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The Dimerization of Propylene over a Nickel Oxide-Silica-Alumina Catalyst

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The composition of hexene isomers produced by the dimerization of propylene over a nickel oxide-silica-alumina catalyst has been examined under the following experimental conditions: 10—300 kg/cm^2, 100 and 200°C. Under a typical set of experimental condition (50 kg/cm^2, 200°C), eight hexene isomers, *i. e.*, 4-methyl-*trans*-2-pentene, 4-methyl-*cis*-2-pentene, 2-methyl-1-pentene, *trans*-2-hexene, *cis*-2-hexene, 3-methyl-*trans*-2-pentene, 3-methyl-*cis*-2-pentene, and 3-methyl-1-pentene, have been found to be the primary products of the dimerization. Among these, more trans isomers are produced initially than the corresponding cis isomers for 4-methyl-2-pentenes and 2-hexenes, but the reverse is true for 3-methyl-2-pentenes. Under higher pressures, 2, 3-dimethylbutenes are also produced at 200°C. A reaction scheme assuming the intermediates of cyclobutane derivatives has been proposed to explain the above findings. The scheme may also explain the unique order of the activity of the present catalyst for a series of *n*-olefins.

The catalyst consisting of nickel oxide, silica, and alumina has been found to be an effective catalyst for the dimerization of olefins.[1-3] One of the remarkable features of this catalyst system is its activity in relation to a series of *n*-olefins. In contrast to usual acid-type catalysts, the nickel oxide-silica-alumina shows a higher activity for a lower olefin, *i. e.*, the highest activity for ethylene.[2,3] Although some efforts have previously been made to elucidate this feature of the catalyst,[2,4] the problem remains practically unsettled.

In the dimerization of ethylene over this catalyst system, the composition of butene isomers was examined in order to get an insight into the mechanism of the reaction.[5-7] It may be expected that more information on the mechanism can be obtained in the dimerization of propylene because of the more complex shape of a propylene molecule, and so the composition of the hexene isomers produced by the dimerization of propylene has been examined in order to determine the primary products of the reaction.[*2] A reaction scheme assuming the intermediates of cyclobutane derivatives has been proposed; this scheme may also suffice to explain the above-mentioned feature of the nickel oxide-silica-alumina catalysts.

Experimental

Materials. A nickel oxide-silica-alumina catalyst composed of 3 atom% nickel, 3 atom% aluminum, and 94 atom% silicon was prepared by a co-precipitation method described elsewhere.[5] The structural characteristics of the catalyst are summarized in Table 1. The specific surface area (S) was obtained by applying the standard B. E. T. method to the adsorption isotherm of nitrogen at −196°C; the mean pore diameter (d) was estimated by the equation, $d=4V_g/S$, where the total pore volume (V_g) was obtained from the amount of nitrogen adsorbed at the relative pressure of 0.967 in the adsorption of nitrogen at −196°C; the acidity was measured by a quinoline chemisorption method at 300°C on the catalyst samples before and after the removal of nickel oxide, and the acidity after the removal was defined as the acidity due to alumina-silica, and the difference between the two, as the acidity due to nickel oxide-silica.[5]

TABLE 1. STRUCTURAL CHARACTERISTICS OF THE CATALYST

Composition (Ni : Al : Si)	3 : 3 : 94 by atom ratio
Specific surface area	342 m^2/g
Mean pore diameter	48.1 Å
Acidity	
Acidity due to nickel oxide-silica	1.50×10^{-4} meq./m^2
Acidity due to alumina-silica	1.73×10^{-4} meq./m^2

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2) M. Koizumi, *J. Institute Polytechnics, Osaka City University*, **4**, 1 (1953).

3) J. P. Hogan, R. L. Banks, W. C. Lanning and A. Clark, *Ind. Eng. Chem.*, **47**, 752 (1955).

4) A. Ozaki, *Bull. Tokyo Inst. Tech., Series-B*, 109 (1960).

