HYDROGENATION OF 1-HEXENES AND 1-OCTENES OVER NICKEL CATALYST SUPPORTED ON POROUS GLASS PREPARED FROM BOROSILICATE GLASS

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Abstract − The pore radius of the silica glass prepared from a borosilicate glass could be controlled by the content of alumina in the starting glass in the range from 1.9 nm (0 wt% alumina) to 1.9 nm (4.5 wt%). The hydrogenation of three kinds of 1-hexenes and 1-octenes, respectively, was carried out over nickel catalysts supported on a series of the porous glasses different in pore size to elucidate the effects of pore size on the rates of hydrogenation. The rates over the catalyst with the largest pore radius (1.9 nm) were almost the same among the 1-hexenes and 1-octenes, respectively. As the pore radius decreased, however, there was observed an increasing tendency that the rates of branched (or more spherical) olefins such as 3,3-dimethyl-1-butene and 2,4,4-trimethyl-1-pentene far exceeded than those of the corresponding linear olefins, i.e. 1-hexene and 1-octene, respectively. This shape selective behavior is quite different from that of the zeolite-supported catalyst. These results confirm that a catalyst support with unique shape selectivity can be synthesized from the borosilicate glass with a small amount of alumina.

Key words: Olefin Hydrogenation, Nickel Catalyst, Porous Glass, Mesoporous Materials, Shape Selectivity

INTRODUCTION

Recently, many kinds of mesoporous materials including MCM series and FSM-16 were synthesized by use of special template compounds [Beck et al., 1992; Inagaki et al., 1993]. It has been found that the porous glasses prepared from a borosilicate glass in the presence of a small amount of alumina added also have mesopores around 2 nm [Takahashi et al., 1986]. The principle of the preparation is as follows. When a borosilicate glass with a specified composition is heated up to a temperature just below the melting point, the glass is split into two layers. One layer is composed mainly of silica, and the other is of sodium oxide, boria and alumina. The network of silica develops during the heat treatment. After the sodium oxide-boria-alumina layer is dissolved into hydrochloric acid or sulfuric acid, a porous glass with mesopores or micropores is obtained [Takahashi et al., 1992]. It has also been reported that the pore size is controlled by the addition of alumina, zirconia or rare earth metal oxide up to 5 wt% [Takahashi et al., 1996]. Since the phase splitting is prohibited by the addition of these metal oxides, the pore size as well as the pore volume decreases with increasing content of the oxides. The specific surface area increases gradually with increasing oxide content up to 3 wt% due to the decrease of the pore size, whereas it suddenly begins to decrease sharply at the content of 3 wt% because of the decrease of the pore volume.

The hydrogenation of benzene and its derivatives with different numbers of methyl groups was carried out over the

nickel and platinum catalysts supported on these porous glasses to examine the effects of pore size of the supports on the hydrogenation rate [Takahashi et al., 1996]. Although the hydrogenation rates of benzene and toluene were little affected by the pore size, those of 1,3,5-trimethylbenzene and o-xylene decreased significantly as the pore size decreased. These results suggest that a catalyst support for the catalyst having unique molecular shape selectivity can possibly be prepared from the borosilicate glass.

It is known that the pore size of zeolite or pillared clay is too small to be accessible to relatively large molecules, such as naphthalene and pyrene. On the other hand, the pore size of the porous glass is large enough and in addition can be controlled by the starting composition and the conditions of the heat and acid treatments. This flexibility appears to be an important advantage of the porous glass prepared from a borosilicate glass.

In the present study, three kinds of 1-hexenes, i.e. 1-hexene, 4-methyl-1-pentene and 3,3-dimethyl-1-butene, and three kinds of 1-octenes i.e. 1-octene, 2,5-dimethyl-1-hexene and 2,4,4-trimethyl-1-pentene were hydrogenated over nickel catalysts supported on a series of the porous glasses prepared from a borosilicate glass. These olefins are larger in molecular size than o-xylene and 1,2,4-trimethylbenzene, which were tested previously. The aim of the present study is to elucidate the molecular shape selectivity of the mesoporous glasses, which can be utterly different from those of zeolites with a micropore size less than 1 nm.

