JOURNAL OF CATALYSIS 44, 197–206 (1976)

An Infrared Spectroscopic Study of the Re_2O_7/Al_2O_3 Metathesis Catalyst

I. Physicochemical Properties, Structure, and Synthesis

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Received August 27, 1975

A new type of Re_2O_7/Al_2O_3 catalyst has been prepared. Its optical properties, which are important in view of the experimental problems of *in situ* infrared spectroscopy of solid catalysts, are excellent. The carrier surface is completely covered with a monolayer of Re_2O_7. The spectrum of the calcined catalyst is characterized by hydroxyl bands at ca. 3500, 3640, and 3700 cm^{-1} and by bands at 2000 and 1980 cm^{-1}. At room temperature water is absorded mainly associatively; its infrared spectrum is characterized by a very broad band centered around 3100 cm^{-1}. At higher temperatures dissociative adsorption occurs, giving two types of hydroxyl groups characterized by infrared bands at 3500 and 3640 cm^{-1}. On reduction with hydrogen at 773 K a considerable amount of the Re_2O_7 is reduced to metal; by X-ray spectroscopy rhenium metal crystals have been found. On subsequent oxidation with oxygen at 823 K the rhenium atoms are spread over the surface, reforming a monolayer of Re_2O_7.

INTRODUCTION

The metathesis reaction, known for a decade, has drawn much interest because of its technological and fundamental importance (*1*). A typical example is the exclusive formation of $CH_2{=}CD_2$ when a mixture of $CH_2{=}CH_2$ and $CD_2{=}CD_2$ is exposed to a metathesis catalyst (*2, 3*):

$$\begin{array}{l} H_2C{=}CH_2 \\ \quad + \quad \rightarrow 2H_2C{=}CD_2. \\ D_2C{=}CD_2 \end{array}$$

Since it was recognized as a transalkylidenation reaction, little definite information has been obtained with regard to the reaction mechanism. Concerning the nature of the catalytic centers several authors conclude that partly oxidized transition metal ions seem to be necessary to bring about this reaction (*4–6*).

Most studies of the heterogeneously catalyzed metathesis have been carried out with or concern WO_3/SiO_2, MoO_3/Al_2O_3, and $MoO_3/CoO/Al_2O_3$ catalysts. The present paper deals with the important Re_2O_7/Al_2O_3 catalyst of which only in a few patents and papers information is published (*1, 7*). This catalyst is active even at subatmospheric pressures and at room temperature, and therefore particularly suited for an *in situ* infrared spectroscopic study: high temperatures and pressures, required by most other metathesis catalysts to effect metathesis, give rise to severe experimental difficulties. The infrared technique is valuable in that it enables one to observe the catalyst surface at a molecular level (*8–10*). At present infrared studies of metathesis catalysts have only been reported on a $Mo(CO)_6/Al_2O_3$ catalyst (*11, 12*). Owing to the complicated nature of that catalyst those studies did not give definite information with respect to metathesis activity (*3, 13*).

The results of our study will be presented in two parts. Part 1, the present paper, describes physicochemical properties of our Re_2O_7/Al_2O_3 catalyst and the rather special technique of preparing a catalyst tailored to the demands of the infrared spectroscopic method. Gravimetry, electron microscopy and X-ray diffraction have been used to obtain information along with infrared spectroscopy. In Part 2, the succeeding paper (*33*), attention will be paid to the catalytic properties of the Re_2O_7/Al_2O_3 catalyst, as well as to the interaction of alkenes with the catalyst surface.

METHODS

1. The Catalyst

The main experimental difficulty of *in situ* infrared spectroscopy of heterogeneous catalysts is caused by conflicting demands on the properties of the catalyst sample. To obtain a satisfactory amount of catalyst surface in the infrared beam, a substantial optical thickness of the sample is required; however, to minimize scattering losses of the incident infrared beam a small optical thickness is needed. A successful and elegant compromise is reached by using catalysts with an aerogel structure as prepared by the method of Kistler (*14*). In their studies of Al_2O_3 and SiO_2 Peri and Hannan (*15, 16*) have been the first to exploit the potentials of this technique for *in situ* infrared studies. The preparation of supported aerogel catalysts requires an extension of the technique of Kistler, such as for example Peri's method of preparing NiO/SiO_2 aerogel catalysts (*17*).

We have been able to prepare effective and highly transparent MoO_3/Al_2O_3, $Mo(CO)_6/Al_2O_3$, WO_3/Al_2O_3, and Re_2O_7/Al_2O_3 aerogel catalysts (*3*). Re_2O_7/Al_2O_3 has been prepared by saturating a piece of alumina aerogel with the volatile Re_2O_7 at temperatures between 773 and 873 K. This was effected by flushing a vessel containing rhenium powder and the aerogel with nitrogen at 773 K in order to dry the aerogel, followed by introducing oxygen at a temperature between 770 and 870 K. At these temperatures the rhenium is readily burned to the heptoxide. The aerogel piece had previously been cut into the dimensions required to fit the sample holder.

