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Metathesis of Propylene over Unsupported Rhenium Trioxide

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The metathesis of C_3H_6 proceeds over unsupported ReO_3 and the activity is enhanced by the slight reduction of the catalyst with CO. As the extent of reduction is increased, the activity becomes lower and the (co)dimerizations among C_2H_4 and C_3H_6 become pronounced. The stereoselectivity of metathesis is found over nonreduced ReO_3 and the *cis/trans* ratio of 2-C_4H_8 extrapolated to a zero reaction period decreases when the catalyst is reduced.

INTRODUCTION

The olefin metathesis reaction (*1*) is known to occur mainly over rhenium, tungsten, and molybdenum compounds and the nonpairwise metal–carbene chain model is widely accepted as a working mechanism especially for homogeneous systems (*2*). Some unsupported heterogeneous catalysts are also considered to work as well (*2*). As for heterogeneous catalysts such as supported oxides (*3–18*), the mechanism is not yet well clarified due to their complex structures though the carbene model is considered to be the most probable one and it has been frequently reported that the reduction of supported oxides is important for raising the activity (*4, 10, 13–15, 17*).

Recently various experimental methods have been developed to study solid surfaces but as they are often applicable under very limited conditions, it is desirable to make a structurally simpler catalyst to apply such a technique. In this case, however, the catalytic reactions will proceed differently from those over supported catalysts. The object of this work is to find how the metathesis of C_3H_6 proceeds over unsupported ReO_3 powders, which are aggregates of fine single crystals with (100) faces, with the extent of reduction.

To compare the results with those over supported catalysts, rhenium oxides/silica gel catalysts were prepared.

EXPERIMENTAL METHODS

1. Materials

Powders of ReO_3 were prepared by reducing 99.99 wt% Re_2O_7 with CH_3OH at about 363 K in a nitrogen atmosphere. They are aggregates of rectangular parallelepiped single crystals with (100) faces. They were annealed at 503 K for 19 h and 553 K for 1 h in air. During the annealing, oxidation of ReO_3 to Re_2O_7 was observed. Then they were degassed at $\sim 10^{-5}$ Torr (1 Torr = 133.3 Nm^{-2}) for 2 h at 553 K. Since the disproportionation of ReO_3 to Re_2O_7 and ReO_2 would not occur under such conditions (*19*), the atomic ratio of O/Re of oxide thus obtained would not be smaller than 3.0. To certify that they were ReO_3, an X-ray diffraction pattern, lattice images by an electron microscope (*20*), and an infrared absorption spectrum (*21*) were taken. The BET surface area was 7.3 ± 0.6 m^2/g. The density of ReO_3 was 7.42 g/cm^3.

Supported rhenium oxides/silica gel catalysts were prepared by impregnating a sample of Wako gel 200 with aqueous Re_2O_7, followed by drying at 453 K in air. Then they were reduced with CH_3OH below 423 K in a nitrogen atmosphere. The nominal atomic ratios, Re/Si, were 1/10 and 1/100. The color of the former was blue with its BET area being 257 ± 10 m^2/g, while that of the latter was dark green with an area 290 ± 10 m^2/g.

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Gases were research grade C_2H_4, C_3H_6, C_4H_8, and CO. Each gas was dried through each column of 3A molecular sieves. The main impurities in C_3H_6 were C_2H_4 (0.01 mol%) and C_2H_6 (0.003 mol%).

2. *Apparatus and Experimental Procedure*

Reactions were carried out in a closed reactor. A cylindrical Pyrex reactor of 45 mm diameter and 30 mm width was held with a horizontal cylindrical axis and was rotated once a second. A ledge was attached on an inner wall of the reactor to make the rotation more effective. Gases and catalysts were fed through a greaseless cock from one end of the cylindrical rotation axis whose inner volume was 1.4 cm^3. The temperature distribution was flat within 3 K in the reactor and was acceptable for carrying out the experiments. The temperature was regulated within 1 K. The reactor was evacuated by a diffusion pump through a liquid nitrogen trap.

