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Hydrogenation and Dehydrogenation of 4-Isopropenyl-1-methylcyclohexene Catalyzed by MgO, CaO, La_2O_3, ThO_2, and ZrO_2

Yasutaka TANAKA, Hideshi HATTORI,* and Kozo TANABE*

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

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Synopsis. 4-Isopropenyl-1-methylcyclohexene undergoes hydrogenation over ZrO_2 and ThO_2 to 4-isopropyl-1-methylcyclohexene, while it undergoes mainly dehydrogenation over MgO, CaO, and La_2O_3 to 1-isopropyl-4-methylbenzene. The activity variation of catalysts with pretreatment temperature and the reaction of 4-isopropyl-1-methyl-1,3-cyclohexadiene suggest that selectivity is determined by relative activity for hydrogenation to that for double bond isomerization.

In hydrogenation of diolefins, certain metal oxide catalysts exhibit characteristic selectivity which distinguishes the metal oxides from metallic hydrogenation catalysts. One characteristic of a metal oxide catalyst is partial hydrogenation to produce monoolefins selectively. Another is the 1,4-addition of hydrogen atoms to conjugated diolefins such as 1,3-butadiene and 2-methyl-1,3-butadiene. MgO,[1] ThO_2,[2] and ZrO_2[3] have been found to be active for hydrogenation as well as double bond isomerization of olefins. We have studied the hydrogenation of 4-isopropenyl-1-methylcyclohexene having two kinds of double bonds in a molecule over MgO, CaO, La_2O_3, ThO_2, and ZrO_2 in order to examine the selectivity-determining factor of each catalyst.

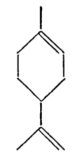
Experimental

Magnesium oxide and CaO were obtained by heating *in situ* $Mg(OH)_2$ and $Ca(OH)_2$, respectively. Lanthanum sesquioxide was obtained by heating *in situ* $La(OH)_3$ prepared by the hydrolysis of $La(NO)_3$. Zirconium oxide was obtained by calcination of $Zr(OH)_4$ in air. The $Zr(OH)_4$ was prepared by hydrolysis of $ZrOCl_2$. Thorium oxide was prepared by pyrolysis of $Th(NO_3)_4$ in air. 4-Isopropenyl-1-methylcyclohexene and 4-isopropyl-1-methyl-1,4-cyclohexadiene were supplied by Takasago Perfumery Co., Ltd.

For the reaction, a microcatalytic pulse reactor directly combined with a gas chromatographic column was employed. The oxides or hydroxides were heated at desired temperatures under a helium stream (flow rate, 80 ml/min) for 2 h. Eight μl of a reactant was injected into a hydrogen stream ahead of the catalyst. The reaction was carried out at room temperature, the flow rate of hydrogen stream being 60 ml/min. The reaction products were trapped in liquid nitrogen and then flash evaporated into a gas chromatographic column. A column (5 m, 6 mm o.d.) was packed with PEG 20 M on Celite 545, which was operated at 100 °C with a flow rate of 60 ml/min.

Results and Discussion

The reaction products of 4-isopropenyl-1-methylcyclohexene (**1**) were 4-isopropyl-1-methyl-1,3-cyclohexadiene (**2**), 4-isopropyl-1-methyl-1,4-cyclohexadiene (**3**), 4-isopropylidene-1-methylcyclohexene (**4**), 1-isopropenyl-4-methylcyclohexane (**5**), 1-isopropyl-4-methylcyclohexene (**6**), 3-isopropyl-6-methylcyclohexene (**7**), 4-isopropyl-1-methylcyclohexene (**8**) and 1-isopropyl-4-methylbenzene (**9**).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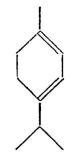
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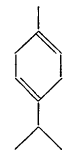
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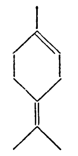
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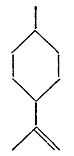
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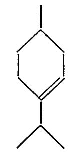
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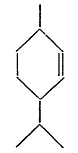
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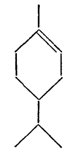
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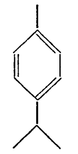
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The composition of products over each catalyst is given in Table 1. In the reaction of **1** over CaO, dehydrogenation occurred producing **9** exclusively. Hydrogenated products **7** and **8** were formed over MgO in addition to the main product **9**. Formation of **4** increased with decrease in the conversion of the reactant. Over La_2O_3, product distribution was similar to that for MgO except that **6** was formed instead of **7**. In the reactions of **1** over ThO_2 and ZrO_2, the main product was **8** formed by the selective hydrogenation of the double bond in