The Re_2O_7 content, as determined by activation analysis, depended on the temperature at which the Re_2O_7 was brought into contact with the carrier. The higher this temperature the lower the Re_2O_7 content and it varied between 20 and 26 wt%. These catalysts had high specific surface area: e.g., the surface area of a 26% catalyst was 195 m^2/g (BET, N_2, 77 K). Optical properties were excellent. Transmission at 4000 cm^{-1} was about 85%, while the optical density was approximately 80 mg/cm^2.

The catalyst had to be stored in reduced form as its optical properties rapidly and irreversibly deterioriated on exposure to air, probably by water which is attracted due to the highly hygroscopic character of the carrier.

The Al_2O_3 carrier was prepared following the method of Peri and Hannan (*15, 16*). Its specific surface area was 330 m^2/g (BET, N_2, 77 K) and according to spectrometric measurements the amounts of impurities (ppm) were Si $\sim$ 100, Na $<$ 100, Ca $\sim$ 5, Fe $\sim$ 10, Cu $\sim$ 10, Mn $<$ 1, and Mo $\sim$ 0.5. X-Ray diffraction indicated a weakly crystalline γ-alumina.

2. Infrared Cell and Apparatus

The catalyst sample was mounted in a stainless steel holder which could be moved from an oven into the proper cell by means of a winch. The cell had an optical pathlength of 10 mm. A reference cell with the same optical pathlength could be connected with the measuring cell. Condensable gases could be trapped in a cold finger. By means of a conventional mercury diffusion pump and cold traps a dynamic vacuum could be reached of 2.6×10^{-8} Pa. Details are given elsewhere (*3*). Grubb–Parsons Mk III and Perkin–Elmer 337 double beam spectrophotometers have been used to obtain the spectra. At times an optical wedge in the reference beam was necessary. Owing to the good optical properties of the samples normal split programs could be used. For the spectra taken with the Grubb–Parsons apparatus the accuracies of the indicated wavenumbers are 3 cm^{-1} and for those taken with the Perkin–Elmer apparatus 5 cm^{-1}. The latter spectra are marked with PE. When the Grubb–Parsons spectrophotometer was used with standard instrument adjustments, the sample was heated to about 333 K by the infrared beam. To prevent extensive heating of the sample this instrument was operated in certain cases with a reduced source intensity. This is critical when recording spectra of adsorbed species in the presence of gaseous reactants, as a hot sample heats the gases in the measuring cell, resulting in a difference in optical densities of the gases in the two cells.

3. Other Techniques

Samples for transmission electron microscopy were cut with an LKB ultramicrotome from catalysts embedded in polymethylmethacrylate; the thickness of the sections was between 4 and 5×10^{-8} m.

Gravimetric data were obtained with a Cahn RG balance.

4. Materials

$^{18}O_2$ was obtained from I.C.N. Its purity was 98%. D_2O (Fluka) had a purity of 98% and the rhenium powder, also from Fluka, contained 0.1% impurities (these values have been given by the manufacturers).

RESULTS

1. Infrared Spectrum of the Re_2O_7/Al_2O_3 Catalyst

Figure 1 shows the infrared spectra of Re_2O_7/Al_2O_3 (23% Re_2O_7) and of the carrier Al_2O_3. Both spectra were obtained

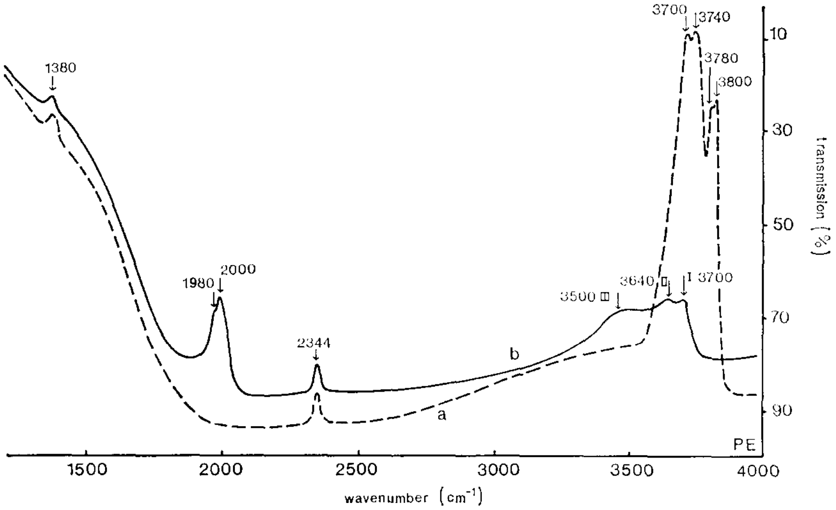


FIG. 1. The infrared spectra of (a) γ-Al_2O_3 and (b) Re_2O_7/Al_2O_3. In both cases the samples have been outgassed for 1 hr at 823 K. The marks I, II and III indicate different hydroxyl groups of the Re_2O_7/Al_2O_3 catalyst surface.

