

## Formation and Structure of the $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ System under Precatalysis Conditions

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Received August 5, 1983; revised November 20, 1984

The formation of the  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst surface in conditions of precatalysis has been investigated by means of various physical and chemical methods. It is suggested that under oxidative conditions a surface aluminum mesoperrhenate, " $\text{AlRe}^{\text{VII}}\text{O}_5$ ," is obtained. The same structure is formed finally, irrespective of the amount of rhenium deposited, as well as its valence state, combination (oxides, salts), the alumina carrier structure ( $\gamma$ ,  $\theta$ , nonporous) and phase (solid mixture or solution) of the starting materials. The structure is thermal and moisture stable, and is characterized by diffuse reflectance spectra with bands at 235 and 340 nm and a shoulder at 395 nm. It is not readily transformed into metallic rhenium. After reduction the structure can be completely restored under oxidative conditions only. On heating dried samples in an inert gas atmosphere or *in vacuo*, low-valence Re(VI) and Re(IV) coexist with Re(VII) on the surface. This is also observed under vacuum treatment of the calcined samples. The formation of a surface mesoperrhenate structure is detected on other carriers as well. © 1985 Academic Press, Inc.

### INTRODUCTION

The catalyst conventionally designated as  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  is well known for its high activity in the olefin metathesis reaction (1). Its structure is a subject of considerable interest, and several ideas referring to it have been suggested (2-9). The interaction of rhenium compounds with the surface of alumina is important for the preparation of the widely used bimetallic catalysts, such as Pt-Re/ $\text{Al}_2\text{O}_3$  (10-12).

In a previous communication (13) the possibility of the formation of a surface aluminum mesoperrhenate (" $\text{AlReO}_5$ ") under precatalysis conditions was reported.

In the present work, the formation of the active catalyst surface, its properties, and its structure are systematically reinvestigated using various physical and chemical methods.

### EXPERIMENTAL

**Sample preparation.** Supported rhenium samples were obtained by impregnation of

slightly crystalline  $\gamma\text{-Al}_2\text{O}_3$  (surface area 210  $\text{m}^2/\text{g}$ , Fe 0.024%, Na 0.01%) with an aqueous solution of  $\text{NH}_4\text{ReO}_4$  (Fluka, pure). The initial rhenium deposition was varied between 0.5 and 25 wt%  $\text{Re}_2\text{O}_7$ . After 24 h storage the slurry was dried at 105°C for 2 h and calcined in air at different temperatures between 200 and 1000°C. Two other aluminas, namely  $\theta\text{-Al}_2\text{O}_3$  (surface area 180  $\text{m}^2/\text{g}$ ) and Degussa Oxyd C (surface area 100  $\text{m}^2/\text{g}$ ) were also used. The carriers were previously calcined in air at 600°C for 6 h.

In order to obtain a bulk phase of aluminum mesoperrhenate ( $\text{AlReO}_5$ ) several attempts have been made mixing aqueous solutions or solid phase of  $\text{AlCl}_3$  (Merck, extrapure) or  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Merck, GR) and  $\text{NH}_4\text{ReO}_4$ . The atomic ratio Al:Re = 1:6.9 and is equivalent to 82.6%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ .

The synthesis of both  $\text{Ba}_3(\text{ReO}_5)_2$  and  $\text{Ba}_5(\text{ReO}_6)_2$ , which have been used as model compounds, was performed starting with  $\text{Ba}(\text{CO}_3)_3$  (Merck, Specpure) and  $\text{HReO}_4/\text{Re}_2\text{O}_7$  (Koch-Light) in accordance with Ref. (14).  $\text{Ba}_3(\text{ReO}_5)_2$  was also obtained

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from  $\text{BaCl}_2 \cdot \text{H}_2\text{O}$  (Merck, Specpure) and  $\text{NH}_4\text{ReO}_4$  solutions. Their structure was checked by X-ray analysis (15) and IR spectroscopy (14).

**Chemical analysis.** The air-calcined samples were reduced for 5 h in a hydrogen gas flow at 550°C and then treated with  $\text{H}_2\text{O}_2$  according to Ref. (16). Rhenium was analyzed colorimetrically (using an improved rhodanide method (17)) or by atomic emission spectroscopy (PGS-2, Carl Zeiss-Jena).

**Apparatus.** X-Ray diffraction measurements were made with a Dron 1 apparatus using filtered  $\text{CuK}\alpha$  radiation.

The thermal analysis data were obtained with a Paulik-Paulik-Erdey instrument, Type OD-103; 200-mg samples were studied in air at a heating rate of  $10^\circ\text{C min}^{-1}$  in the range 25–1000°C.

Diffuse reflectance spectra were recorded at room temperature in the range 220–2000 nm on a Carl Zeiss Jena VSU-2P spectrophotometer supplied with a 0/45 geometry attachment and milk glass as reference. The other commonly used references, such as MgO and  $\text{BaSO}_4$ , turned out to be less suitable owing to the high absorption of the  $\text{Al}_2\text{O}_3$  support below 350 nm (Fig. 1), which greatly reduced the resolution of the spectra, as may be observed in Ref. (5). The spectra obtained against  $\text{Al}_2\text{O}_3$  are similar to those of milk glass. The latter is preferred because it is not influenced by the atmospheric humidity.