The products were analyzed chromatographically with a 10-m column of sebaconitrile at 333 K. CO and CO_2 were analyzed using a Porapak-Q and/or a Unibeads-C column. The products were taken out through the cylindrical axis after discarding the dead volume gas of 1.4 cm^3 and were charged to the gas chromatograph. To see the homogeneity of these products, the gases were also collected into a small vessel cooled at 78 K in 2 min and after thawing they were expanded rapidly to an evacuated large vessel and a part of them was quickly analyzed. Since both results coincided within the error range, the former method was applied. Peak areas of signals were corrected for sensitivity factors of 0.67 (C_2H_4), 1.0 (C_3H_6), 1.4 (C_4H_8), 1.7 (C_5H_{10}), and 2.1 (C_6H_{12}). For CO/CO_2, 1/1.4 was used.

Reaction experiments were done in two ways: One was a successive experiment over 1 g of the same ReO_3. With that experiment, an effect of Re_2O_7, if it existed, was eliminated since Re_2O_7 was easily reduced with C_3H_6 to ReO_3 as will be described later. So even if a residue of Re_2O_7 would exist in the starting material, it would no longer exist after the first metathesis experiment. After degassing ReO_3 at 553 K for 60 min at 10^{-5} Torr, 600 Torr of C_3H_6 was fed and the reaction was done at 473 K for 20 min. Then after degassing at 553 K for 40 min, the same catalyst was reduced with CO at 553 K for 60 min in the closed reactor and was degassed at 553 K for 20 min. Then C_3H_6 was fed and the reaction was repeated. The same procedure was repeated a few times thereafter. The other method of experimentation was as follows: 5 g of ReO_3 powders was divided into ten parts. Each reaction of C_3H_6 was carried out over 0.5 g of the fresh catalyst. The methods of degassing and reducing were the same as those for the successive experiment. The latter will be termed the batch experiment hereafter. In the successive experiments, it was impossible to eliminate certain effects of the antecedent experiment such as reactions of the catalysts with gases if they occurred but in the batch experiments the reactions were always performed over the fresh catalysts. H_2 was not used to reduce ReO_3 to avoid the formation of H_xReO_3 (*22*).

As for the supported catalysts, successive experiments were carried out under the same conditions.

RESULTS

1. *C_2H_4 and C_4H_8 from C_3H_6 over Unsupported Rhenium Oxides*

Figure 1 shows the time dependence of the cumulative olefin concentrations over nonreduced ReO_3 at 473 K. C_3H_6 was charged at 600 Torr. The concentrations were normalized to the unit area of ReO_3. The catalyst was degassed at 10^{-5} Torr for 1 h at 553 K. The activity decreased gradually with the reaction period and when the reactions were repeated after the prolonged reactions followed by the degassing, the activity was low from the beginning as shown in Fig. 1 suggesting certain poison

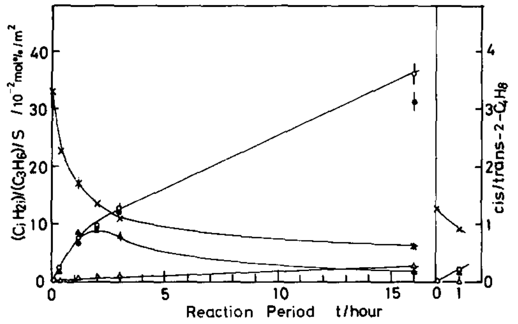

FIG. 1. Concentrations of olefins accumulated in the closed reactor were plotted against the reaction period at 473 K over nonreduced ReO_3. After 16 h, reactions were repeated for 1 h. On the right-hand ordinate, *cis*/*trans* ratios of C_4H_8 were plotted. ○, C_2H_4; ●, C_4H_8; △, C_5H_{10}; ▲, C_6H_{12}; and x, *cis*/*trans* ratio of C_4H_8.

effects. As will be explained later, the reduction of ReO_3 with C_3H_6 was not appreciable at that temperature. In Fig. 1, the (*cis*)/(*trans*) ratio of 2-C_4H_8 is also shown. It includes the conversion effect during the reaction. It is noted that C_6H_{12} was produced initially as much as C_4H_8 as shown in Fig. 1. In other words, the metathesis activity was very low. In the following experiments, the reaction period was 20 min as described above, except for special cases, and discussions are limited to the initial stage of the reactions where the amounts of the products seem to be nearly proportional to the reaction period.