5) H. Uchida and H. Imai, This Bulletin, **35**, 989, 995 (1962).

6) H. Imai and H. Uchida, *ibid.*, **38**, 925 (1965).

7) T. Matsuda and T. Shiba, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **88**, 308 (1967).

[*2] Recently, Schultz *et al.* have studied the product distribution in the dimerization of propylene over cobalt-oxide-on-carbon catalysts; R. G. Schultz, J. M. Schuck and B. S. Wildi, *J. Catalysis*, **6**, 385 (1966).

Polymerization-grade propylene (purity>99.9%) was obtained from the Nippon Petrochemicals Co., Ltd., and was further purified by passing it successively through alkaline silica gel, sodium hydroxide, a supported copper catalyst, and alkaline silica gel. The standard samples of hexene isomers were obtained from the Tokyo Kagaku Seiki Co., Ltd.

Apparatus and Procedures. The dimerization of propylene was carried out by using a high-pressure flow system. The reactor body consisted of 25 mm-I. D. (50 mm-O. D.) stainless steel tubing, 50 cm long. A 5-m*l* portion of the catalyst was placed after the 10 cm preheating section at the entrance of the reactor. A thermocouple junction for measuring the reaction temperature was located at the center of the catalyst bed in a 2 mm-I. D. (4 mm-O. D.) stainless steel tube inserted through the bottom of the reactor. The temperature of the reactor was controlled by fluidizing heated iron powder around the reactor. The purified propylene was fed to the reactor by a high-pressure plunger pump, and the reactor effluent was cooled to −20°C in order to condense the dimerization products. A correction was made for uncondensed products by analyzing the uncondensed effluent gas.

The total dimers, trimers, and tetramers were determined by gas chromatographic analysis with a 3% silicon oil on a diasolid column (1 m) at 200°C, a hydrogen flame ion detector being used. All the hexene isomers, except for the *cis*-3-hexene from *trans*-3-hexene, were separated from one another and analyzed by gas chromatography using a 75-m silicon oil-coated capillary coulmn.

Prior to the reaction, the catalyst was treated *in situ* in a stream of dried air for 16 hr at 500°C, and then in a stream of purified nitrogen for 4 hr at the same temperature. After the temperature of the catalyst had been lowered to a reaction temperature in the nitrogen atomosphere, the feeding in of propylene was started.

Results

The conversion of propylene and the composition of the hexene isomers obtained under typical experimental conditions (200°C, 50 kg/cm^2) are plotted against the contact time*3 in Fig. 1. Under these experimental conditions more than 80% of the products were dimers. The figure shows that the contents of eight isomers, *i. e.*, 4-methyl-*trans*-2-pentene, 4-methyl-*cis*-2-pentene, 2-methyl-1-pentene, *trans*-2-hexene, *cis*-2-hexene, 3-methyl-*trans*-2-pentene, 3-methyl-*cis*-2-pentene, and 3-methyl-1-pentene, decrease as the contact time is increased, while those of the other isomers increase with an increase in the contact time.

As only three types of chain structure were found in the hexenes produced, the contents of the hexene isomers with the same chain structure were summed up to give the total amounts of *n*-hexenes, 2-methylpentenes, and 3-methylpentenes.