XPS spectra were recorded with an ES-100 spectrometer at room temperature. The C *s* line ( $E_b = 285$  eV) of adsorbed diffusion pump oil and Al 2*p* ( $E_b = 75.0$  eV) were used as standards to calibrate the energy position of the peaks. The pressure in the spectrometer was  $10^{-7}$  Torr (1 Torr = 133.3 N m<sup>-2</sup>), which excluded the possibility of rhenium oxidation during the recording of the spectra.

IR spectra were recorded in the region 400–4000  $\text{cm}^{-1}$  by a Carl Zeiss Jena IR-20 spectrophotometer, using Nujol or KBr technique.

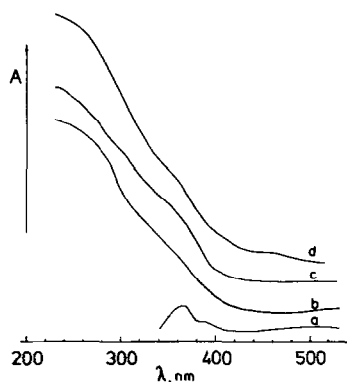


FIG. 1. Diffuse reflectance spectra of  $\gamma\text{-Al}_2\text{O}_3$  against different references. (a) Milk glass, (b)  $\text{SiO}_2$  (Degussa), (c) MgO, (d)  $\text{BaSO}_4$ .

## RESULTS

### (a) Thermal Treatment of Pure and Supported $\text{NH}_4\text{ReO}_4$ in Air

The thermal treatment in air of a pure, i.e., unsupported,  $\text{NH}_4\text{ReO}_4$  (sample A) was followed by means of different physical methods and compared to that of samples supported on  $\text{Al}_2\text{O}_3$  (samples B).

**X-Ray analysis.** As X-ray analysis has previously given controversial results (4, 5), an attempt was made to repeat them. Samples containing 5, 10, 15, 18, and 20 wt%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  as well as pure  $\text{NH}_4\text{ReO}_4$  were investigated. After drying, seven intense lines were clearly observed at  $d$  (Å) = 5.361, 3.504, 2.581, 2.1791, 1.9133, 1.8479, and 1.7885. Upon heating to 360°C they gradually decreased in intensity and broadened. Above 400°C  $\text{NH}_4\text{ReO}_4$  completely sublimed. On the samples B only the main lines of the support were registered (JCPDS File No. 29-63) after calcining at 400–800°C.

**Thermal analysis (TA).** The  $\text{NH}_4\text{ReO}_4$ -impregnated  $\gamma\text{-Al}_2\text{O}_3$  samples containing up to 20 wt%  $\text{Re}_2\text{O}_7$  afforded TA Scans identical with the curves of pure carrier. However, 25 wt%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  exhibited a shallow broad endothermic peak at 350°C on its DTA curve indicative of  $\text{NH}_4\text{ReO}_4$  decomposition. The weight loss after 650°C shown

by TG curves revealed the sublimation of the products.

**IR spectra.** The characteristic metal–oxygen bond vibrations can be recorded in the region  $400\text{--}1100\text{ cm}^{-1}$ . The dried samples with 13%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  gave absorption bands at  $905\text{ cm}^{-1}$  (strong) and  $925\text{--}935\text{ cm}^{-1}$  (weak). After calcining, the bands became more diffuse, but an appearance of new bands was not detected. The increase of Re content enhanced the band intensity in both dried and calcined samples. The carrier exhibits strong absorption below  $900\text{ cm}^{-1}$ .

**Diffuse reflectance spectra (DRS).** It is seen from Fig. 2a that the white crystalline  $\text{NH}_4\text{ReO}_4$  absorbed intensely at 235 and 270 nm. This is of interest, since above 220 nm the aqueous  $\text{NH}_4\text{ReO}_4$  solution absorbs only in the range  $225\text{--}235\text{ nm}$  (18). Upon heating, its color turned from light pink ( $180^\circ\text{C}$ ) to grey ( $250\text{--}320^\circ\text{C}$ ) and new absorption bands appeared at 365, 395, 460, and 520 nm (Figs. 2b, c, d). As already mentioned, after  $360^\circ\text{C}$  the unsupported  $\text{NH}_4\text{ReO}_4$  sublimed.