With the slight reduction of ReO_3, the amount of C_2H_4 and C_4H_8 increased and reached maxima at $x \approx 0.005–0.01$ both in the successive (Fig. 2) and the batch (Fig. 3) experiments where the extent of reduction was expressed by $x = (CO_2)/(ReO_3)$. The parentheses mean the number of the molecules. Thus if the composition of the initial rhenium oxide would be stoichiometric, the averaged composition of the reduced oxide might be expressed as ReO_{3-x}. As the diffusion constant of oxygen is not known, it is not clear how homogeneous the oxide was. As the vaporization of Re_2O_7 was observed during the annealing of ReO_3 in air, there is a possibility that the surface of ReO_3 was contaminated with Re_2O_7 and CO was oxidized with Re_2O_7. To see whether Re_2O_7 remained even after the metathesis reaction, C_3H_6 was fed over Re_2O_7 at 393 K. Re_2O_7 was found to have been reduced to ReO_3 in 20 min. Thus at least in the successive experiments, no Re_2O_7 may have remained after the first metathesis reaction and Re_2O_7 would not have contributed to the appearance of the activity peak in Figs. 2 and 3. Physisorbed oxygen, if it existed, would be also reduced

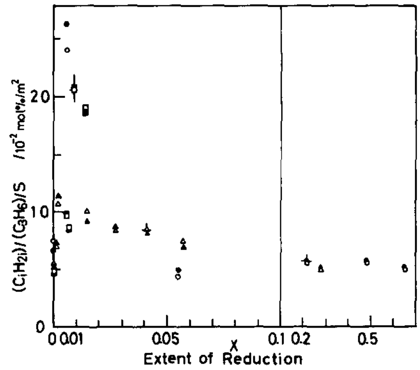

FIG. 2. Relative concentrations of C_2H_4 (open symbols) and C_4H_8 (solid symbols) after 20-min reactions at 473 K over the unsupported catalysts in the successive experiments. The results of the same series of experiments are shown by the common symbols. The extent of reduction is expressed by $x = (CO_2)/(ReO_3)$ in molar ratio. If the oxide is uniform in composition, it is represented as ReO_{3-x}. *S*; surface area of the catalyst.

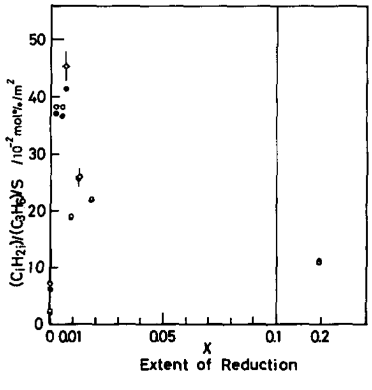

FIG. 3. Relative concentrations of C_2H_4 (○) and C_4H_8 (●) after 20-min reactions at 473 K over the unsupported catalysts in the batch experiments. The extent of reduction is expressed as in Fig. 2. *S*; surface area of the catalyst.

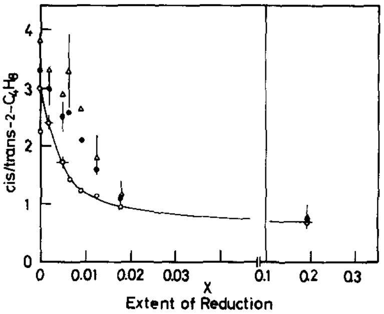

FIG. 4. The *cis*/*trans* ratio of C_4H_8 after 3.7-(●) and 20-(○) min reactions at 473 K over the unsupported catalysts in the batch experiments. △; the ratio extrapolated to the zero reaction period. (iso-C_4H_8)/(C_4H_8) is less than 17 mol% after 20-min reactions. The extent of reduction is expressed as in Fig. 2.

with C_3H_6. Moreover, some amount of CO always remained without being oxidized after the reduction of rhenium oxide at 553 K for 60 min. Thus no physisorbed oxygen may have remained at least after the first reduction reaction in the successive experiments.

In Fig. 3, two sets of data are shown at $x = 0$. As shown the amounts of olefins increased by prolonging the degassing from 1 to 3.5 h but no additional increase was found.

