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The Reaction of *n*-Heptane on Rhodium Catalysts in the Presence of Steam

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The catalytic activities of rhodium supported on γ-alumina for steam reforming and dehydrocyclization (aromatization) have been investigated as a function of the degree of dispersion of rhodium. The state of dispersion of rhodium was characterized by measurements of hydrogen and carbon monoxide chemisorption. The specific catalytic activity expressed by the initial rate at 550°C per unit surface area of rhodium was found to depend on the degree of dispersion of rhodium. It was suggested that the steam reforming activity was associated with surface atoms existing in crystal faces and the aromatization activity with edge atoms.

INTRODUCTION

It was predicted by Dowden *et al.* (*1*) in 1968 that noble metals would be catalytically active for steam reforming (gasification) of hydrocarbons. Experimentally it has been revealed that rhodium and ruthenium catalysts are more active for steam reforming of ethane (*2*) and also of other hydrocarbons including *n*-heptane (*3*, *4*) than nickel catalysts which have exclusively been used as industrial catalysts for the production of hydrogen by steam reforming.

On the other hand, rhodium has been shown by Rabinovich *et al.* (*5*) to be a catalyst for the dehydrocyclization of *n*-heptane to toluene and benzene (aromatization) in the presence of steam at the temperature range 430–480°C, when supported on γ-alumina. It has been found by ourselves (*6*) that aromatization is an important reaction taking place concurrently with steam reforming of *n*-heptane at temperatures above 500°C, which are thermodynamically favorable for the production of hydrogen.

The purpose of the present work was to determine the effect of the degree of dispersion of rhodium on its catalytic activity and also on its selectivity for steam gasification against aromatization.

EXPERIMENTAL METHODS

Apparatus and Procedure

The experimental study on the reactions of *n*-heptane in the presence of steam was made in a flow system with the fixed bed of a catalyst. A weighed amount of catalyst packed with quartz wool was placed almost at the central section of the quartz reactor tube (14 mm ϕi.d.). The reactants, *n*-heptane and water were fed separately from microfeeders, mixed and evaporated in the preheating section. The amount of catalyst (W) and the feed rate of *n*-heptane (F) were varied in the range 0.10–1.00 g and 1.01×10^{-4}–18.1×10^{-4} moles/min, respectively. The time factor was defined by the conventional reciprocal space velocity W/F. The catalyst was reduced in hydrogen at 600°C for 2 hr prior to reaction, and then cooled in a stream of nitrogen to the

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reaction temperature (550°C). The partial pressures of the hydrocarbon and steam were fixed to be 0.05 and 0.95 atm, respectively.

Product gas compositions were determined by a gas chromatographic analysis (TCD) after the condensation and the removal of unreacted n-heptane, excess steam and liquified products. Chromatographic separations of hydrogen, carbon monoxide, carbon dioxide, and methane were made with the use of an activated carbon column (4 m) at 80°C. Product hydrocarbons other than methane were analyzed by way of an FID gas chromatography with a capillary column of squarane.

The apparatus used for the adsorption measurements was a conventional high vacuum glass system. The catalyst sample was reduced in hydrogen for 2 hr at 600°C. After evacuation to 10^{-6} Torr (1 Torr = 133.3 N m^{-2}) at the reduction temperature, the sample was cooled to room temperature (25°C) for the measurement of adsorption isotherms of hydrogen and carbon monoxide.

Materials

The rhodium catalysts used in the present work were prepared by impregnating γ-alumina with an aqueous solution of $RhCl_3 \cdot 3H_2O$. The γ-alumina and rhodium trichloride were obtained from Nikka Seiko Co. Ltd. and Nippon Engelhard Ltd., respectively. The rhodium concentration in the catalysts was varied in the range of 0.1–5.0% by weight. The preparation of the catalysts with two extremes of rhodium concentration, 0.1 and 5.0 wt% was duplicated.

The n-heptane used in the catalytic study was an extra pure reagent. Any impurities in the n-heptane were below the level of detection of the chromatographic analysis. Commercial cylindrical hydrogen was used for the catalyst reduction and the adsorption measurements, after purified through a Deoxo unit to remove trace amounts of oxygen.