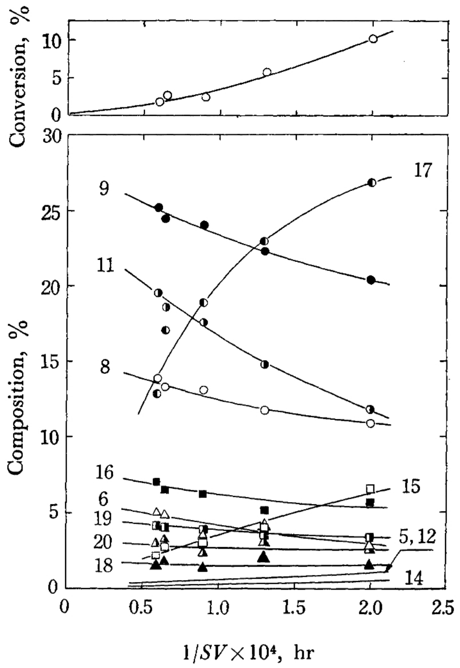

Fig. 1. Conversion of propylene as well as the composition of hexenes produced plotted against contact time.
Experimental condition: 200°C, 50 kg/cm^2
5: 4-methyl-1-pentene, 6 △: 3-methyl-1-pentene, 8 ○: 4-methyl-*cis*-2-pentene, 9 ●: 4-methyl-*trans*-2-pentene, 11 ◑: 2-methyl-1-pentene, 12: 1-hexene, 14: 2-ethyl-1-butene, 15 □: *cis*- and *trans*-3-hexene, 16 ■: *trans*-2-hexene, 17 ◐: 2-methyl-2-pentene, 18 ▲: 3-methyl-*trans*-2-pentene, 19 ◨: *cis*-2-hexene, 20 ◭: 3-methyl-*cis*-2-pentene.

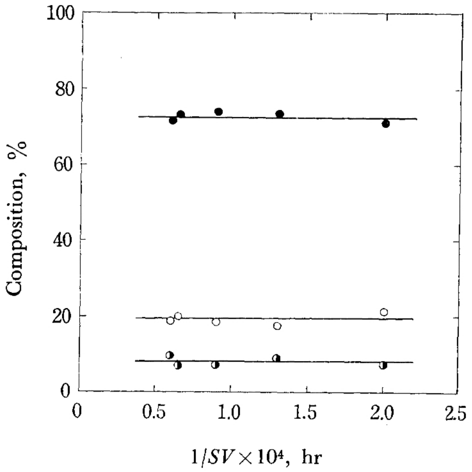

Fig. 2. Composition of hexenes expressed in terms of their chain structures as the function of contact time.
○: *n*-hexenes, ●: 2-methylpentenes,
◑: 3-methylpentenes

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*3 Contact time is defined by 1/*SV*, where the space velocity (*SV*) is expressed in terms of m*l* of propylene (at NTP) per hr per m*l* of the catalyst.

The composition of the product was classified in this way, and is plotted against the contact time in Fig. 2. The figure reveals that the content of the individual type remains constant with an increase in the contact time.

In Fig. 3, the ratios of trans- and cis-isomers are plotted against the contact time. The ratios of trans- and cis-isomers remain almost constant with an increase in the contact time; this is consistent with the results obtained in the dimerization of ethylene.⁵⁾ The figure also indicates the following fact; in the cases of 2-hexenes and 4-methyl-2-pentenes, more trans isomers are produced initially than the corresponding cis isomers, while in the case of 3-methyl-2-pentenes the reverse is true.

The composition of the products, expressed in terms of their chain structures, remained almost constant with an increase in the contact time under all the experimental conditions studied; in Fig. 4 the average values are plotted against the reaction pressures for the reactions carried out at 100 and at 200°C. The figure shows that n-hexenes, 2-methylpentenes, and 3-methylpentenes are produced under all the experimental conditions studied, and that, at 200°C, 2, 3-dimethylbutenes are produced at higher pressures. The 2, 3-dimethylbutene content was too small for us to determine the primary product of the dimerization.

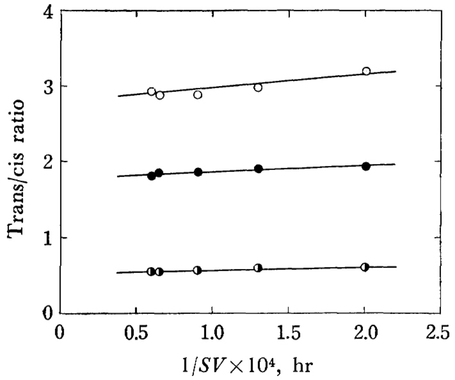

Fig. 3. Trans/cis ratios plotted against contact time.
○: 2-hexene, ●: 4-methyl-2-pentene,
◐: 3-methyl-2-pentene