2. *Stereoselectivity*

Figure 4 shows the (*cis*)/(*trans*) ratio of 2-C_4H_8 in the batch experiments. Solid and open circles represent those ratios after 3.7- and 20-min reactions, respectively. As shown in Fig. 4, those ratios decreased rapidly with the extent of reduction. To find out whether or not the ratio extrapolated to a zero reaction period also decreases, the conversion rate of *cis*-2-C_4H_8 was investigated. *cis*-2-C_4H_8 (8%) in N_2 gas of 600 Torr was introduced over 0.5 g of heavily reduced rhenium oxide for which $x = 0.65$. The (*cis*)/(*trans*) ratios were 4.7 ± 0.3, 0.93 ± 0.06, 0.66 ± 0.04, and 0.64 ± 0.04 after 1, 4, 7, and 10 min, respectively. The (*cis*)/(*cis* + *trans*) ratio was found to decrease single exponentially with a decay constant of 1.8 ± 0.3 min. At the same time, in the case of the metathesis reaction, the (*cis*)/(*trans*) ratios of 2-C_4H_8 were 0.73 ± 0.07 and 0.68 ± 0.07 at 80 ± 10 and 220 ± 10 sec, respectively, over the same catalyst at 473 K. By using the aforementioned decay constant, the (*cis*)/(*trans*) ratio at a zero reaction period was found to be 0.8 ± 0.2 where it was taken into account that 2-C_4H_8 was continuously produced from C_3H_6 during the reaction. Thus the ratio at a zero reaction period also decreased with the extent of reduction. This is seen again in Fig. 4. Open triangles show the ratios at a zero reaction period. Estimated errors are very large as the ratios were obtained from those at 3.7 and 20 min assuming a single-exponential decay and a uniform production of C_4H_8 as before.

3. *C_5H_{10} and C_6H_{12} from C_3H_6 over Unsupported Rhenium Oxides*

In Fig. 5, concentrations of C_5H_{10} and C_6H_{12} are plotted against the degree of reduction in the case of the successive experiments. Similar results were obtained in the batch experiments as shown in Fig. 6. As seen from Fig. 5, (C_6H_{12}) is large where the metathesis reaction is active and also increases as the catalyst is much more reduced. Similar results were obtained also for C_5H_{10}. They may be produced both by the metathesis reaction and by (co)dimerization. If they are produced only

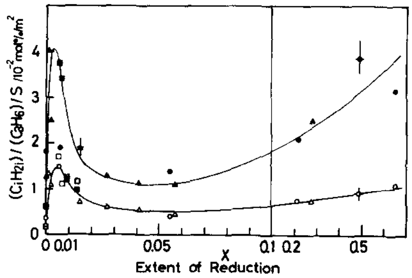

FIG. 5. Relative concentrations of C_5H_{10} (open symbols) and C_6H_{12} (solid symbols) after 20-min reactions at 473 K over the unsupported catalysts in the successive experiments. (C_2H_4) and (C_4H_8) are shown in Fig. 2 with the common symbols. x = (CO_2)/(ReO_3); S, surface area of the catalyst.

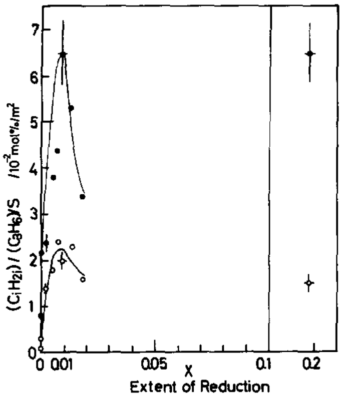

FIG. 6. Relative concentrations of C_5H_{10} (○) and C_6H_{12} (●) after 20-min reactions at 473 K over the unsupported catalysts in the batch experiments. $x = (CO_2)/(ReO_3)$; S, surface area of the catalyst.

by the metathesis reactions among C_2H_4, C_3H_6, and C_4H_8, then it may be said that $\{(C_2H_4) - (C_4H_8)\}$ should be larger than $2\{(C_5H_{10}) + (C_6H_{12})\}$ assuming that such reactions as $C_4H_8 + C_4H_8 \rightarrow C_2H_4 + C_6H_{12}$ and $\rightarrow C_3H_6 + C_5H_{10}$, etc., would occur. As seen from Figs. 2, 3, 5, and 6, this inequality does not hold especially for the heavily reduced catalysts. Therefore, most C_5H_{10} and C_6H_{12} might have been produced by (co)dimerization. At the same time the reaction of C_2H_4 with C_3H_6, 300 Torr each, was carried out over unsupported rhenium oxides with $x = 0.01$ and 0.28 under the same conditions as the metathesis. The results are shown in Table 1. As seen from Table 1, (C_5H_{10}) became larger than (C_6H_{12}) when C_2H_4 was added, indicating that C_5H_{10} was produced mainly by the codimerization of C_3H_6 with C_2H_4.