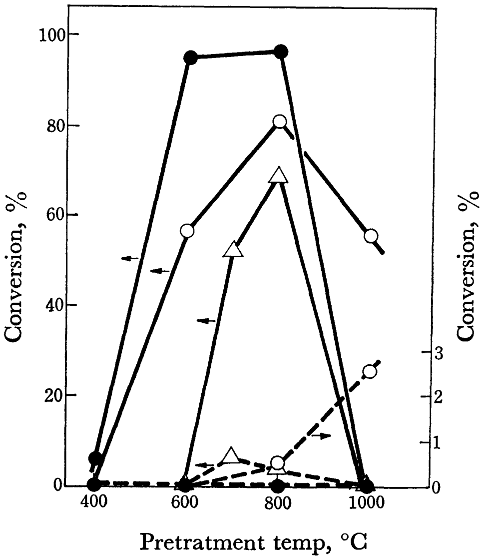


Fig. 1. Variations in conversions to 4-isopropyl-1-methylcyclohexene **8** and 1-isopropyl-4-methylbenzene **9** at the second pulse with pretreatment temperature of catalysts.

○, MgO (0.050 g); ●, CaO (0.050 g); △, La_2O_3 (0.050 g). Broken line, for **8**; solid line, for **9**.

Table 1. Composition of product in reactions of 4-isopropenyl-1-methylcyclohexene **1** and 4-isopropyl-1-methyl-1,3-cyclohexadiene **2** in hydrogen stream at room temperature

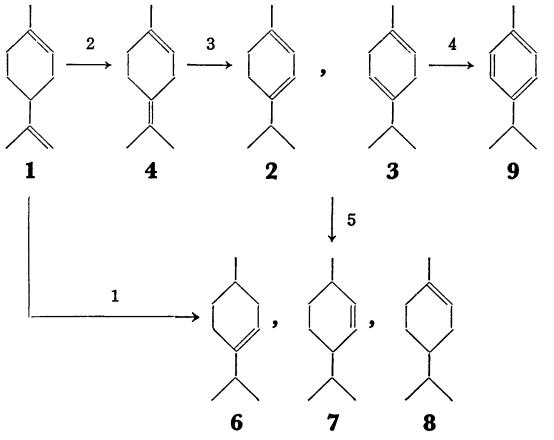
Catalyst	Weight g	Pretreatment temp °C	Pulse No.	Reactant	Mol % each product								
					1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
MgO	0.050	1000	2	**1**	30	<1	0	29	0	0	2	3	36
			3	**1**	54	<1	<1	46	0	0	<1	<1	1
MgO	0.10	1000	3	**1**	0	0	0	0	0	0	7	13	80
			4	**2**	0	0	0	0	0	0	7	12	81
CaO	0.050	800	2	**1**	2	0	0	0	0	0	0	0	98
			4	**1**	8	0	0	0	0	0	0	0	92
La_2O_3	0.10	700	1	**1**	0	0	0	0	0	15	0	8	77
			3	**2**	0	2	3	0	0	18	0	8	69
ThO_2	0.20	650	3	**1**	34	0	0	0	<1	4	0	59	3
			5	**2**	0	19	<1	0	<1	19	0	21	41
ZrO_2	0.20	700	2	**1**	81	0	0	0	0	0	0	15	4
			4	**2**	0	80	1	0	0	0	0	<1	19

the isopropenyl group of the reactant.

In the reaction of **2**, MgO and La_2O_3 gave almost the same product composition as in the reaction of **1**. Over ZrO_2 and ThO_2, however, the product compositions differed from those in the reaction of **1**. Zirconium oxide gave mainly **9** and ThO_2 gave **6** and **8** in addition to **9**.

