

## Heterogeneous Olefin Hydrogenation Catalysis of Metal Cluster Compounds Consisting of Rhodium-Boron Cluster Anion and Rare Earth Cations

### INTRODUCTION

The ternary system of rare earth elements (Ln) rhodium and boron gives metal cluster compounds with characteristic ionic structure, and we have synthesized single crystals of  $\text{Ln}[\text{Rh}_4\text{B}_4]$  (1),  $\text{Ln}[\text{Rh}_3\text{B}]$  (2), and  $\text{Ln}[\text{Rh}_3\text{B}_2]$  (Ln = lanthanoid elements in 3+ state) (3). They give not only quite characteristic electric and magnetic properties, but also exhibit remarkable substrate-selective activity as heterogeneous catalyst for hydrogenation of linear olefins (4). Although alloys containing rare-earth metals and nickel or cobalt have been known to be active for hydrogenation after high-temperature activation by hydrogen under pressure (5), present crystalline catalysts are unique in their potentiality to be activated at ambient temperature and atmospheric pressure of hydrogen.

### METHODS AND RESULTS

$\text{TbRh}_4\text{B}_4$  and  $\text{PrRh}_3\text{B}$  were prepared in molten copper from stoichiometric amounts of the elements in helium atmosphere at 1400°C for several hours and their single crystals formed on slow cooling (several K per hour) to 1000°C. The copper was removed with nitric acid, and the single crystals were crushed in an agate mortar to powders of ca. 100 mesh. Their purity was checked by chemical analysis and X-ray powder diffractometry. X-ray lines of metallic rhodium were not detected. The powder (ca. 0.1 g) was suspended in benzene (ca. 100 cm<sup>3</sup>) containing hexene (5 g) in 1 atm hydrogen. The progress of hydrogenation at room temperature was moni-

tored by gas-liquid chromatography with sebaconitrile as stationary phase.

There was an induction period for the hydrogenation of the hexene by  $\text{PrRh}_3\text{B}$ , the apparent half-period being ca. 60 min. The hydrogenation was completed in 10 h. After the reaction the benzene suspension was filtered in air, and similar experiments were repeated several times by use of the same powder. The hydrogenation required no induction period and the activity was remarkably increased. The activity was further increased (0.3 mol h<sup>-1</sup> g<sup>-1</sup> cat) on repeated usage of the powder even on the tenth run (see Fig. 1).

The used powder contained a sufficient amount of hydrogen to hydrogenate hexene in benzene in the absence of gaseous hydrogen. The amount of *absorbed* hydrogen was measured by the hexane produced and it corresponded to 12-14 cm<sup>3</sup>/0.1 g catalyst. The molar ratio  $\text{H}_2/\text{PrRh}_3\text{B}$  is appreciably more than unity.

The hydrogenation was accompanied by only a little isomerization of the olefin. Thus a very small amount of *cis*-2-hexene (less than 1% *n*-hexane) was formed during the hydrogenation of 1-hexene, but only in the presence of dissolved hydrogen in benzene.

A significant substrate selectivity was observed for 1-hexene among several other hexenes or hexadienes examined (Table 1). The rate of hydrogenation of the other hexene isomers was so small that only the lower limit of the half-period could be measured. No significant difference in the catalytic activity was found between the powders from single crystals and polycrys-

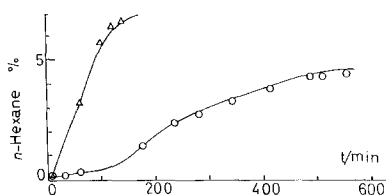


FIG. 1. Increase in concentration of *n*-hexane on the reaction of 1-hexene with hydrogen in benzene in the presence of PrRh<sub>3</sub>B under room temperature and atmospheric pressure (ca. 0.1 g PrRh<sub>3</sub>B for ca. 6% 1-hexene in 100 cm<sup>3</sup> benzene); ○, first run, △, tenth run.

talline ingots (prepared ca. 2000°C by Ar arc melting with rapid cooling) and between TbRh<sub>4</sub>B<sub>4</sub> and PrRh<sub>3</sub>B within the experimental error.