4. *Supported Rhenium Oxides*

Supported rhenium oxide catalysts were also prepared. Reactions were done under the same conditions as for the unsupported oxides. Table 2 shows some results for 1/10 and 1/100 (Re)/(Si) catalysts. Reduction by CO was also tried but no peak in (C_2H_4) was found and (C_2H_4) decreased with the extent of reduction. Instead propylene oxide was found during the metathesis reaction showing that the catalyst was reduced appreciably with C_3H_6. So in Table 2, the results are shown only for those catalysts which were not reduced prior to the reactions. Each concentration was not normalized to the surface area. If it is assumed that rhenium oxide formed a monolayer on the support, then the parenthetical results are obtained when normalized to thus estimated surface areas of rhenium oxides. These normalized values of C_2H_4 are three to ten times larger than the peak value of the batch experiments over the unsupported catalysts.

(*cis*)/(*trans*) ratios of 2-C_4H_8 after 20-min reactions were nearly equal to the equilibrium value and the ratios after 1-min reactions were 0.84 ± 0.05 and 0.81 ± 0.05 for 1/10 and 1/100 catalysts, respectively.

As for C_5H_{10} and C_6H_{12}, the ratio

TABLE 1

Reactions of C_2H_4 with C_3H_6 for 20 min at 473 K in the Batch Experiments over the Unsupported Rhenium Oxides with $x = 0.01$ and 0.28[a]

Oxide	$(C_4H_8)/(C_3H_6)/S$	$(C_5H_{10})/(C_3H_6)/S$	$(C_6H_{12})/(C_3H_6)/S$
$x = 0.01$	4.4 ± 0.3	11 ± 1	2.2 ± 0.2
	(18 ± 1)	(1.2 ± 0.1)	(1.0 ± 0.1)
$x = 0.28$	2.0 ± 0.1	10 ± 1	2.1 ± 0.2
	(5.1 ± 0.3)	(0.7 ± 0.07)	(2.5 ± 0.3)

[a] Concentrations were normalized to the unit area of the catalysts. When C_3H_6 alone is supplied over the catalysts, the parenthetical results are obtained. The unit is 10^{-2} mol%/m^2. S, surface area; $x = (CO_2)/(ReO_3)$.

TABLE 2

Relative Concentrations of Olefins after 20-min Reactions at 473 K over the Supported Catalysts Whose Re/Si Ratios Were 1/10 and 1/100[a]

Catalyst	$(C_2H_4)/(C_3H_6)$	$(C_4H_8)/(C_3H_6)$	$(C_5H_{10})/(C_3H_6)$	$(C_6H_{12})/(C_3H_6)$
1/10	27 ± 2 (150)	23 ± 2 (120)	1.7 ± 0.2 (9.2)	0.30 ± 0.03 (1.6)
1/100	6.0 ± 0.4 (480)	6.2 ± 0.4 (490)	0.18 ± 0.02 (14)	0.10 ± 0.01 (8)

[a] Total weights and the BET surface areas were 0.20 g and 257 m^2/g and 0.11 g and 290 m^2/g for 1/10 and 1/100 catalysts, respectively. When normalized to the unit area of ReO_3, the parenthetical results are obtained. Surface areas of ReO_3 were estimated assuming a monolayer coverage of ReO_3. The unit of the parenthetical quantity is 10^{-2} mol%/m^2 and otherwise mol%.

$(C_5H_{10} + C_6H_{12})/(C_2H_4 + C_4H_8)$ was smaller than those for the unsupported oxides and C_5H_{10} was produced more than C_6H_{12} in contrast to the case of the unsupported catalysts as shown in Table 2. Moreover, the inequality $(C_2H_4) - (C_4H_8) > 2\{(C_5H_{10}) + (C_6H_{12})\}$ seems to have been fulfilled. Those results suggest that C_5H_{10} and C_6H_{12} may have been produced mainly by the metathesis reaction in the case of the supported catalysts.

DISCUSSION

As stated above the experimental results shown are those of the first 20-min reactions where olefins seem to have been produced in proportion to the reaction period and nearly equal amounts of C_2H_4 and C_4H_8 were produced.