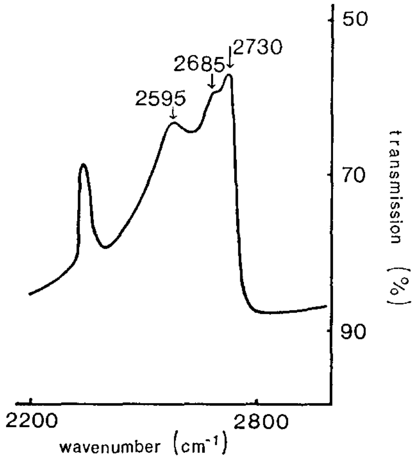


FIG. 2. The infrared spectrum of the deuteroxyl groups on a deuterated Re_2O_7/Al_2O_3 catalyst.

after treating the samples with oxygen (13×10^3 Pa) at 823 K for 1 hr, followed by 1 hr pumping at the same temperature; this procedure is the standard calcination procedure.

In the hydroxyl region of the spectrum alumina hydroxyl bands at 3700, 3780, 3800, and 3740 cm^{-1} are observed. This spectrum closely resembles spectra of alumina obtained by other authors (*10*, *18*). The spectrum of Re_2O_7/Al_2O_3 shows in this region three bands at 3700 (I), 3640 (II), and 3500 cm^{-1} (III). To clarify the origin of these bands H–D exchange was effected. From the spectrum of the deuterated metathesis catalyst it can be concluded that there are three different types of hydroxyl groups (Fig. 2).

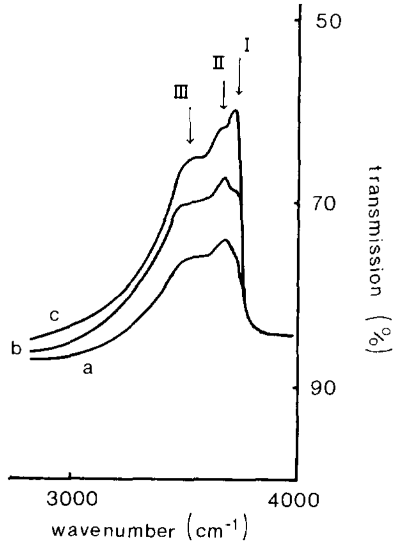


FIG. 3. The relative amounts of different hydroxyl groups as a function of the Re_2O_7 content of the catalyst. (a) 26%, (b) 23% and (c) 20%.

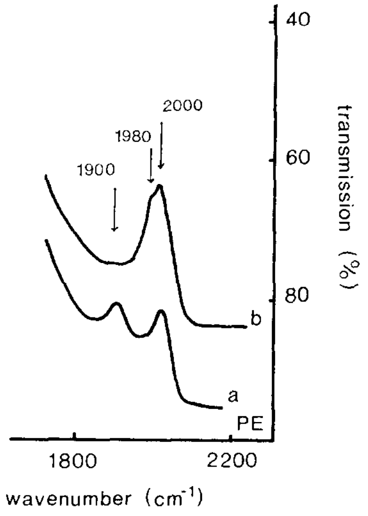


FIG. 4. The effect of ^{16}O–^{18}O exchange on the bands at 2000 and 1980 cm^{-1}. (a) $Re_2{}^{16}O_7/Al_2O_3$ and (b) $Re_2{}^{18}O_7/Al_2O_3$.

Figure 2 shows bands at 2730 (I), 2685 (II) and 2595 (III) cm^{-1} which, according to the isotope rule, correspond with the hydroxyl bands. H–D exchange was effected by adsorbing D_2O at room temperature, followed by pumping at 823 K.

The relative intensities of these three bands proved to be a function of the Re_2O_7 content; the lower this content, the higher the intensity of the type I band (Fig. 3).