EXPERIMENTAL

The purities of the commercially obtained 1-olefins were

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checked by gas chromotography. The olefins were used without further purification. It was reported that the hydrogenation rate of 2-olefins was smaller than that of 1-olefins with the same carbon skeleton over a platinum catalyst supported on alumina [Germain, 1969]. Then, to simplify the effect of molecular structure on hydrogenation rate, only 1-hexenes and 1-octenes were used in this study.

A series of borosilicate glasses [BSGs], as a mother glass containing alumina up to 5 wt%, were supplied from Japan Electric Glass Co. Ltd. The compositions of BSGs used are shown in Table 1, where the figures attached after BSG like BSG-3 stands for the alumina content (wt%) in BSG. The basic compositions of the BSGs are designed such that the silica content be 62.5 wt% and the Na_2O/B_2O_3 ratio be 0.27. The total content of sodium oxide and boria was thus reduced with increasing alumina content. It is known that these compositions of oxides are the most suitable for preparing the porous glass with a sharp pore size distribution [Takahashi et al., 1992]. The preparation procedures for the porous glass were reported in a previous paper [Takahashi et al., 1996]. The BSG was crushed and sieved in the range of 32 to 60 mesh. After washing with distilled and deionized water, followed by drying in an oven at 393 K for 24 h, the crushed glass was heated at 823 K for 30 h in an electric furnace for the phase splitting. The glass was then immersed into 1 mol/l hydrochloric acid at 353 K for 2 h to leach out the Na_2O-B_2O_3-Al_2O_3 phase. The porous glass left behind was washed with the deionized water repeatedly until no chloride ions were detected in the water. The porous glass thus prepared was named like PVG-3, which means porous vycor glass prepared from BSG-3.

The preparation of PVG-supported nickel catalyst [Ni-PVG] using an impregnation method was described in a previous report [Takahashi et al., 1992]. As 1-hexenes and 1-octenes are more reactive to hydrogenation than benzene, the nickel content in most of the catalysts was lowered to 1.0 wt% as listed in Table 2. The exact nickel content was measured by an atomic absorption method, after the catalyst was completely dissolved in aqua regia. Since this nickel content is lower than that of silanol groups of the porous glass, a major part of nickel ions impregnated were presumably exchanged with the protons of the silanol groups.

The hydrogenation of olefins was carried out in a fixed bed reactor at an atmospheric pressure for 2 h. The apparatus and experimental procedures were reported in a previous

Table 1. Chemical composition of borosilicate glass with alumina

Name	SiO_2 [wt%]	B_2O_3 [wt%]	Na_2O [wt%]	Al_2O_3 [wt%]
BSG-0	62.3	29.3	8.33	0.03
BSG-1	62.3	28.7	8.04	0.92
BSG-2	62.3	27.9	7.90	1.93
BSG-3	62.2	27.2	7.70	2.89
BSG-4	62.8	26.3	7.26	4.05
BSG-4.5	62.6	25.6	7.06	4.45
BSG-5	61.9	25.9	6.93	4.93

Table 2. Surface area and nickel dispersion of Ni (1.0 wt%)-PVG

Catalyst name	Surface area [m^2/g]	Dispersion [−]
Ni-PVG-0	276	0.087
Ni-PVG-1	288	0.079
Ni-PVG-2	306	0.093
Ni-PVG-3	318	0.10
Ni-PVG-4	266	0.082
Ni-PVG-4.5	87	0.067
Ni-PVG-5	12	0.025

paper [Takahashi et al., 1987]. A prescribed mass of supported nickel catalyst, mixed with the same volume of porous glass particles with the same mean diameter, was reduced at 773 K for 5 h in hydrogen atmosphere for activation. Olefins fed by a microfeeder as a liquid phase at a constant flow rate were diluted to 10 % with hydrogen in an evaporator, before being supplied to the reactor. The reaction products were collected in a toluene trap chilled with ice at prescribed time intervals, and analyzed by a gas chromatograph equipped with an FID detector.