The supported rhenium sample containing 13 wt%  $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$  (most frequently used as catalyst in our investigations) was also investigated. Generally, the color changes and the spectra were similar to

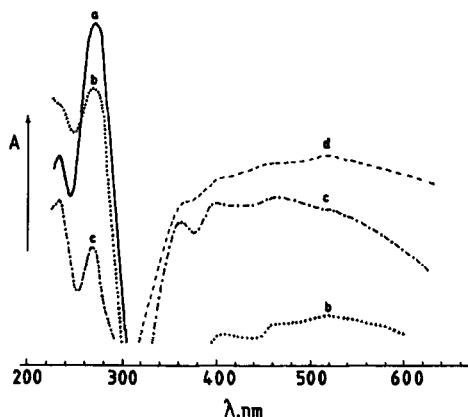


Fig. 2. Diffuse reflectance spectra of  $\text{NH}_4\text{ReO}_4$  after heating in air. (a)  $\text{NH}_4\text{ReO}_4$ ,  $25^\circ\text{C}$ , (b)  $\text{NH}_4\text{ReO}_4$  heated for 1 h at  $180^\circ\text{C}$ , (c)  $\text{NH}_4\text{ReO}_4$  heated for 1 h at  $250^\circ\text{C}$ , (d)  $\text{NH}_4\text{ReO}_4$  heated for 1 h at  $320^\circ\text{C}$ .

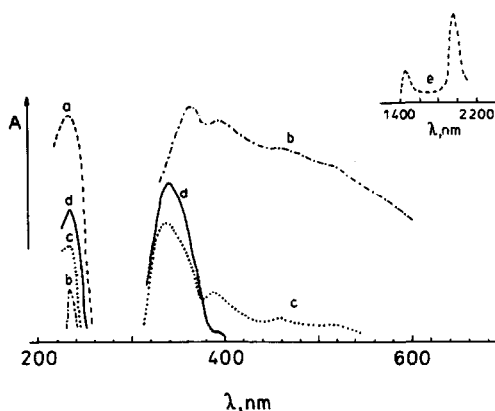


Fig. 3. Diffuse reflectance spectra of 13 wt%  $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$  after heating in air. (a) Dried at  $105^\circ\text{C}$  for 2 h, (b) heated at  $360^\circ\text{C}$  for 1 h, (c) heated at  $360^\circ\text{C}$  for 4 h, (d) heated at  $450^\circ\text{C}$  for 2 h, (e) on air storage.

those of pure  $\text{NH}_4\text{ReO}_4$ , but there were some peculiarities. In the dry sample only the band at 235 nm was recorded, and the band at 270 nm was missing (Fig. 3a). Further heating gave rise to the same additional bands (Fig. 3b). Above  $360^\circ\text{C}$  there was a drastic difference from pure  $\text{NH}_4\text{ReO}_4$ . The band at 365 nm shifted to 340 nm and the bands at 395, 460, and 520 nm gradually disappeared (Figs. 3b, c). The color of the samples turned from greyish to pale yellow. Bands at 235 and 340 nm with a shoulder at 395 nm appeared at  $400\text{--}450^\circ\text{C}$  (Fig. 3d). The band at 235 nm was observed throughout the whole temperature interval, its intensity passing through a minimum at  $320^\circ\text{C}$ . Atmospheric humidity diminished the band intensity and bands at 1450 and 1950 nm arose in the near infrared (NIR) (Fig. 3e).

It should be noted that if the dried samples were heated to  $450^\circ\text{C}$  in an inert atmosphere or *in vacuo*, they turned lilac in color, and bands at 235, 340, 460, 520, and 1650 nm appeared. The band at 340 nm broadened owing to the overlapping of the band at 365 nm. However, the air-calcined sample was treated in an inert gas flow, no new bands were detected, while those at 235 and 340 nm sharpened and became more intense.

### (b) Model Samples and Comparative Reactions

With a view to obtaining additional data to interpret diffuse reflectance spectra identification and to model the reactions which may occur on the surface, several air-stable rhenium oxides and salts were synthesized (see Experimental) and their spectra were recorded.

Some spectra, namely those of  $\text{ReO}_2$  and  $\text{ReO}_3$ , were reported elsewhere (19). The spectra of  $\text{Re}_2\text{O}_7$  and  $\text{Ba}_3(\text{ReO}_5)_2$ , both pale-yellow colored, are shown in Figs. 4a and c.  $\text{Re}_2\text{O}_7$  absorbed at 235 and 350 nm with a shoulder at 260 nm.  $\text{Ba}_3(\text{ReO}_5)_2$  absorbed at 235, 345, and 395 nm with a shoulder at 255 nm. Both spectra resembled the spectrum of the calcined catalyst (Fig. 3d). In the orange-colored  $\text{Ba}_2(\text{ReO}_6)_2$  a band at 430 nm was recorded.

The following samples were prepared and calcined in air:

(a) mixture of solid  $\text{ReO}_3$  and  $\gamma\text{-Al}_2\text{O}_3$ ;  $\text{ReO}_2$  (orthorhombic) and  $\gamma\text{-Al}_2\text{O}_3$ ;  $\text{ReO}_2$  (orthorhombic) and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ;  $\text{Re}_2\text{O}_7$  ( $\text{HReO}_4$ ), and  $\gamma\text{-Al}_2\text{O}_3$ ; (b) rhenium complexes, supported on  $\gamma\text{-Al}_2\text{O}_3$ , such as:  $\text{Re}_2\text{O}_7 \cdot \text{dioxan}$  (decomposing to  $\text{ReO}_3$ ) (20) and  $\text{K}_2\text{ReCl}_6$  (hydrolyzing to  $\text{ReO}_2$ ) (17).