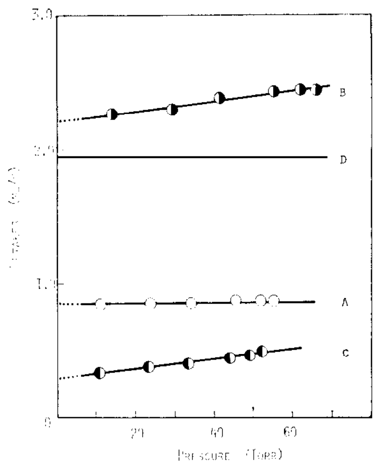

FIG. 1. Adsorption isotherms at room temperature on a 1.0% Rh–alumina catalyst: (A) hydrogen isotherm; (B) carbon monoxide isotherm; (C) carbon monoxide isotherm after pumping out sample at end of isotherm B for 2 min; (D) difference between B and C.

RESULTS

1. Chemisorption of Hydrogen and Carbon Monoxide

Figure 1 illustrates typical isotherms of hydrogen and carbon monoxide adsorption. The amounts of hydrogen uptaken by surface rhodium atoms were determined by extrapolating the isotherm to zero pressure of hydrogen. For the adsorption of carbon monoxide, the contribution of physical adsorption (reversible) cannot be neglected. Therefore, carbon monoxide chemisorption values were determined by obtaining an isotherm between 10 and 50 Torr, evacuating for 2 min to remove reversibly held carbon monoxide, obtaining a second isotherm in the same manner as the first, then taking the difference between the first and second uptakes. The differences were almost constant in the studied range of carbon monoxide pressure, and they were taken as the monolayer points.

TABLE 1

Summary of Chemisorption Data on Rh–Alumina Catalysts

Rh concn (wt%)	Gas uptakes (ml STP/g)			H/Rh (atoms/ atom Rh)	CO/Rh (molecules/ atom Rh)	CO/H	Surface area of Rh (m^2/g)
	H_2	CO	H_2 titration				
0.1 (A)	0.11	0.30	0.33	1.01	1.38	1.37	0.45
(B)	0.11	—	—	1.01	—	—	0.45
0.2	0.21	0.54	0.62	0.96	1.24	1.29	0.85
0.5	0.45	1.13	1.36	0.83	1.04	1.25	1.82
1.0	0.84	1.95	—	0.77	0.90	1.17	3.40
2.0	1.30	2.44	—	0.60	0.56	0.93	5.26
5.0 (A)	2.44	3.97	7.03	0.45	0.36	0.80	9.87
(B)	2.56	—	—	0.47	—	—	10.36

From the amounts of hydrogen and carbon monoxide chemisorbed by rhodium, a calculation can be made of the number of hydrogen atoms or carbon monoxide molecules adsorbed per atom of metal in the catalyst. In Table 1, the results of measurements and such calculations are listed as well as the results of hydrogen titration uptakes. The titration experiments were carried out according to the procedure described by Benson and Boudart (*7*).

Rhodium surface areas were calculated from the monolayer values of hydrogen chemisorption on the assumption that hydrogen is chemisorbed dissociatively on rhodium, and that one hydrogen atom is adsorbed by a surface rhodium atom at saturation. The number of surface rhodium atoms per unit area was taken to be $1.33 \times 10^{19}\ m^{-2}$ (*8*). The degree of dispersion of rhodium varied by more than twofold of magnitude with the concentration of the metal.

The ratio of molecules of carbon monoxide adsorbed to atoms of hydrogen adsorbed depended considerably on the concentration of rhodium in the catalyst. If each carbon monoxide molecule is adsorbed to one surface metal atom in a linear configuration, the ratio would be unity. For the catalysts with higher rhodium concentration, the ratio was unity or lower. These data can be explained either by the linear structure of adsorbed carbon monoxide, or in combination with the bridged configuration. The ratio, however, increased with decreasing concentration of rhodium, and it exceeded unity. With the 0.1% Rh catalyst, the number of carbon monoxide molecules adsorbed was 1.38 times of the number of rhodium atoms in the catalyst, suggesting the existence of the surface site

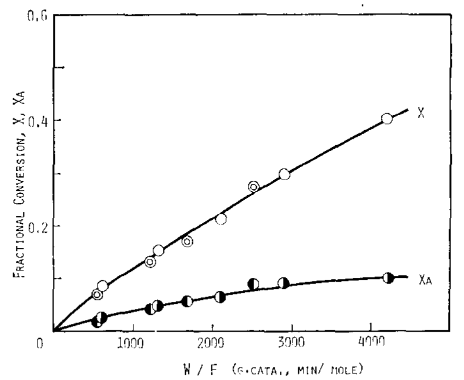

FIG. 2. Typical runs at 550°C, H_2O:*n*-heptane =20:1 on a 0.2% Rh–alumina catalyst: (○ and ◑) X and X_A obtained with 0.5 g of the catalyst; (◎ and ◐) X and X_A with 1.0 g of the catalyst.