As follows from Fig. 1 carrier and catalyst spectra are both characterized by bands at 2344 and 1380 cm^{-1}. The bands at 2344 cm^{-1} can be assigned to CO_2 in closed pores of Al_2O_3 aerogel, and are characteristic for spectra of this type of material (*19*). The origin of the band at 1380 cm^{-1}, which has also been observed in spectra of other types of alumina, is not

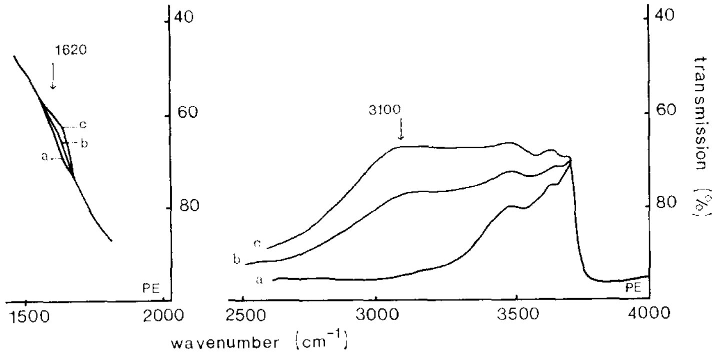


FIG. 5. Adsorption of H_2O on a Re_2O_7/Al_2O_3 catalyst at ambient temperatures. (a) Base spectrum and (b) and (c) after adsorption of increasing amounts of H_2O.

clear (*20, 21*). No further attention has been paid to these bands because they showed no change in shape and position during the experiments.

A remarkable feature of the Re_2O_7/Al_2O_3 catalyst is a band at 2000 cm^{-1} with a shoulder at 1980 cm^{-1}. The latter band shifted to 1900 cm^{-1} on reduction of the catalyst with hydrogen (773 K, 1 hr, 27×10^3 Pa), followed by oxidation with $^{18}O_2$ (723 K, 1 hr, 52×10^3 Pa) (Fig. 4). Deuteration of the catalyst had no effect on these bands.

2. Adsorption of Water

Figures 5 and 6, respectively, show H_2O and D_2O adsorbed at 307 K on the Re_2O_7/Al_2O_3 catalyst, calcined in the standard way. The first spectrum shows a band at ca. 1620 cm^{-1}, which can be assigned to a H_2O deformation vibration (*22*) and thus indicates associative adsorption. The extremely broad band centered around 3100 cm^{-1} should then be due to hydroxyl-stretch vibration of associatively adsorbed H_2O. The results of D_2O adsorption experiments (Fig. 6) are in agreement with this view, as follows from the isotope rule. Figure 6 shows also that the shape of the original hydroxyl bands is hardly influenced by the adsorbed D_2O; evidently adsorption does not occur through hydrogen bonding between the surface hydroxyl

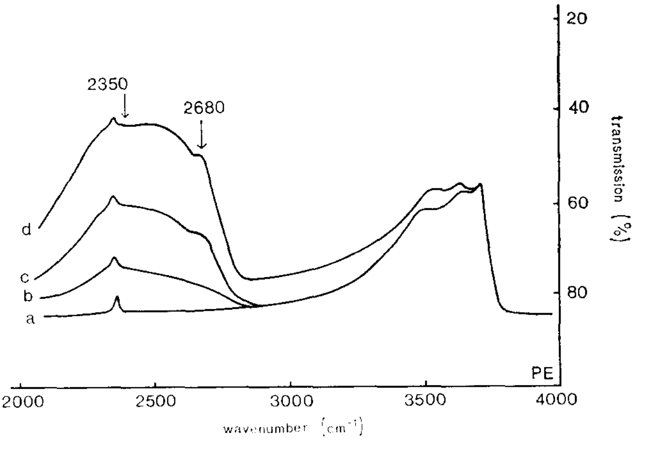


FIG. 6. Adsorption of D_2O at ambient temperatures on a Re_2O_7/Al_2O_3 catalyst. (a) Fresh catalyst and (b), (c), and (d) increasing amounts of adsorbed D_2O.

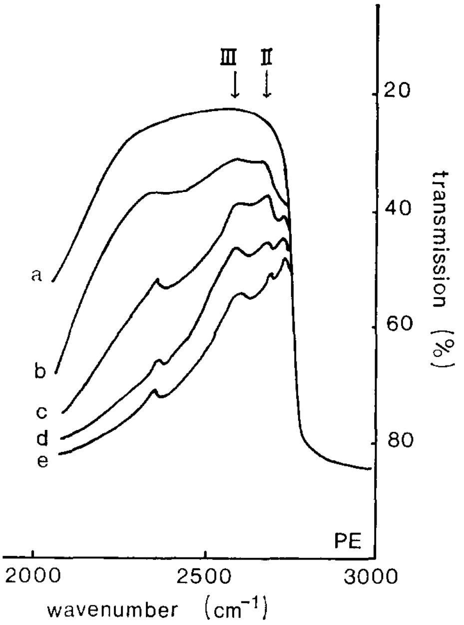


FIG. 7. Desorption and dissociation of adsorbed D_2O. (a) "Wet" catalyst, (b) to (e) after subsequent outgassing for 1 hr at 523, 573, 673, and 773 K.

groups and the D_2O. A second feature of the spectrum is a small band at 2680 cm^{-1}. Being close to the type II deuteroxyl band (2685 cm^{-1}) it appears that associative as well as dissociative adsorption occurred. From adsorption–desorption experiments with catalysts at various temperatures it can be concluded that at higher temperatures dissociative adsorption increases.