All samples after heating in air at 450°C for 2 h gave rise to pale-yellow products absorbing at 235 and 340 nm and with a

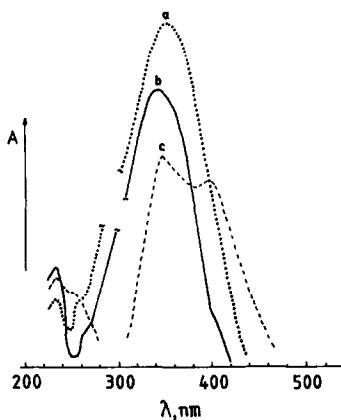


FIG. 4. Diffuse reflectance spectra of (a)  $\text{Re}_2\text{O}_7$ , (b) "AlReO<sub>5</sub>," (c)  $\text{Ba}_3(\text{ReO}_5)_2$ .

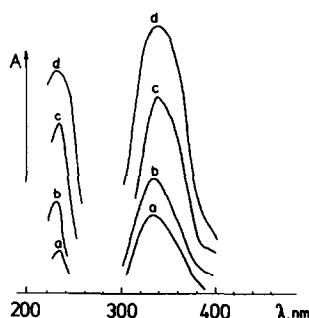


FIG. 5. Diffuse reflectance spectra of  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  (a) 0.5%  $\text{Re}_2\text{O}_7$ , (b) 5%  $\text{Re}_2\text{O}_7$ , (c) 10%  $\text{Re}_2\text{O}_7$ , (d) 20%  $\text{Re}_2\text{O}_7$ .

shoulder at 395 nm. In samples with low-valent Re oxides, the initial bands in the visible region disappeared. The band at 365 nm was shifted to 340 nm and a band at 235 nm arose. The samples impregnated with  $\text{HReO}_4$  were optically clear up to 300°C. Above this temperature, the characteristic bands appeared and increased in intensity.

The alumina used ( $\gamma$ ,  $\theta$ , Degussa Oxyd C) had no observable effect on the results reported here. The carriers are optically clear in the whole range under study, excluding NIR bands at 1450 and 1950 nm (Fig. 3e).

### (c) Physicochemical Properties

Further investigations have been carried out for the elucidation of the physicochemical properties of the structure formed upon calcining in air up to 450°C.

*The influence of rhenium loading.* The increase of Re content from 0.3 to 20 wt%  $\text{Re}_2\text{O}_7$ , i.e., 0.3, 0.5, 1, 5, 10, 13, 15, and 20 wt%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  enhances the intensity of the bands without changing their position or shape (Fig. 5). This is valid both for dried and calcined samples. It is worthy of note that the intensity of the bands depends strongly on the time of air storage (see Experimental). In view of this, comparative studies should be carefully made under similar conditions. The position of maxima and the shape of the spectra persisted for years.

On heating to 450°C from the samples designed to give a bulk phase of aluminum

mesoperrhenate ( $\text{AlReO}_5$ ) a considerable amount of rhenium sublimates was observed. The spectrum recorded contained a shoulder at 265 nm and bands at 235, 340, and 395 nm (Fig. 4b). No X-ray diffraction patterns were registered. The rhenium content was 18.3 wt%  $\text{Re}_2\text{O}_7$ .

The increase of Re loading has no measurable effect on the specific area.

**Thermal stability.** The characteristic bands for all kinds of supported rhenium samples, air calcined at 450°C, persisted after prolonged heating (8 h) at 800°C and was accompanied by a loss of 23 wt% Re (calculated as  $\text{Re}_2\text{O}_7$ ) in the sample containing initially 13 wt%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ . The bands disappeared only after calcining at 1000°C.

**Reduction.** It has already been reported (13, 21) that the reduction of the air-calcined samples with  $\text{CO}$ ,  $\text{H}_2$ , or olefins leads to color changes and the appearance of new bands at 365, 395, 460, 520, and 1650 nm. No lines were detected in the diffractograms after reduction at 350°C with  $\text{H}_2$  of the sample with 13 wt%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ . The sample remained X-ray amorphous after treatment for 3.5 h at 550°C. If the reduction was carried out for 5 h, metallic rhenium ( $d = 2.36, 2.23, \text{ and } 2.11 \text{ \AA}$ ) (JCPDS File No. 5-702) was registered. In samples richer in rhenium (20.5 wt%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ ) the metallic form is present after a shorter reduction time (1 h).

Upon air calcining at 450–500°C the reduced samples restored their pale-yellow color and the bands at 235 and 340 nm reappeared, while bands in the UV–visible and NIR regions disappeared. The samples turned X-ray amorphous again. During catalytic activity tests in metathesis the catalyst (13 wt%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ ) undergoes 80 cycles of reduction by olefins and regeneration in air without changing its spectrum. At the end of experiments it contained 11.8 wt%  $\text{Re}_2\text{O}_7$  instead of the theoretically calculated 13 wt%  $\text{Re}_2\text{O}_7$  loading.