Although the rate of olefin hydrogenation is expressed generally by a complex Langmuir Hinshelwood type equation [Mezaki and Inoeu, 1991], it follows Eq. (1) at a low conversion level [Hashimoto, 1993].

$$-r_m = F \cdot \Delta x/\Delta W \tag{1}$$

where, $-r_m$ is disappearance rate of olefin [mol/(kg·s)], F is feed rate of olefin [mol/s], Δx is differential olefin conversion [−] and ΔW is that of catalyst mass [kg].

The specific surface areas of PVG and Ni-PVG were measured by the nitrogen adsorption method in which the BET equation was used for calculation.

RESULTS AND DISCUSSION

Fig. 1 shows the effect of alumina content on the specific surface areas of PVG and Ni-PVG. The surface area of PVG increased with increasing alumina content up to 3 wt%, but it suddenly decreased when alumina content exceeded 4 wt%. The surface area of Ni-PVG with 8.5 wt% nickel was almost a half of the corresponding value of PVG, because of a part of pores of PVG were blocked by the nickel impregnation. On the other hand, the area of Ni-PVG with 1 wt% nickel was fairly close to that of PVG, indicating that the microporous structure of PVG remained almost intact at such low nickel content. Nickel content was fixed to 1.0 wt% in this study unless otherwise specified.

Fig. 2 shows the rate of 1-hexene over Ni-PVG-3 (see Table 2) as a function of reaction temperature. The reaction rate gradually increased with increasing reaction temperature up to 473 K, above which it gradually decreased with increasing reaction temperature. This behavior can be explained as follows. The rate of the hydrogenation is expressed by a Langmuir-Hinshelwood type equation [Hashimoto, 1993]. The intrinsic reaction rate constant increases with increasing temperature, while the adsorption equilibrium constants of the re-

Fig. 1. Relationship between surface area of PVG and Ni-PVG, and alumina content.

Key	Ni content
O	0 wt%
△	1·0
□	8·5

actants decreased with increasing temperature. As a result, the increase of the rate constant overcomes the opposite effect due to the decreases of the adsorption constants in the lower temperature range, while the reverse occurs in the higher temperature range. The hydrogenation rate of benzene or other olefins has similar temperature dependence. Considering such tendency, we focused attention to the rate of hydrogenation at 473 K, at which the rate was maximum.

Fig. 3 shows the hydrogenation rates of three kinds of 1-hexenes over Ni-PVG with 8.5 wt% nickel at 473 K as a function of alumina content. The hydrogenation rates of the
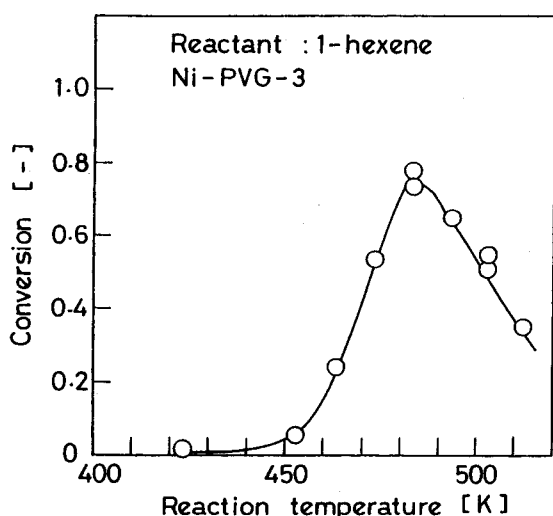
three olefins were almost the same to each other up to 2 wt% alumina content, all increasing somewhat with increasing alumina content. With alumina content above 2 wt%, however, the rates decreased with increasing alumina content. The decrease was the most remarkable for 1-hexene followed by, 4-methyl-1-pentene, leaving 3,3-dimethyl-1-butene to be the most reactive over Ni-PVG-4.5.