Figure 7 shows the spectra of a deuterated catalyst on which D_2O is adsorbed at ambient temperature and next pumped at successively higher temperatures. It appears that, relatively speaking, type II and III deuteroxyl bands first increase in relative intensity, indicating dissociative adsorption, and only on pumping at higher temperatures (573–673 K) diminish. The decrease in intensity is presumably caused by condensation of the deuteroxyl groups. It is striking that type I deuteroxyl groups are not formed under these conditions. The character of this type of group is different from the two others, as is also indicated by the effect of the rhenium oxide content on the relative amount of these groups (Fig. 2).

3. Reduction of the rhenium heptoxide/alumina catalyst

Reduction and subsequent oxidation was studied by various techniques.

a. X-Ray diffraction. The diffractogram of the oxidic catalyst showed only lines attributable to the carrier. After reduction (H_2, 773 K, 1 hr) the diffractogram showed rather weak lines at $d = 2.39$, $d = 2.23$ and $d = 2.10$ Å, indicating the presence of metallic rhenium (*22*). From line widths a mean particle diameter of 15×10^{-9} m was estimated.

b. Gravimetry. Weight changes were monitored with a microbalance. Treatment with H_2 (26×10^2 Pa) at 823 K resulted in a rapid decrease of weight. By repeated evacuation and treating with H_2 a stable reduction level was obtained. Approximately the original weight was readily obtained in O_2 (26×10^2 Pa) at the same temperature.

Assuming that weight increase is exclusively caused by oxidation of rhenium metal to Re_2O_7, a Re_2O_7 content of 16% is calculated. However, activation analysis of this sample established a Re_2O_7 content of 20%. Such discrepancies were also found for catalysts with different amounts of Re_2O_7 and different methods of preparation (*24*).

c. Electron microscopy. Catalysts studied by this technique were prepared by impregnation of a commercial gamma alumina (Ketjen H.D.S. base) with an ammonium perrhenate solution. These catalysts contained about 12% Re_2O_7. Transmission electron micrographs of the oxidic catalyst did not differ from those of the carrier (Fig. 8).

It can therefore be concluded that, if Re_2O_7 crystals are present, these crystals have mean diameters smaller than 2×10^{-9} m. The electron micrograph of the reduced