The reduction–oxidation cycles were followed by ESCA measurements (Fig. 6). The spectra of the model samples Ba

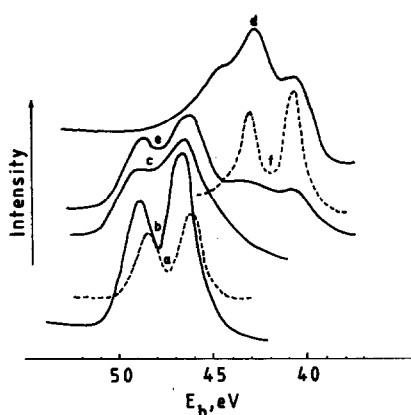


FIG. 6. (a)  $\text{Ba}(\text{ReO}_4)_2$ , (b)  $\text{Ba}_3(\text{ReO}_5)_2$ , (c) 13 wt%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  calcined at 580°C for 2 h, (d) sample (c) after hydrogen treatment for 1 h at 550°C, (e) sample (d) after air storage, (f) metallic rhenium.

( $\text{ReO}_4$ )<sub>2</sub>,  $\text{Ba}_3(\text{ReO}_5)$ , and metallic Re were also obtained.

In the air-calcined sample (13 wt%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ ) the Re  $4f$  line shows  $E_b = 46.6 \text{ eV}$  (Fig. 6c). It coincides with the  $4f_{7/2}$  line of the reference  $\text{Ba}_3(\text{ReO}_5)_2$  (Fig. 6b) and differs in the position of the  $4f_{7/2}$  line of  $\text{Ba}(\text{ReO}_4)_2$  ( $E_b = 46.0 \text{ eV}$ ) (Fig. 6a) of both Re(VII) compounds. The catalyst line is somewhat broadened.

After treatment with  $\text{H}_2$  for 1 h at 550°C the Re  $4f$  line shifted to lower energies. The comparison with the  $4f_{7/2}$  line of metallic Re ( $E_b = 40.6 \text{ eV}$ ) (Fig. 6c) showed the presence of both metallic rhenium and other low-valent forms, e.g.,  $\text{Re}^{n+}$  ( $0 \leq n \leq 4$ ) on the surface (Fig. 6d). After air exposure of the sample, two marginal forms of Re  $4f_{7/2}$  were detected, such as  $E_b = 40.6$  and  $46.0 \text{ eV}$  (Fig. 6c), indicative of immediate partial surface oxidation. On air calcination the initial spectrum was completely recovered (Fig. 6c).

**Water solubility.** Treatment with water of the air-calcined samples provides some additional data about the nature of the structure formed.

The washing water absorbs intensely at 206 nm ( $\epsilon = 6060$ ) and 220 nm ( $\epsilon = 3610$ ), which is an evidence for the presence of  $\text{ReO}_4^-$  ( $\text{Re}^{\text{VII}}$ ) (18). On concentration the

washing water exhibits an acid reaction. Careful evaporation to dryness leads to the appearance of pale-yellow crystals of  $\text{Re}_2\text{O}_7$ , which readily adsorb moisture from the air and are transformed reversibly into perrhenic acid ( $\text{HReO}_4$ ).

A semiquantitative analysis of the washing waters (rinsing waters) at  $\lambda = 220$  nm and  $\epsilon = 3610$  of a sample containing 13 wt%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ , air calcined at  $550^\circ\text{C}$  for 2 h, was performed. It was established that after cold water treatment about 35 wt% of Re was extracted. Further treatment with boiling water increases this percentage up to 61%, and after prolonged treatment with warm water 83 wt% of rhenium loading is extracted. The same results are obtained treating the samples with 0.5, 1, and 18 wt%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ . The incomplete extraction of rhenium is confirmed by the diffuse reflectance spectra, which reveal the presence of bands both at 235 and 340 nm. Their intensity decreases simultaneously upon the treatment with cold and warm water.

#### d. Catalytic Activity

The activity for metathesis of propene over Re-containing catalysts, calcined in air, at different temperatures between 360 and  $450^\circ\text{C}$  was investigated (Table 1).

It is clear that after catalyst calcination at an appropriate temperature the conversion almost reaches equilibrium (22).

### DISCUSSION

#### 1. Identification of Bands in DRS

In agreement with the literature data for  $\text{ReO}_4^-$  spectra in solution (23) the band at

235 nm in solid  $\text{NH}_4\text{ReO}_4$  can be attributed to a charge transfer transition  $t_1 \rightarrow 2e$  in  $\text{Re(VII)} (T_d)$ . The new more intense band at 270 nm may be due to the  $C_{2v}$  deformation of tetrahedral  $\text{ReO}_4^-$  ion in the crystal state (24). The symmetry lowering leads to splitting of the  $t_1$  and  $2e$  levels, thus allowing the new charge transfer. This band arises also in the DRS of solid  $\text{KReO}_4$ ,  $\text{Ba(ReO}_4)_2$ ,  $\text{Mg(ReO}_4)_2$  (25), and is not present in their solution spectra.