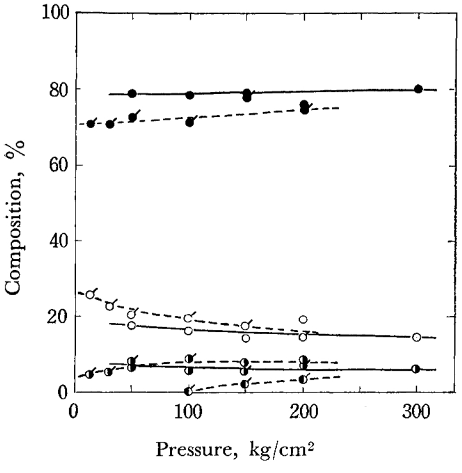

Fig. 4. Chain structures of hexenes produced at different experimental conditions.
n-hexenes at 100 (○) and 200°C (○′)
2-methylpentenes at 100 (●) and 200°C (●′)
3-methylpentenes at 100 (◑) and 200°C (◑′)
2, 3-dimethylbutenes at 200°C (◐′)

Discussion

Figure 1 shows that eight hexene isomers, *i. e.*, 4-methyl-*trans*-2-pentene, 4-methyl-*cis*-2-pentene, 2-methyl-1-pentene, *trans*-2-hexene, *cis*-2-hexene, 3-methyl-*trans*-2-pentene, 3-methyl-*cis*-2-pentene, and 3-methyl-1-pentene, are the primary products of the dimerization. It should be noticed that the 3-methyl-pentenes are primary dimerization products. The presence of 3-methylpentenes in the products of propylene dimerization was previously reported by Wachter,⁸⁾ who attributed them to the products of the secondary rearrangement. Indeed, the 3-methylpentenes cannot be explained as the primary products of the dimerization by a carbonium-ion mechanism⁹⁾ nor by any other mechanisms which assume an open-chain hydrocarbon as the activated intermediate, but they can be explained as being produced by secondary skeletal isomerization. Figure 2 shows that the composition of the hexene isomers, as expressed by their chain structures, does not change with the contact time, remaining at a constant value which is far from the equilibrium.¹⁰⁾ This fact indicates that no skeletal isomerization occurs under the experimental conditions studied, although double-bond-shift reactions are taking place. Thus, it may be concluded that the 3-methylpentenes are not produced by the secondary skeletal isomerizations of n-hexenes or 2-methylpentenes, but are produced directly by the dimerization of propylene.

The above conclusion, as well as the facts shown in Figs. 3 and 4, cannot be explained by the carbonium-ion mechanism nor by any other cation polymerization mechanisms which assume an open-chain hydrocarbon as the activated intermediate, although the catalyst activity is proportional to the number of nickel acid sites, as determined by the chemisorption of a basic molecule.⁵⁾

Schoepfle and Ryan¹¹⁾ proposed a mechanism

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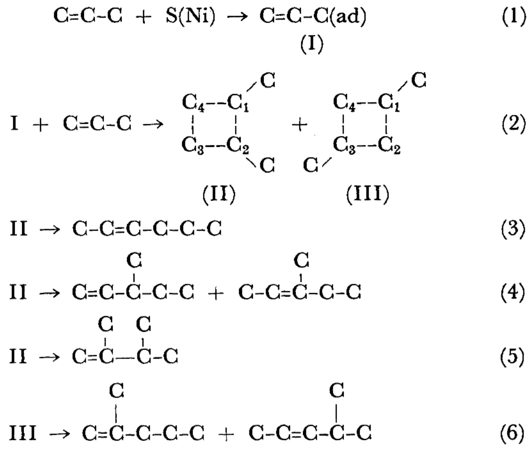
8) A. Wachter, *Ind. Eng. Chem.*, **30**, 822 (1938).