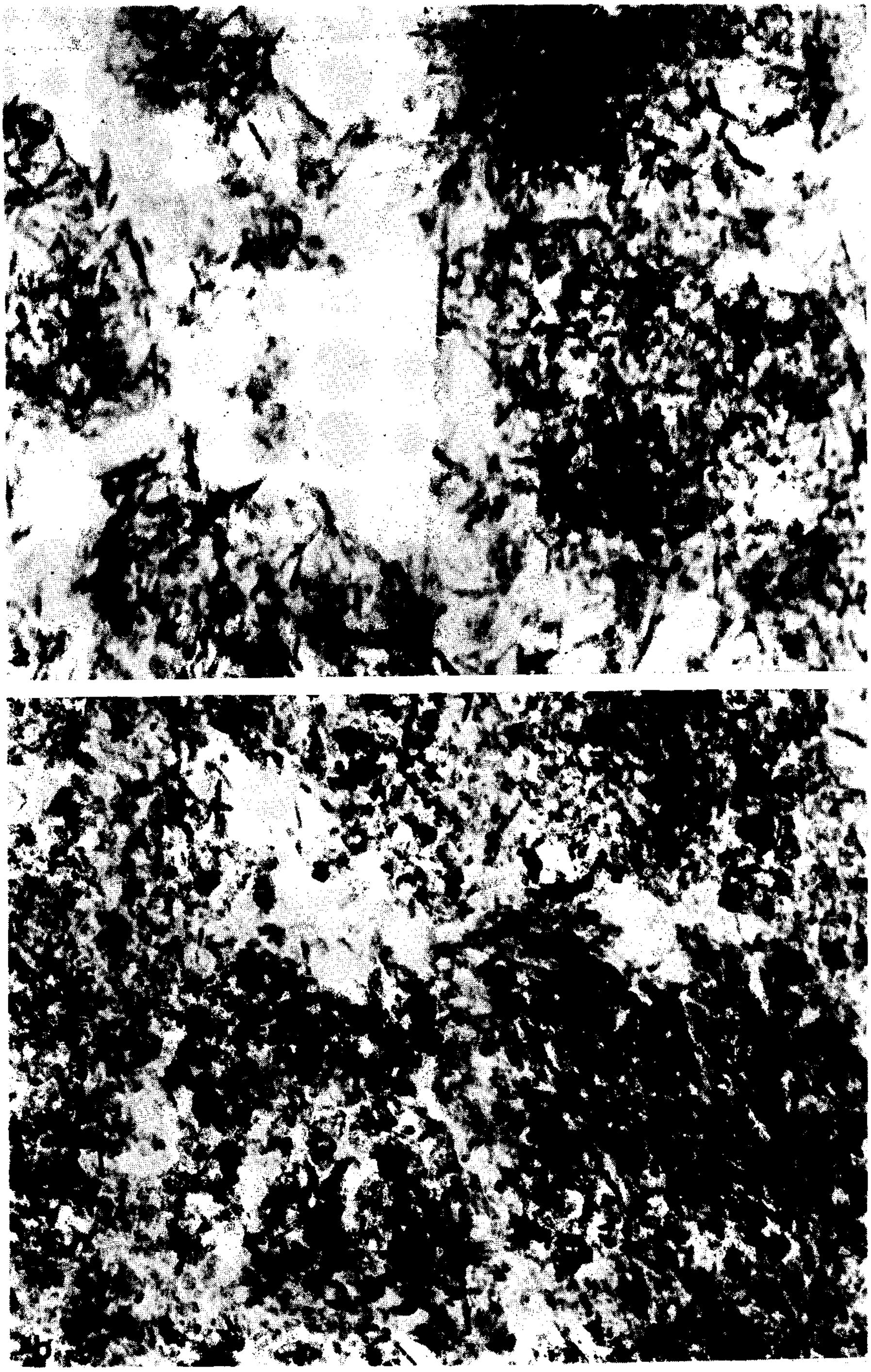


FIG. 8. Electron micrographs of (a) Al_2O_3 and (b) a reduced Re_2O_7/Al_2O_3 catalyst. Reduction was effected by reducing with hydrogen (1.0×10^5 Pa) for 1 hr at 823 K. Thickness of the sections 5×10^{-8} m. Magnification 250,000 ×.

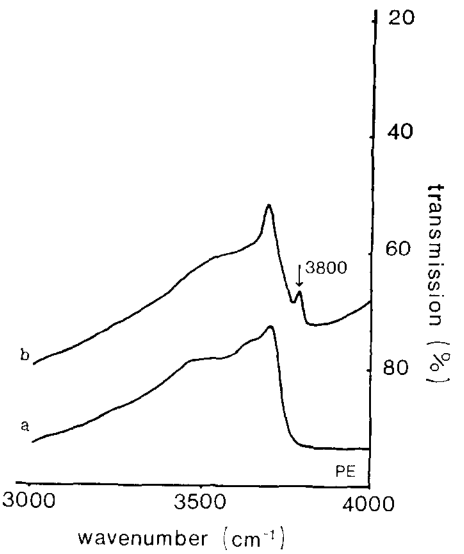


FIG. 9. Partial reduction of a Re_2O_7/Al_2O_3 catalyst. (a) before reduction and (b) after reduction with NH_3. This reduction was effected by adsorbing NH_3 on the catalyst at ambient temperatures followed by pumping at successively higher temperatures up to 823 K.

catalyst clearly shows black spots which, in view of the results of the X-ray diffraction measurements, we assign to metal crystals of rhenium (Fig. 8). According to this micrograph, the mean diameter of these crystals is approximately 15×10^{-9} m.

d. Infrared spectroscopy. Catalysts when reduced had a zero transmission. A partial reduction was effected with NH_3: the catalyst was saturated with NH_3 at ambient temperature and next pumped at successively higher temperatures up to 773 K. The resulting infrared spectrum is shown in Fig. 9.

The effect of reduction on the transmission is evident. The spectrum shows a relative decrease of the type II and III hydroxyl groups. Furthermore a band at 3800 cm^{-1} is shown. We assign this band to a hydroxyl group because the corresponding deuteroxyl band appeared in a similar experiment with a deuterated catalyst. Analogous results were obtained when the catalyst was reduced with CO at temperatures between 573 and 773 K.

After several reduction–oxidation cycles the infrared spectrum of the oxidic catalyst did not differ from the original one.

DISCUSSION

1. Structure

The absence of characteristic Al_2O_3 hydroxyl groups in the infrared spectrum of the Re_2O_7/Al_2O_3 catalyst indicates a complete coverage of the carrier surface with Re_2O_7.