According to Ref. (26) the crystal structure of  $\text{Re}_2\text{O}_7$  represents double polymer sheets of equal numbers of almost regular tetrahedra and strongly distorted octahedra. The double sheets are linked by weak van der Waals bonds. By means of DRS spectra the bands at 235 and 260 nm may be ascribed to  $\text{Re(VII)} (T_d)$ , and that at 350 nm to  $\text{Re(VII)} (O_h)$ . However,  $\text{Ba}_3(\text{ReO}_5)_2$ , i.e.,  $\text{Re(VII)}$  in the  $\text{ReO}_3^{3-}$  anion, possesses a similar spectrum. It is obvious that some more data should be considered with the view to interpreting these bands.

As seen from the DRS data of  $\text{ReO}_2$  and  $\text{ReO}_3$  (19),  $\text{Re(IV)}$  at 365, 395, 460, and 570 nm, and  $\text{Re(VI)}$  at 520 and 1650 nm can be detected in the products of thermal decomposition of both unsupported (Fig. 2) and supported (Fig. 3)  $\text{NH}_4\text{ReO}_4$ , as well as in reduced and vacuum-treated samples.

The bands in the NIR region can be attributed to the carrier (Fig. 3e). The band at 1450 nm is ascribed to an OH stretching overtone and that at 1950 nm to a combination band of physically adsorbed water molecules, by analogy with  $\text{SiO}_2$  spectra in this region (27). Similar bands were detected on a noncalcined  $\text{MgO}$  carrier (25).

#### 2. Structure of Calcined Samples

On the basis of the X-ray data mentioned above, it can be concluded that, after drying,  $\text{NH}_4\text{ReO}_4$  remains as a phase on the catalyst surface (JCPDS File No. 10-252). During calcination in air  $\text{NH}_4\text{ReO}_4$  decomposes into a mixture of rhenium oxides,

TABLE 1

Influence of the Calcination Temperature of Catalyst on Metathesis<sup>a</sup>

$T$ ( $^\circ\text{C}$ )	360	400	450
Conversion (%)	5.4	23	38

<sup>a</sup> Reaction conditions: pulse reactor; 1.1 g, 13 wt%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ . After calcining, all samples were treated with  $\text{N}_2$  for 1 h at  $450^\circ\text{C}$ ,  $T_{\text{react}} = 150^\circ\text{C}$ .

namely  $\text{ReO}_2$ ,  $\text{ReO}_3$ , and  $\text{Re}_2\text{O}_7$  (28). Their presence could not be proved by X-ray analysis, most probably owing to a high dispersion on the alumina surface. However, the DRS results revealed the appearance of Re(VI) and Re(IV) even above 200°C (Figs. 2, 3). The lowering in intensity of the Re(VII) band at 235 nm may be associated with  $\text{NH}_4\text{ReO}_4$  decomposition, and its further increase with temperature with the appearance of the new rhenium structure.

Proceeding from the comparative reactions and the DRS, it can be assumed that the oxide-support interactions lead to the same final structure, irrespective of the rhenium valence state in the starting material, as well as its combination (oxides, salts), phase (mixture or solutions), or carrier structure ( $\gamma$ -,  $\theta$ -, nonporous  $\text{Al}_2\text{O}_3$ ). Certainly, the possibility of a direct interaction between  $\text{ReO}_4^-$  ( $\text{NH}_4\text{ReO}_4$  and  $\text{HReO}_4$ ) and  $\text{Al}_2\text{O}_3$  is not excluded.

The thermal analysis results indicated that an amount of ca. 20–25 wt%  $\text{Re}_2\text{O}_7$  "saturated" the surface of the alumina used. The excess was sublimed. The attempts to obtain bulk aluminum mesoperrhenate ( $\text{AlReO}_5$ ) by mixing rhenium and aluminum in a stoichiometric ratio failed. The "trapped" amount of rhenium (18 wt%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ ) is almost equal to the highest amount "trapped" as a result of rhenium deposition by impregnation, i.e., instead of a bulk compound, only surface forms are obtained. Contrary to this, in the rhenium-magnesium system magnesium oxide trapped all the rhenium deposited to form pale-yellow colored magnesium mesoperrhenate,  $\text{Mg}_3(\text{ReO}_5)_2$  (80 wt%  $\text{Re}_2\text{O}_7$ ), and white magnesium perrhenate,  $\text{Mg}(\text{ReO}_4)_2$  (92.3 wt%  $\text{Re}_2\text{O}_7$ ), both being bulk compounds (25).

The alumina "saturation," along with the lack of diffraction pattern, and the insignificant variation of specific surface area with the increase of rhenium loading supports the idea already given by other authors (2, 3, 5) that the structure formed represents a monolayer. The latter is characterized by

its DRS, where bands at 235 and 340 nm prevail with a shoulder at 395 nm.