These observations indicate that the hydrogenation results from reaction between absorbed hydrogen in the catalyst and 1-hexene. The change in crystalline state of the catalyst was examined by X-ray powder diffractometry. Table 2 shows the change in  $2\theta$  values of the peak at 35.875° on use as a heterogeneous catalyst. The  $2\theta$  value decreases upon hydrogenation, whereas the half-value width increases. A similar change is also seen on the contact with hydrogen in benzene in the absence of 1-hexene. It is worth noting that the  $2\theta$  goes back to the original value when the powder is kept in contact with 1-hexene in benzene

TABLE 1

Relative Rates of the Hydrogenation of Hexenes and Hexadienes in Benzene in the Presence of TbRh<sub>4</sub>B<sub>4</sub>

Substrate	Relative rates	Note <sup>a</sup>
1-Hexene	1.0 <sup>b</sup>	Trace (ca. 1%) of <i>cis</i> -2-hexene
<i>cis</i> -2-Hexene	0.05	No isomerization (<0.1%)
<i>trans</i> -2-Hexene	0.03	No isomerization (<0.1%)
<i>trans</i> -3-Hexene	0.03	Traces of <i>cis</i> - and <i>trans</i> -2-hexene
1,5-Hexadiene	0.5	1-Hexene as intermediate
2,4-Hexadiene	0.05	Various isomers of hexene

<sup>a</sup> No isomerization in the absence of H<sub>2</sub>.

<sup>b</sup> The relative rates increases on repeated usage of a given powder of TbRh<sub>4</sub>B<sub>4</sub>.

TABLE 2

X-Ray Powder Diffractometry of TbRh<sub>4</sub>B<sub>4</sub>

Reaction time <sup>a</sup> (h)	$2\theta$ (deg)	$a$ (Å)	$c$ (Å)	$\beta_{1/2}$ (10 <sup>-3</sup> rad)
0	35.875	5.31 <sub>6</sub>	7.43 <sub>3</sub>	4.36
32	35.725	5.33 <sub>9</sub>	7.47 <sub>5</sub>	3.93
	*35.738	5.33 <sub>7</sub>	7.47 <sub>1</sub>	4.15 <sup>b</sup>
53	35.763	5.33 <sub>2</sub>	7.47 <sub>3</sub>	5.24
	*35.768	5.33 <sub>1</sub>	7.48 <sub>5</sub>	4.80 <sup>b</sup>
62 + 8 <sup>c</sup>	35.800	5.32 <sub>5</sub>	7.47 <sub>1</sub>	5.67
	*35.857	5.31 <sub>6</sub>	7.43 <sub>8</sub>	5.24 <sup>b</sup>

<sup>a</sup> The powder (0.1 g) was in contact with H<sub>2</sub> in 1-hexene (ca. 6%) in benzene (100 cm<sup>3</sup>) at room temperature.

<sup>b</sup> \*In the absence of 1-hexene in benzene.

<sup>c</sup> After the reaction for 62 h the powder was kept in contact with 1-hexene in benzene in the absence of H<sub>2</sub> for 8 h.

in the absence of hydrogen. Evacuation *in vacuo* at room temperature and at 80°C did not result in the restoration of the original lattice. The crystal lattice of TbRh<sub>4</sub>B<sub>4</sub> is thus found to expand on absorption of hydrogen so as to decrease the  $2\theta$  value. The original lattice dimension is restored when the absorbed hydrogen is consumed by reaction with 1-hexene. The particle size, however, decreases irreversibly on absorption of hydrogen followed by reaction with 1-hexene (see Table 2,  $\beta_{1/2}$  values).

Another cluster catalyst, LnRh<sub>3</sub>B, has a perovskite structure (2) but its magnetic susceptibility indicates that it consists of Ln<sup>3+</sup> and a cluster anion [Rh<sub>3</sub>B]<sup>3-</sup>. The  $2\theta$  value (36.650°) of the (111) plane of PrRh<sub>3</sub>B increased on use as catalyst indicating the contraction of the lattice. The reversibility of the change is similar to that of TbRh<sub>4</sub>B<sub>4</sub>.

The experimental results clearly indicate that single crystals of the ionic cluster exhibit hydrogenation activity as a heterogeneous catalyst under mild conditions, and with substrate selectivity. The high surface area of the catalyst resulting from absorption of hydrogen is advantageously utilized for hydrogenation with remarkably

increased activity and prolonged catalyst life.

## REFERENCES

1. Takei, H., Shishido, T., Iwasaki, H., and Muto, Y., *Japan J. Appl. Phys.* **22**, 1463 (1983).
2. Takei, H., and Shishido, T., *J. Less-Common Met.* **97**, 223 (1984).
3. Takei, H., Kobayashi, N., Yamauchi, H., Shishido, T., and Fukase, T., *J. Less-Common Met.* **125**, 223 (1986).
4. See a recent monograph for olefin hydrogenation: Rylander, P. N., "Catalytic Hydrogenation in Organic Syntheses," pp. 31-43. Academic Press, New York, 1979.
5. Soga, K., Imamura, H., and Ikeda, S., *J. Phys. Chem.* **81**, 1762 (1977); *Chem. Lett.* 1387 (1976).

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