TABLE 2

Specific Catalytic Activities and Initial Reaction Products

Rh concn (wt%)	Specific activity ($\times 10^4$ moles/min·m^2 Rh) for		Initial products (mole%) of Steam gasification				Aromatization		r_A/r
	Gasification	Aromatization	H_2	CO	CO_2	CH_4	Toluene	Benzene	
0.1 (A)	0.41	0.28	74	21	5	0	100	0	0.41
(B)	0.46	0.36	74	21	5	0	100	0	0.44
0.2	1.24	0.56	74	21	5	0	84	16	0.31
0.5	2.56	0.64	73	19	8	0	27	73	0.20
1.0	2.84	0.67	72	19	9	0	18	82	0.19
2.0	4.31	0.59	72	18	10	0	8	92	0.12
5.0 (A)	5.00	0.26	72	16	12	0	9	91	0.05
(B)	5.14	0.27	73	14	13	0	9	91	0.05

which adsorbed more than one carbon monoxide molecule.

2. *Reaction of n-Heptane in the Presence of Steam*

All the rhodium catalysts used were found to catalyze steam gasification of n-heptane to methane, hydrogen, carbon monoxide and dioxide, as well as dehydrocyclization to toluene and benzene. Formation of C_2–C_6 aliphatic hydrocarbons was far smaller than that of methane.

Figure 2 shows typical results of the conversion on a 0.2% Rh catalyst. The values of X and X_A represent the fractions of n-heptane totally converted and converted to aromatics, respectively. The overlap of data taken with two different amounts of a catalyst showed that external mass transfer was not important under the conditions studied.

The initial rates of overall conversion (r) and aromatization (r_A) were determined from the initial gradients of the curves of X and X_A versus (W/F), respectively. As the gasification took place concurrently with aromatization, the initial rate of gasification (r_G) was determined from the difference: $r - r_A$. The specific catalytic activities were defined by the initial rates per unit surface area of rhodium, and were calculated using the surface areas given in Table 1. A comparison of specific catalytic activities determined in this way is given in Table 2. The specific activity of rhodium for gasification varied by more than tenfold, while that for aromatization varied at most threefold.

The initial reaction products were determined by extrapolating the product distributions to zero conversion of n-heptane. They are also listed in Table 2. The distributions of gasification and aromatization products depended on the concentration of rhodium. No other dehydrocyclization products, such as methylcyclopentane, were found in the reaction products.

It is interesting to note that the specific gasification activity increased in a monotonous fashion with increasing concentration of rhodium in the catalyst. It is obvious from the values of r_A/r in Table 2 that the selectivity for aromatization decreases with increasing rhodium concentration.

DISCUSSION

The results of the present study show that both gasification and aromatization on

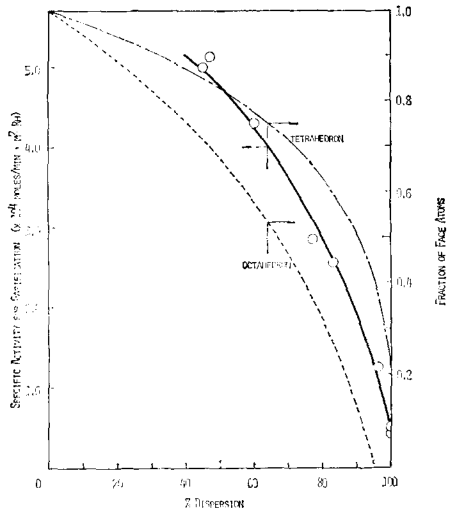

FIG. 3. Theoretical proportion of face atoms to total surface atoms on a fcc octahedron or tetrahedron Rh crystal and the specific activity for gasification as a function of the degree of dispersion.

rhodium–alumina catalysts are of demanding nature, according to the classification by Boudart (*9*). The specific catalytic activity of rhodium, expressed by the reaction rate per unit surface area of rhodium, changed considerably with the degree of dispersion of rhodium. The specific activity for gasification decreased as the dispersion of rhodium increased.