The invariability of the position and shape of the bands with increase of rhenium content or temperature leads to the conclusion that after calcination the rhenium ions exist in a unique structure, i.e., in the same valence state and coordination. This conclusion is supported by the similar behavior of samples containing low and high  $\text{Re}_2\text{O}_7$  amounts, including the simultaneous lowering of intensity of all bands upon treatment with cold and warm water. This is at variance with the other metathesis catalysts, such as  $\text{MoO}_3/\text{Al}_2\text{O}_3$  (29a) and  $\text{WO}_3/\text{Al}_2\text{O}_3$  (29b).

By comparing the DRS results for  $\text{Re}_2\text{O}_7$  and air-calcined catalyst (Figs. 3d and 4a), it might be concluded that a double oxide structure is formed on the surface, namely  $x\text{Re}_2\text{O}_7 \cdot y\text{Al}_2\text{O}_3$ . However, such a conclusion must be rejected for of several reasons. First,  $\text{Re}_2\text{O}_7$  is a highly hygroscopic substance and is rapidly converted into  $\text{HReO}_4$  (30). This would lead to drastic changes in the spectra under moist conditions, which were not observed. Second,  $\text{Re}_2\text{O}_7$  begins to sublime at 200°C, whereas the structure formed demonstrates high stability on air calcining. Third, under dynamic conditions  $\text{Re}_2\text{O}_7$  sublimed before reduction (31) while the catalyst suffered numerous reduction-oxidation cycles with insignificant loss of rhenium. Moreover, the average surface area of  $\text{Re}_2\text{O}_7$  in crystal form is 0.25 nm<sup>2</sup> (26), but for one molecule of  $\text{Re}_2\text{O}_7$  on 18 wt%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst, it is 0.90 nm<sup>2</sup>, i.e., not such closely packed units. Similar results were reported in Ref. (5).

An interaction between rhenium oxides and the support may be assumed under oxidative conditions leading to formation of a surface aluminum perrhenate analogue,  $\text{Al}(\text{ReO}_4)_3$ , i.e., the presence of  $\text{ReO}_4$  groups on the surface. Both the IR data (9) and the Raman spectra (7) of the pure and calcined supported  $\text{NH}_4\text{ReO}_4$  point to this conclusion. However, if the spectra of dried and

calcined samples are compared, no significant difference is evident, although rhenium state on their surfaces is markedly different, as shown by the diffuse reflectance spectra (Fig. 3). Most probably, this is due to the fact that the observed bands in IR are typical not only for  $\nu_{as}\text{ReO}_4$  in  $\text{NH}_4\text{ReO}_4$  (32) but they are detected in other rhenium structures as well (33). Furthermore, it is worthy of note that according to Ref. (34) aluminum perrhenate is a white-colored, strongly hygroscopic substance. On air calcination at  $300^\circ\text{C}$  it begins to decompose into  $\text{Al}_2\text{O}_3$  and  $\text{Re}_2\text{O}_7$ . The latter is sublimed completely at  $700^\circ\text{C}$ , which allows quantitative determination of the rhenium. The reduction of  $\text{Al}(\text{ReO}_4)_3$  with  $\text{H}_2$  begins at  $200^\circ\text{C}$  and reaches completion at  $300^\circ\text{C}$  leading to  $\text{Al}_2\text{O}_3$  and Re metal formation. The structure formed on calcining has quite different features. The XPS results (Fig. 6) also testify to the fact that the  $\text{ReO}_4^-$  structure is different from that of the calcined catalyst. The conditions of preparation excluded the possibility of  $\text{AlRe}^{\text{VO}}_4$  formation (58,000 atm,  $1200\text{--}1300^\circ\text{C}$ ) (35).

The bands at 235 and 265 nm (Figs. 3, 4) in DRS should not be examined separately as  $\text{Re}(\text{VII}) T_d$  bands, but should be taken together with the band at 340 nm and the shoulder at 395 nm, indicative of another type of Re structure.

It is known in the literature (15) that on calcination in air at  $400\text{--}800^\circ\text{C}$  of alkaline and alkali earth oxides and salts with their perrhenates of the same metal, new types of oxygen-containing  $\text{Re}(\text{VII})$  compounds are formed, such as pale-yellow mesoperrhenates ( $\text{ReO}_3^{3-}$ ) and orange or green-yellow *ortho*-perrhenates ( $\text{ReO}_6^{5-}$ ). These structures exist in the solid state in other substances (36–38). In water solution they are transformed into  $\text{ReO}_4^-$ .

In contrast to those of the alkali metals, the alkali-earth meso- and *ortho*-perrhenates are comparatively stable to moisture in the air. Barium *ortho*- and mesoperrhenates have been studied in detail (14).

The band at 430 nm, characteristic of or-

ange  $\text{Ba}_5(\text{ReO}_6)_2$ , was not observed in the spectrum of the calcined samples B, which excluded the possibility of a similar structure formation on the surface, i.e.,  $\text{Re}(\text{VII})$  in octahedral environment.

The pale-yellow barium mesoperrhenate,  $\text{Ba}_3(\text{ReO}_5)_2$ , is of particular interest. The conditions of its preparation, thermal and moisture stability, as well as diffuse reflectance spectra [see Fig. 4c and Refs. (14, 39)] strongly resemble those of the air-calcined catalyst (Fig. 3).

