[†1)]，神谷　裕一[†1)]

[†1)] 北海道大学大学院地球環境科学研究院，060-0810 札幌市北区北10条西5丁目

[†2)] 北海道大学大学院地球環境科学研究科，060-0810 札幌市北区北10条西5丁目

種々の担持貴金属触媒を用い，反応温度493 K，常圧，水素共存下でメチルシクロヘキサン転換反応を行った。提案されている反応ルートならびに検討した中で最良の触媒（Ir/H-β）を用いた時の反応速度解析から，実施した反応条件下において目的生成物であるジメチルペンタン類の最大収率が18% と低く，かつ望ましくないメチルヘキサン類の収率が25% と高いのは次の二つが原因であると結論した：(1) 低転化率域でエチルシクロペンタン（メチルヘキサン類の前駆体）が高選択的に生成すること，(2) エチルシクロペンタンの水素化開環の速度がジメチルシクロペンタン類（ジメチルペンタン類の前駆体）のそれよりも速いこと。この結果を踏まえ，ジメチルペンタン類の収率向上を目指し，メチルシクロヘキサンからシクロペンタン類への環縮合反応を高選択的に進行させる触媒（Pt–$H_4SiW_{12}O_{40}$/SiO_2 もしくは Pt/H-β）とシクロペンタン類の水素化開環反応を進行させる触媒（Ir/Al_2O_3）を物理混合して一つの反応器に充填した，もしくは，それぞれの触媒を別々の反応器に充填し，それらを直列に接続した連続二段反応器を用いて水素共存下でのメチルシクロヘキサン転換反応を行った。前者の場合（Pt–$H_4SiW_{12}O_{40}$/SiO_2 と Ir/Al_2O_3 の物理混合）では，ジメチルペンタン類収率の向上はわずかであり（収率20%），望ましくないメチルヘキサン類とクラッキング生成物が多く生成した。これに対して後者（前段反応器に Pt/H-β，後段反応器に Ir/Al_2O_3 をそれぞれ充填）では，メチルシクロヘキサン転化率65% において，ジメチルペンタン類収率は30% に達した。このとき，望ましくない生成物であるメチルヘキサン類の収率は約15% にとどまった。

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