In Figs. 1 and 2, the conversion into **8** and **9** in the reaction of **1** is plotted against pretreatment temperature of catalysts. Magnesium oxide exhibited maximum activity for dehydrogenation at pretreatment temperature, 800 °C, while for hydrogenation, the activity increased with a rise in pretreatment temperature up to 1000 °C. Calcium oxide showed only dehydrogenation activity over the whole range of pretreatment temperature and maximum activity at pretreatment temperatures 600—800 °C. Over La_2O_3, dehydrogenation and hydrogenation changed nearly parallel with pretreatment temperature, the maximum activities being observed at pretreatment temperatures 700—800 °C. Over ThO_2 and ZrO_2, hydrogenation was predominant over the entire pretreatment temperature range, the maximum activities being obtained at pretreatment temperature 700 °C.

The reaction scheme might be as follows.



The catalytic feature of each catalyst could be explained as follows.

Over ZrO_2 and ThO_2, **1** undergoes hydrogenation by step 1 before it undergoes double bond migration by steps 2 and 3 to form **2** which would easily be converted into **9**. Step 5 is negligible with ZrO_2 but fast with ThO_2.

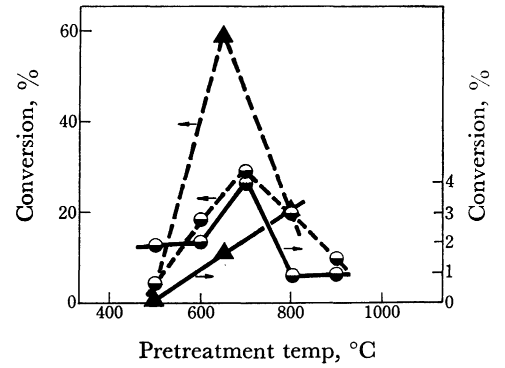


Fig. 2. Variations in conversions to 4-isopropyl-1-methylcyclohexene **8** and 1-isopropyl-4-methylbenzene **9** at the second pulse with pretreatment temperature of catalysts. ◒, ZrO_2 (0.20 g); ▲, ThO_2 (0.20 g). Broken line, for **8**; solid line, for **9**.

Over MgO, CaO, and La_2O_3, hydrogenation step 1 should be slower than steps 2, 3, and 4. Double bond isomerization by steps 2 and 3 quickly occurs to produce **2** or **3** which undergoes fast dehydrogenation to **9**. Since the product distribution of **6**, **7**, and **8** from **1** was practically the same as from **2**, step 5 is much faster than step 1.

Variations in the activities of MgO and CaO were reported for the isomerization of butenes and hydrogenation of olefins as a function of pretreatment temperature.[4-6] The activity of MgO for isomerization exhibited a maximum at 600 °C, while that for hydrogenation did not appear at 600 °C and reached a maximum around 1100 °C. The activity for dehydrogenation of **1** to **9** correlates better with that for isomerization of butenes.

Since the hydrogenation step in the reaction of **1** to **9** is considered to proceed on the hydrogenation sites, a correlation of dehydrogenation activity to **9** with isomerization activity suggests that dehydrogenation to **9** involves an isomerization step which is slower than the dehydrogenation step. This is in line with the proposed reaction scheme.

High selectivity of ThO_2 and ZrO_2 for hydrogenation is considered to be due to a relatively high activity for hydrogenation as compared with that for double bond isomerization, as actually observed in hydrogenation and isomerization of butenes.[2,3]

References

1) H. Hattori, Y. Tanaka, and K. Tanabe, *J. Am. Chem. Soc.*, **98**, 4652 (1976).

2) Y. Imizu, H. Hattori, and K. Tanabe, *Shokubai*, **19**, 64 (1977).

3) T. Yamaguchi and J. W. Hightower, *J. Am. Chem. Soc.*, **99**, 4201 (1977).

4) H. Hattori, N. Yoshii, and K. Tanabe, *Proc. 5th Intern. Congr. Catalysis*, Miami Beach, 1972, **10**, 233 (1973).

5) H. Hattori, Y. Tanaka, and K. Tanabe, *Chem. Lett.*, **1975**, 659.

6) Y. Tanaka, H. Hattori, and K. Tanabe, *Chem. Lett.*, **1976**, 37.

7) T. Yamaguchi and J. W. Hightower, *Shokubai*, **19**, 257 (1977).