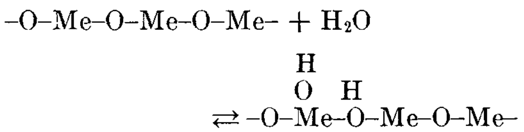
With regard to the structure of the Re_2O_7 layer on the carrier surface it is useful to take account of ideas on the structure of another metathesis catalyst, MoO_3/Al_2O_3. In the latter the presence of a monolayer has been stated by several authors (*25–28*). Its structure has been described as epitactic (*25*), or, in corresponding terms, it has been said that monolayer and carrier form a continuum (*26*). The question as to what kind of Re_2O_7 layer is present may be answered by comparing the surface densities of the rhenium and molybdenum cations on the respective catalyst surface. Sonnemans and Mars (*26*) found a mean surface density of one molybdenum per 17×10^{-20} m^2 catalyst surface. A 26% Re_2O_7/Al_2O_3 catalyst had a specific surface area of 195 m^2/g, corresponding with a mean surface density of one rhenium ion per 30×10^{-20} m^2. It is permissible to compare the catalysts because in both cases the preferentially exposed carrier surface is of the (100) type (*18, 26*). Considering now that the Re_2O_7/Al_2O_3 surface is completely covered with Re_2O_7, the low value of the rhenium cation surface density strongly suggests that the Re_2O_7 is a monolayer.

The nature of this monolayer does not appear to be epitactic. This is suggested when one takes into account the large difference in surface densities with the relatively small difference in transition metal ion densities in bulk Re_2O_7 and MoO_3, given one rhenium cation per 66.7×10^{-30} m^3 and one molybdenum cation per 57.7×10^{-30} m^3, respectively (*29*). Furthermore, the structure of an epitactic monolayer by definition cannot depend on the amount of metal oxide on the carrier surface. On the Re_2O_7/Al_2O_3 surface the relative amounts of hydroxyl groups depend on the Re_2O_7 content of the catalyst, which can only be explained by assuming different structures with changing Re_2O_7 content.

We suggest that the Re_2O_7 layer on the carrier surface consists of small aggregates of Re_2O_7, and those catalysts with smaller amounts of Re_2O_7 (20% or less) have atoms of the Al_2O_3 surface layer exposed. In the arrangement of the Re_2O_7 aggregates the row-like structure of the Al_2O_3 (100) surface might be reflected.

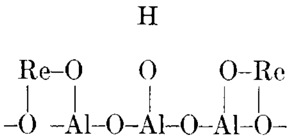
2. Hydroxyl Groups

Under atmospheric circumstances metal oxide surfaces are as a rule covered with hydroxyl groups (*30*). On evacuation at higher temperatures water is formed through a condensation process and coordinatively unsaturated ions will be exposed on the surface (*31*). This process is reversible, as indicated in the following scheme:



$$\text{–O–Me–O–Me–O–Me–} + H_2O \rightleftarrows \text{–O–}\overset{\overset{H}{O}}{\text{Me}}\text{–}\overset{H}{\text{O}}\text{–Me–O–Me–}$$

By dissociative adsorption hydroxyl groups are formed in pairs. This is observed for the type II and III hydroxyl groups of the Re_2O_7/Al_2O_3 surface. Type I hydroxyl group is not formed on adsorption of water. Therefore, this group is not part of a pair. The fact that the number of type I groups relatively increases with decreasing Re_2O_7 content can be explained by assuming bonding of hydroxyl groups to Al ions which are exposed between the Re_2O_7 patches. For instance:



$$\begin{array}{ccccccccc} & & & & \text{H} & & & & \\ \text{Re–O} & & & & \text{O} & & & & \text{O–Re} \\ | & & | & & | & & | & & | \\ \text{–O} & & \text{–Al} & \text{–O–} & \text{Al} & \text{–O–} & \text{Al} & & \text{–O–} \end{array}$$

We assume that the type II and III hydroxyl groups are bonded to Re^{7+} cations. This is in accordance with the relative decrease of the amounts of type II and III groups on reduction of the catalyst.

3. Reduction Properties

A remarkable property of the catalyst is that on reduction Re crystals are formed; therefore, a sintering must occur, while on subsequent oxidation this Re is spread out again to a monolayer. This agrees with the idea that the 3800 cm^{-1} band, which is observed in the infrared spectra of partial reduced catalysts, might be the 3800 cm^{-1} band seen in the infrared spectrum of the carrier and, therefore, might be assigned to carrier hydroxyl groups. Such groups become possible when parts of the carrier surface are exposed on sintering.

The reduction to the metal is also remarkable in comparison with the reduction properties of MoO_3/Al_2O_3 and WO_3/Al_2O_3 catalysts. Under comparable reduction circumstances these supported transition metal oxides are only slightly reduced, while all the corresponding transition metal oxides in pure form are reduced to metals under the same conditions (hydrogen, 823 K, 1 hr) (*27, 32*). As far as a comparison is allowed this suggests a difference in the structures of the Re_2O_7 and MoO_3 layers on alumina. This was previously suggested from the difference in the surface densities.

Our gravimetric data indicate only a partial reduction of the Re_2O_7 in spite of a severe reduction procedure. This can be explained by assuming a distribution in bonding strengths between the Re atoms and the Al_2O_3 surface. Analogous results have also been reported for a MoO_3/Al_2O_3 catalyst (*27*).