The metathesis activity was enhanced with the slight reduction of ReO_3. Aldag *et al.* suggested that anion vacancies on the rhenium oxide surface are responsible for an enhanced activity (*17*) and Westhoff and Moulijn showed that a slight reduction enhanced the activity of a supported WO_3 catalyst (*14*). LoJacono and Hall found that the olefin metathesis reaction is catalyzed by anion vacancies over a molybdena–alumina catalyst (*15*). As explained in the previous section, it may be said that ReO_3 was really reduced with CO and that the reduction of physisorbed oxygen and/or Re_2O_7 might have no primary importance to the appearance of the enhanced activity even if they existed on the surface. A phase equilibrium study showed that there is no oxide between Re_2O_7 and ReO_3 (*19*).

As for the stereoselectivity, the (*cis*)/(*trans*) ratio of 2-C_4H_8 was larger than 3 and it decreased with the extent of reduction. Though it is not clear whether or not this obtained ratio is the kinetic one for one site reaction, it may be said that the large ratio is characteristic of the reaction center at least for the slightly reduced catalysts. Lin *et al.* found that the (*cis*)/(*trans*) ratio of 2-C_4H_8 becomes smaller as the anion vacancies increase over a rhenium/alumina catalyst (*13*). Davie *et al.* reported that *cis*-2-C_4H_8 was sometimes produced more than *trans*-2-C_4H_8 initially from C_3H_6 when a supported molybdenum hexacarbonyl catalyst was used (*27*). Basset *et al.* found that the (*cis*)/(*trans*) ratio of C_4H_8 from *cis*-2-C_5H_{10} is larger using a supported catalyst than using a homogeneous one (*28*). Katz and McGinnis explained the stereoselectivity by the metal–carbene model (*29*) and Leconte and Basset explained it in more detail by taking into account the various static interactions among substituents in the metallocyclobutane transition states (*23*).

Now the metal–carbon model is a widely accepted mechanism especially for homogeneous catalysts. On a surface of rhenium oxide enough free space is necessary around a Re ion for the formation of metallocyclobutane and a number of such ions will increase by reduction. Thus over a heavily reduced rhenium oxide there is a possibility that the metathesis reaction proceeds with the metallocyclobutane mechanism. Leconte and Basset found that the stereoselectivity is absent for the case of C_3H_6 with $Mo(NO_2)Cl_2(PPh_3)_2$, that is, the (*cis*)/(*trans*) ratio of C_4H_8 is equal to unity (*23*). The stereoselectivity seems to be absent also for the heavily reduced rhenium oxide.

Now on a surface of ReO_3, there may be variously coordinated Re ions (*24*). Sixfold- and fivefold-coordinated ions may be inactive as there is not enough free space and available *d* orbitals. Second, there may be three kinds of fourfold-coordinated ions. One is on an edge and the structure may be similar to that of $PtCl_2Py_2C_3H_6$ (*25*). Another is on the (100) plane adjacent to an oxygen vacancy. The third is on a corner. The first may be more or less active since an active center in a homogeneous catalyst will have a similar structure. The activity peak and the stereoselectivity will be explained if this Re ion is the most active and stereoselective. However, this assumption will not be so easily accepted since the stereoselectivity is absent for C_3H_6 over $Mo(NO_2)Cl_2(PPh_3)_2$ (*23*). In the case of the second fourfold-coordinated Re ion, which is adjacent to an oxygen vacancy, the structure around the ion is quite different from that of the former. The oxygen vacancy is sandwiched by two Re ions which are only 3.75 Å apart. When there is an oxygen ion, $p\pi$ and $d\epsilon$ orbitals overlap to form a bonding band (*26*). Thus C_3H_6 will also interact with two Re ions when it enters into the vacant site and the metallocyclobutane will not be formed. Thus if this fourfold-coordinated ion is active, another intermediate state is to be considered in which two Re ions are involved. From this point of view, it is suggestive that (C_6H_{12}) increases when the metathesis reaction is active. One more ion is on a corner but the structure of the metallocyclobutane there might be the same as that on an edge as the number of involved atoms and/or ions are the same. As for less coordinated Re ions, they might be active but it is doubtful whether they contribute to the appearance of the activity peak and the stereoselectivity since their number densities will increase with reduction.