Fig. 4 illustrates a similar relationship for the hydrogenation of 1-octenes. The reaction rates went through maximum with increasing alumina content, similar to the previous case of 1-hexenes. 2,4,4-trimethyl-1-pentene and 1-octene showed the largest and the smallest rates of hydrogenation among the tested octenes over Ni-PVG-4.5.

As shown in Figs. 3 and 4, the decreases in hydrogenation rate with increasing alumina content above 2 wt% were much more extensive for 1-hexene and 1-octene than for the branched olefin isomers of the same carbon numbers. This indicates that the hydrogenation rates of straight-chain molecules is more strongly hindered than that of the corresponding branched-chain isomers at higher alumina content. Just an opposite situation was reported over a zeolite [Venuto, 1994], where a linear olefin showed higher reactivity than its branched isomers. Since the pore size of zeolite, less than 1 nm, is not much larger than the size of methyl group, 1-hexene diffuses more easily into the pores than 4-methyl-1-pentene, whose size normal to the molecular axis is larger than that of 1-hexene. On the other hand, as compared in the arithmetic average size of molecule, i.e. a half of molecular length plus molecular width, 4-methyl-1-pentene is smaller than 1-hexene, so that the former would penetrate more easily into the mesopore of Ni-PVG than the latter. As a result, the reaction rate of a branched olefin would be larger than that of the corresponding linear olefin.

To clarify the effect of pore size, the rates of hydrogena-

Fig. 2. Relationship between hydrogenation rate of 1-hexene and reaction temperature.

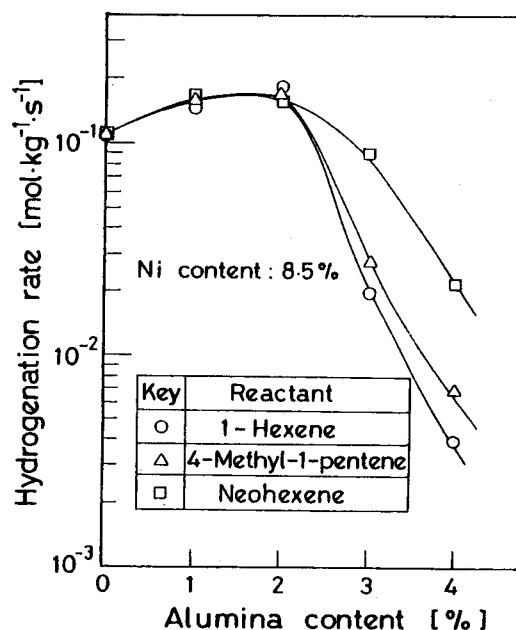| Key	Reactant
O	1-Hexene
△	4-Methyl-1-pentene
□	Neohexene

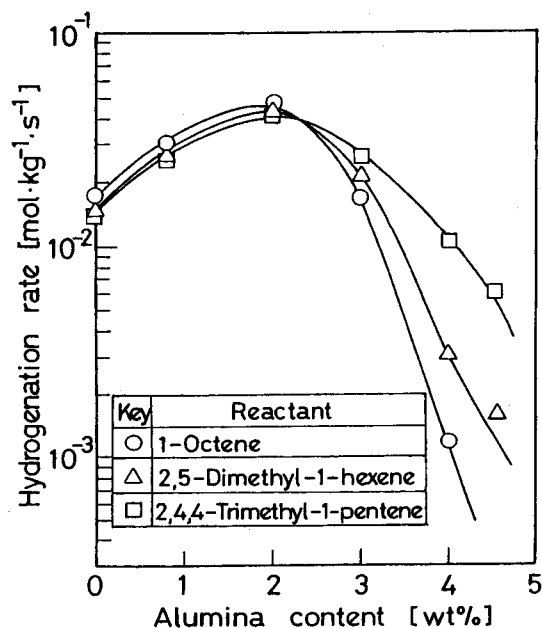Fig. 3. Effect of alumina content on hydrogenation rate of 1-hexenes over Ni (8.5 wt%)-PVG.