4. Bands at 2000 and 1980 cm^{-1}

Finally we wish to draw attention to the bands at 2000 and 1980 cm^{-1}. In view of its shift to 1900 cm^{-1} on ^{16}O–^{18}O exchange, the band at 1980 cm^{-1} can be assigned to a rhenium–oxygen vibration. The results of our gravimetric experiments indicate that only part of the rhenium–oxygen bonds is broken on reduction. Therefore, it is possible that also the 2000 cm^{-1} band is caused by such vibration. As metal–oxygen bonds generally (*22*) have frequencies in the region between 1000 cm^{-1} these bands are probably caused by overtones.

It is interesting that also in the spectra of our MoO_3/Al_2O_3 and WO_3/Al_2O_3 catalysts bands have been found at 2004 and 2030 cm^{-1}, respectively, suggesting a relationship in the structures of these catalysts (*3*).

ACKNOWLEDGMENTS

Thanks are due to R. Westhoff of our laboratory for his gravimetric measurements. We further gratefully acknowledge the cooperation of B. Koch of the Laboratory for Crystallography of the University of Amsterdam, as well as W. Woldringh of the Laboratory for Electron microscopy. Finally we mention that the activation analysis have been carried out by the Reactor Centrum Nederland, Petten NH, The Netherlands.

REFERENCES

1. Mol, J. C., and Moulijn, J. A., *in* "Advances in Catalysis" **24**, p. 131. Academic Press, New York, 1975; and references therein.
2. Mol, J. C., Visser, F. R., and Boelhouwer, C., *J. Catal.* **17**, 114 (1970).
3. Olsthoorn, A. A., PhD thesis, Amsterdam, 1974.
4. Henrici-Olivé, G., and Olivé, S., *Angew. Chem.* **85**, 148 (1973).
5. Nakamura, R., and Echigoya, E., *Bull. Japan. Petrol. Inst.* **14**, 187 (1972).
6. Howe, R. F., and Leith, I. R., *J. Chem. Soc. Faraday I*, **69**, 1967 (1973).
7. Lin, C. B., Aldag, A. W., and Clark, A., *J. Catal.* **34**, 494 (1974).
8. Little, L. H., "Infrared Spectra of Adsorbed Species." Academic Press, New York, 1966.
9. Hair, M. L., "Infrared Spectroscopy in Surface Chemistry." Dekker, New York, 1967.
10. Basila, M. R., *Appl. Spectrosc. Rev.* **1**, 289 (1968); and references therein.
11. Davie, E. S., Whan, D. A., and Kemball, C., *Chem. Commun.* 1202 (1971).
12. Howe, R. F., Davidson, D. F., and Whan, D. A., I.C.S. Farad. I **68**, 2266 (1972).
13. Burwell, R. L., and Brenner, A., "Relations entre processus catalytiques hétérogènes et homogènes." Colloque Int., Bruxelles, 1974.
14. Kistler, S. S., *J. Phys. Chem.* **36**, 52 (1932).
15. Peri, J. B., and Hannan, R. G., *Spectrochim. Acta* **16**, 237 (1960).
16. Peri, J. B., and Hannan, R. G., *J. Phys. Chem.* **64**, 1562 (1960).
17. Peri, J. B., *Discuss. Faraday Soc.* **41**, 121 (1966).
18. Peri, J. B., *J. Phys. Chem.* **69**, 211 (1965).
19. Parkyns, N. D., *Chem. Commun.* 152 (1969).
20. Kiselev, A. V., and Uvarov, A. V., *Surface Sci.* **6**, 399 (1967).
21. Parkyns, N. D., *J. Chem. Soc. A.* 410 (1969).
22. Nakamoto, K., "Infrared Spectra of Inorganic and Coordination Compounds." Wiley, New York, 1970.
23. X-Ray Powder Data File, Card 50702m ASTM, 1960.
24. Westhoff, R., private communication.
25. Schuit, G. C. A., and Gates, B. C., *AIChE J.* **19**, 417 (1973).
26. Sonnemans, J., and Mars, P., *J. Catal.* **31**, 209 (1973).
27. Massoth, F. E., *J. Catal.* **30**, 204 (1973).
28. De Beer, V. H. J., PhD thesis, Eindhoven, 1975.
29. Krebs, B., Müller, A., and Beyer, H. H., *Inorg. Chem.* **8**, 436 (1969).
30. Morimoto, T., Nagao, M., and Tokuda, F., *J. Phys. Chem.* **73**, 243 (1969).
31. Burwell, R. L., Haller, G. L., Taylor, K. C., and Read, J. F., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 20 p. 1. Academic Press, New York, 1969.
32. Biloen, P., and Pott, G. T., *J. Catal.* **30**, 169 (1973).
33. Olsthoorn, A. A., and Boelhouwer, C., *J. Catal.* **44**, 207 (1976).