Finally it must be emphasized that the results reported here are mainly for the aggregates of single crystals and that their characteristic features are different from those for rhenium oxide/silica gel catalysts. It is known that rhenium oxide/silica gel catalysts are more easily reduced than rhenium oxide/alumina catalysts and that the metathesis activity of the latter is higher than that of the former (*13*). These results suggest that there might be many kinds of active centers on heterogeneous catalysts and their activities will differ from one another. For instance, Iwasawa *et al.* designed various active centers containing Mo on alumina and silica supports and found that their metathesis activities differ from one another (*30*).

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REFERENCES

1. Banks, R. L., and Bailey, G. C., *Ind. Eng. Chem. Prod. Res. Develop.* 3, 170 (1964).
2. Grubbs, R. H., *in* "Progress in Inorganic Chemistry" (S. J. Lippard, Ed.), Vol. 24, p. 1. Wiley, New York, 1978.
3. Moffat, A. J., Clark, A., and Johnson, M. M., *J. Catal.* 22, 379 (1971).
4. Luckner, R. C., and Wills, G. B., *J. Catal.* 28, 83 (1973).
5. Biolen, P., and Pott, G. T., *J. Catal.* 30, 169 (1973).
6. Sonnemans, J., and Mars, P., *J. Catal.* 31, 209 (1973).
7. Pennela, F., and Banks, R. L., *J. Catal.* 31, 304 (1973).
8. Kobylinski, T. P., and Swift, H. E., *J. Catal.* 33, 83 (1974).

9. Johnson, M. F. L., and LeRoy, V. M., *J. Catal.* **35,** 434 (1974).
10. Olsthoorn, A. A., and Boelhouwer, C., *J. Catal.* **44,** 197 and 207 (1976).
11. Laverty, D. T., Rooney, J. J., and Stewart, A., *J. Catal.* **45,** 110 (1976).
12. Maksivov, Yu. V., and Kushnerev, M. Ya., *J. Catal.* **45,** 114 (1976).
13. Lin, C. J., Aldag, A. W., and Clark, A., *J. Catal.* **45,** 287 (1976).
14. Westhoff, R., and Moulijn, J. A., *J. Catal.* **46,** 414 (1977).
15. LoJacono, M., and Hall, W. K., *J. Colloid Interface Sci.* **58,** 76 (1977).
16. Sodesawa, T., Ogata, E., and Kamiya, Y., *Bull. Chem. Soc. Japan* **50,** 988 (1977).
17. Aldag, A. W., Lin, C. J., and Clark, A., *J. Catal.* **51,** 278 (1978).
18. Kerkhof, F. P. J. M., Moulijn, J. A., and Thomas, R., *J. Catal.* **51,** 278 (1978).
19. Martens, V. H., and Ziegenbalg, S., *Z. Anorg. Allg. Chem.* **401,** 141 (1973).
20. Horiuchi, S., Kimizuka, N., and Yamamoto, A., *Nature* **279,** 226 (1979).
21. Ishii, M., Tanaka, T., Akahane, T., and Tsuda, N., *J. Phys. Soc. Japan* **41,** 908 (1976).
22. Kimizuka, N., Akahane, T., Matsumoto, S., and Yukino, K., *Inorg. Chem.* **15,** 3178 (1976).
23. Leconte, M., and Basset, J. M., *J. Amer. Chem. Soc.* **101,** 7296 (1979).
24. Tsukada, M., Tsuda, N., and Minami, F., *J. Phys. Soc. Japan* **49,** 1115 (1980).
25. Gillard, R. G., Keeton, M., Mason, R., Pilbrow, M. F., and Russel, D., *J. Organometal. Chem.* **33,** 247 (1971).
26. Mattheiss, L. F., *Phys. Rev. B* **2,** 3918 (1970).
27. Davie, E. S., Whan, D. A., and Kemball, C., *J. Catal.* **24,** 272 (1972).
28. Basset, J. M., Bilhou, J. L., Martin, R., and Theolier, A., *J. Amer. Chem. Soc.* **97,** 7376 (1975).
29. Katz, T. J., and McGinnis, J., *J. Amer. Chem. Soc.* **97,** 1592 (1975).
30. Iwasawa, Y., Kubo, H., Yamagishi, M., and Ogasawara, S., *Chem. Lett.,* 1165 (1980).