Fig. 4. Effect of alumina content on hydrogenation rate of 1-octenes over Ni (1.0 wt%)-PVG.

tion of 1-octenes over Ni-PVGs were correlated with the pore radius involved. The results are shown in Fig. 5. The radius was calculated from the data of specific surface area and pore volume by use of Eq. (2).

$$r_e = 2 \cdot V_g / S_g \qquad (2)$$

where, r_e is pore radius [m], V_g is pore volume [m³/g] and S_g is surface area [m²/g]. It was shown that the pore radius of the catalyst decreased monotonously with increasing alumina content of the starting BSG, from 1.9 nm (0 wt% alumina) to 0.8 nm (4.5 wt%). The hydrogenation rates of 1-oc-
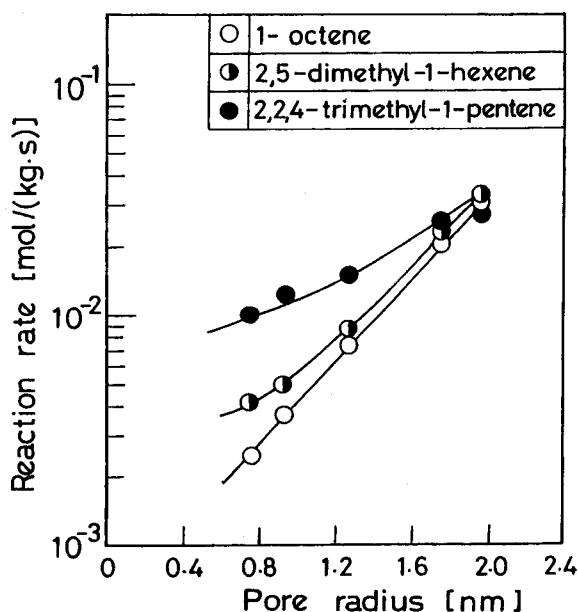
tenes were found to decrease exponentially with a decrease in the pore radius, the steepest decrease being observed for 1-octene among the 1-octenes tested.

The nickel dispersion of Ni-PVGs was measured by a hydrogen adsorption method at 298 K. The apparatus and experimental procedure were reported in a previous paper [Takahashi et al., 1996]. As shown in Table 2, the dispersion was almost constant up to 3 wt% of alumina content, since the nickel was deposited on the surface largely by ion-exchange. It follows that the differences in the hydrogenation rate in this range of alumina content should be caused by the differences in the diffusion rate in the mesopore of Ni-PVG among the hydrocarbons.

Fig. 6 demonstrates the relationship between the apparent activation energy and pore radius for the hydrogenation of 1-octenes over Ni-PVGs prepared at various alumina contents. To obtain the activation energy, the hydrogenation rate was measured in the temperature range from 413 to 463 K in which the rate increased exponentially with arise of temperature as shown in Fig. 2. The same measurement was also carried out over a nickel catalyst supported on silica, whose average pore radius was 50 nm. The activation energy values for 1-olefins over Ni-PVG-O with 1.9 nm of pore radius were close to each other and, in addition, were comparable to the value obtained over the nickel catalyst supported on silica. These results suggest that diffusion does not affect the activation energy over Ni-PVG-O so seriously. With an increase in starting alumina content or a decrease in pore radius, the activation energy values decreased sharply, giving rise to the lowest value of 12 kJ/mol for the 1-octene hydrogenation over Ni-PVG-4.5 ξ with the smallest pore radius (0.8 nm). These tendencies suggest that in this range of pore radius the over-
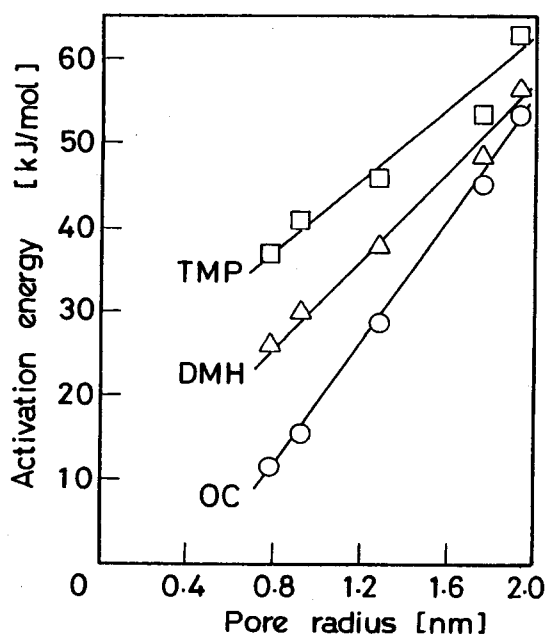