Poltorak and Boronin (*10*) have pointed that, if crystal size is expected to alter the specific catalytic activity, it must be observed with crystals in the size smaller than ca. 40 Å. Van Hardeveld and Hartog (*11*) determined how, in (different) crystals with fcc, bcc, and hcp structures, the proportions of various types of surface atoms depend on the crystallite size. According to their calculation, the most drastic changes in the composition of the surface take place in particles smaller than ca. 40 Å. Assuming any particle shapes of rhodium crystal, the calculation can show that the particle size of rhodium in the catalysts of the present work is smaller than 40 Å.

It has been proposed by Van Hardeveld and Hartog (*12*) that the adsorption of carbon monoxide yields information about the relative numbers of surface atoms with different coordination numbers. The results of the present work indicate that the ratio of molecules of carbon monoxide adsorbed to atoms of hydrogen adsorbed increased from 0.80 to 1.37 with increasing degree of rhodium dispersion, namely with decreasing particle size of rhodium. It has been shown from infrared studies (*13–15*) that a certain surface rhodium atom can adsorb more than one carbon monoxide molecule. To explain the results of the present study, the proportion of such special surface atoms should increase with increasing degree of dispersion. For nickel (*12*), it has been suggested that only the surface atom with a low coordination number, such as a corner or edge atom, can adsorb more than one carbon monoxide molecule.

It is interesting to interpret the specific catalytic activities determined in the present work in terms of the surface composition calculated according to the method of Van Hardeveld and Hartog (*11*). Assuming that rhodium crystals comprise the fcc octahedron or tetrahedron structure, the proportions of corner, edge, and face atoms to the total surface atoms were calculated. The results obtained for face atoms are given in Fig. 3. Both crystal models gave a similar trend, and the proportion of face atoms decreased with increasing degree of dispersion, as anticipated. Similarly, the octahedron and tetrahedron models showed a similar trend in the appearance of corner and edge atoms on the crystal surface, and only the results based on octahedron crystals are given in Fig. 4.

The specific catalytic activity of rhodium for gasification is plotted in Fig. 3 against the dispersion of rhodium. The activity decreases in accordance with the proportion of face atoms as the degree of dispersion of rhodium increases. If the faces of the crystal are more active for gasification than the corners and the edges, the specific activity will decrease with the dispersion

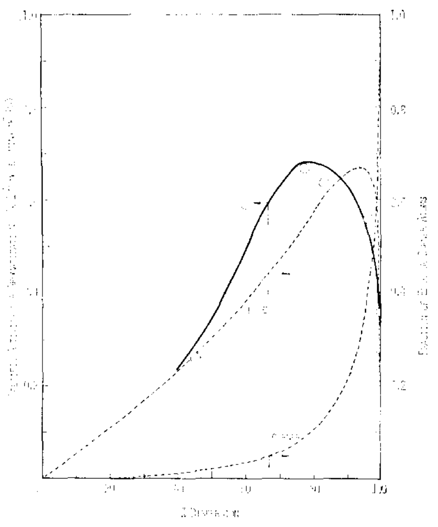

FIG. 4. Theoretical proportion of corner or edge atoms to total surface atoms on a fcc octahedron Rh crystal and the specific activity for aromatization as a function of the degree of dispersion.

On the contrary, the specific activity for aromatization, as shown in Fig. 4, was found to increase with the dispersion of rhodium in the range upward of approximately 80% and then decrease.

The proportion of the various types of surface atoms was the one determined by assuming an ideal, complete crystallite shape. Real crystallites would have a higher proportion of atoms in low coordination positions than ideal crystallites. Furthermore, when catalysts received different thermal treatment, they would have different degree of crystalline nonideality, as well as having different average crystalline size. Although our catalysts were reduced by hydrogen at constant and relatively high temperature (600°C), they would still have different crystalline nonideality. However, it would be reasonable to suppose that the proportion of face atoms decreases as the dispersion of rhodium increases. It is thus obviously tempting to associate the gasification activity of rhodium with the surface atoms existing in crystal faces.

It has been shown by Anderson (*16*) that the specific catalytic activities of platinum for isomerization and dehydrocyclization of *n*-hexane decrease with increasing particle size of platinum from 10 to 50 Å. These reactions via a C_5 cyclic intermediate were suggested to take place preferentially at platinum atoms of low coordination, such as corner atoms in a crystal. Although the dehydrocyclization mechanism on rhodium catalysts is uncertain, the variation of the specific activity for aromatization with the degree of dispersion seems to suggest that this reaction takes place preferentially on the active centers including edge atoms in the crystal of rhodium.

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