9) F. C. Whitmore, *ibid.*, **26**, 94 (1934).

10) Calculated from the thermodynamic data; F. C. Rossini *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pa. (1953).

11) C. S. Schoepfle and J. D. Ryan, *J. Am. Chem. Soc.*, **52**, 4021 (1930).

of the dimerization of diphenylethylene which assumed an intermediate of a cyclobutane derivative. An examination of the present results has shown that the same mechanism may hold for the present reaction. A reaction scheme assuming the intermediates of cyclobutane derivatives can be described as follows:



$$\mathrm{C{=}C{-}C + S(Ni) \rightarrow \underset{(I)}{C{=}C{-}C(ad)}} \quad (1)$$

$$\mathrm{II \rightarrow C{-}C{=}C{-}C{-}C{-}C} \quad (3)$$

$$\mathrm{II \rightarrow C{=}C{-}\overset{C}{\overset{|}{C}}{-}C{-}C + C{-}C{=}\overset{C}{\overset{|}{C}}{-}C{-}C} \quad (4)$$

$$\mathrm{II \rightarrow C{=}\overset{C}{\overset{|}{C}}{-}\overset{C}{\overset{|}{C}}{-}C} \quad (5)$$

$$\mathrm{III \rightarrow C{=}\overset{C}{\overset{|}{C}}{-}C{-}C{-}C + C{-}C{=}C{-}\overset{C}{\overset{|}{C}}{-}C} \quad (6)$$

A propylene molecule is chemisorbed on a nickel acid site (Eq. (1)). The chemisorbed propylene molecule, I, then further reacts with a propylene molecule to form the intermediates of cyclobutane derivatives, II and III, on the nickel acid site (Eq. (2)). In the intermediate II, the breaking of the C_1–C_2, C_2–C_3, and C_3–C_4 bonds leads to the formation of 2-hexenes (Eq. (3)), 3-methylpentenes (Eq. (4)), and 2, 3-dimethylbutene (Eq. (5)) respectively. In the intermediate III, the same ring-opening processes lead to the formation of 2-methyl-1-pentene and 4-methyl-2-pentenes as the primary products (Eq. (6)). In this way, the reaction scheme can explain the presence of all the primary products found. Under the experimental conditions of 200°C and 50 kg/cm^2, no 2, 3-dimethylbutene was formed, and more *n*-hexenes than 3-methylpentenes were formed. This fact may be explained by assuming that the order of ease in the C–C bond breaking of the cyclobutane intermediate II is C_1–$C_2 > C_2$–C_3 ($= C_1$–C_4) $> C_3$–C_4. These cyclobutane intermediates, however, may not be the activated complexes which are at the top of the energy barrier, because the selectivity in the ring-opening reactions changes with the experimental conditions, as Fig. 4 shows.

Figure 3 shows that more of the trans isomers were produced initially than the corresponding cis isomers for 2-hexenes and 4-methyl-2-pentenes, and that the reverse was true for 3-methyl-2-pentenes. This fact can be explained on the reasonable assumptions that the two propylene molecules are chemisorbed on the catalyst surface so that the two methyl groups of the cyclobutane intermediate direct opposite to the catalyst surface (the cyclobutane ring lies horizontally on the catalyst surface), and that during the course of the ring-opening process on the catalyst surface the rotation of a C–C bond of the cyclobutane ring is retarded by the steric hindrance of the methyl groups.

Finally, we wish to refer to an interesting feature of the nickel oxide-silica-alumina catalysts. Unlike the usual acid-type catalysts over which the polymerization of olefins is considered to take place *via* a carbonium-ion mechanism, the nickel oxide-silica-alumina catalysts exhibit a higher activity for a lower olefin, *i. e.*, the highest activity for ethylene.[2,3] This fact cannot be explained by the carbonium-ion mechanism. The present mechanism may suffice to explain this fact, in view of the steric hindrance of the alkyl group in the formation of the intermediates of cyclobutane derivatives.