Fig. 5. Relationship between hydrogenation rate of 1-octenes and pore radius.

Fig. 6. Relationship between apparent activation energy and pore radius.
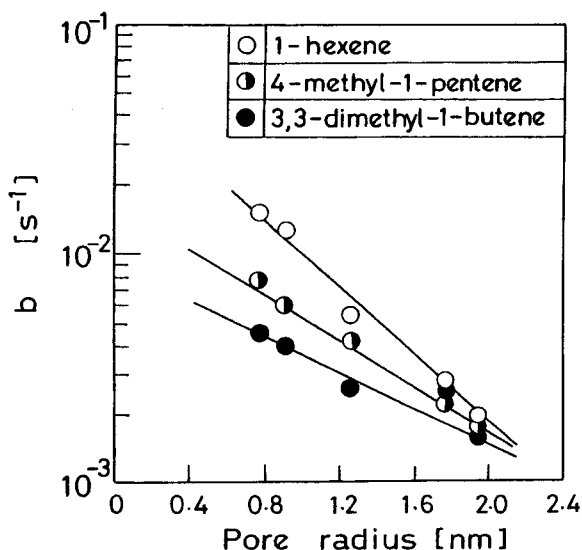OC: 1-octene, DMH: 2,5-dimethyl-1-hexene, TMP: 2,4,4-trimethyl-1-pentene

Fig. 7. Effect of pore radius on deactivation coefficient.

all rate of hydrogenation should be controlled by the diffusion into the micropore.

The rate of catalyst deactivation was evaluated from the relationship between reaction rate and time on stream. The reaction rate decreased exponentially with time on stream, following Eq. (3)

$$r_m(t) = r_m(0) \cdot \exp(-b \cdot t) \tag{3}$$

where, $r_m(t)$ is reaction rate at time on stream t [mol·kg^{-1}·s^{-1}], $r_m(0)$ is initial reaction rate [mol·kg^{-1}·s^{-1}], b is deactivation coefficient [s^{-1}] and t is time on stream [s]. The relationships between deactivation coefficient and pore radius in the hydrogenation of 1-hexenes are shown in Fig. 7. The deactivation coefficients increased exponentially with a decrease in pore radius, the steepest change being again observed with the unbranched olefin (1-hexene). The coke deposits on the catalysts increased with an increase in reaction temperature and time on stream, but remained almost constant irrespective of the deactivation coefficients, when compared under the same conditions. These results suggest that the coke deposits would block the pore mouth, causing the nickel catalyst supported inside smaller pores to lose the catalytic activity more rapidly.

As mentioned so far, the pore size of the porous glass prepared from the borosilicate glass can be controlled in a wide range from micropore to mesopore by the alumina content in the starting borosilicate glass. The shape selective behavior of the catalyst supported on the porous glass is quite different from that of the same catalyst supported on zeolite, that

is, the reaction rate of a spherical molecule is larger than that of a straight molecule with the same molecular weight. It is considered that such unique shape selectivity a remarkable feature of a mesoporous material. The porous glass with controlled mesopores can thus be a unique and useful support for various catalysts.

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