These data suggested that a mesoperrhenate structure might be formed on the support surface under the oxidative conditions of precatalysis.

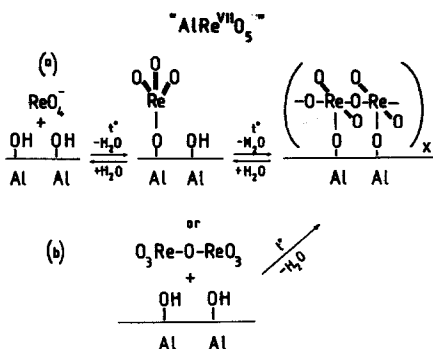
Further information in support of this was provided by the XPS spectra (Fig. 6). The Re 4f line of the catalyst (Fig. 6c) coincides with the Re 4f line of the reference  $\text{Ba}_3(\text{ReO}_5)_2$  (Fig. 6b). The line broadening observed in the catalyst spectrum indicated some energetic nonequivalency of the rhenium ions on the alumina surface. The latter was attributed to the presence of low-valence rhenium ions, namely  $\text{Re}(\text{IV})$  and  $\text{Re}(\text{VI})$  following high-temperature treatment under vacuum of the air-calcined samples (21).

An attempt was made to model the structure of the surface aluminum mesoperrhenate. X-Ray analysis of a single crystal of  $\text{Ba}_3(\text{ReO}_5)_2$  showed that in the  $\text{ReO}_3^{3-}$  anion  $\text{Re}(\text{VII})$  is surrounded by five oxygen atoms in a slightly distorted tetragonal pyramid geometry ( $C_{4v}$  symmetry) (40).

It is assumed that upon oxidative heating in air,  $\text{ReO}_4^-$  interacts with  $\text{Al}_2\text{O}_3$  according to Scheme 1: (a) On heating,  $\text{ReO}_4^-$  from  $\text{NH}_4\text{ReO}_4$  or  $\text{HReO}_4$  interacted with alumina hydroxyls evolving  $\text{H}_2\text{O}$  and forming surface aluminum mesoperrhenate. The process is reversible, i.e., upon treatment with water the monolayer is gradually destroyed, separating  $\text{ReO}_4^-$  in solution. The gradual solubility is attributed to different reactivity of surface hydroxyls, which leads to a different strength of the bonding between rhenium and alumina. Finally, some



amount of rhenium which could hardly be extracted, remained on the surface. (b) The low-valence rhenium oxides are transformed into  $\text{Re}_2\text{O}_7$ . With increasing temperature, the polymeric structure of  $\text{Re}_2\text{O}_7$  in the solid state is easily destroyed and transformed into almost linear  $\text{O}_3\text{Re}-\text{O}-\text{ReO}_3$  molecules (30). They are retained on the surface as shown in (b) of Scheme 1.



Obviously, irrespective of the mode of interaction, rhenium is stabilized on the surface up to a definite amount depending on the specific surface area and concentration of OH groups of the support. Above this loading the rhenium sublimes.

The necessity of OH groups is supported by the fact that Re cannot be deposited by the described method of impregnation on the thermodynamically stable  $\alpha\text{-Al}_2\text{O}_3$ , where OH groups are absent.

The lack of the characteristic vibrations of OH groups in samples containing 20–26 wt%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ , reported in Ref. (2), also confirms the above scheme for their participation in the formation of the catalytic surface.

This scheme accounted for the thermal stability of the surface structure as well as its gradual solubility in water. The bulk phase of magnesium mesoperrhenate,  $\text{Mg}(\text{ReO}_5)_2$ , formed on  $\text{Re}_2\text{O}_7/\text{MgO}$  catalyst is readily dissolved (5).

Moreover, the scheme interpreted the effectiveness of another method for rhenium deposition, namely not by impregnation, but by sublimation of  $\text{Re}_2\text{O}_7$  on to  $\text{Al}_2\text{O}_3$  calcined in the range 400–500°C (41).

If the dried sample is heated in an inert atmosphere or *in vacuo*, the low-content rhenium oxides are not completely oxidized to  $\text{Re}_2\text{O}_7$ . In this case, Re(VI) and Re(IV) coexisted in considerable amounts along with the mesoperrhenate structure. This was also observed for air-calcined samples subsequently treated *in vacuo* as if the surface suffered a moderate reduction by CO or olefin treatment (21). Both these findings should be taken into account by those workers employing the vacuum technique with a view to avoiding errors in adsorption (3) or gas titration measurements (8) used for the determination of the Re valence state. On air calcination the reduced samples completely recover the "surface aluminum mesoperrhenate" structure.

It is suggested that Re(VII) stabilizes through insertion in the carrier lattice (4). Unlike a normal spinel,  $A^{2+}B_2^{3+}O_4$ , the defective pseudo-spinel structure of  $\gamma\text{-Al}_2\text{O}_3$  may be designated as  $\text{Al}_{\frac{2}{3}}^{3+}(T_d)[\text{Al}_{\frac{1}{3}}^{3+}(O_h)]O_4$ , i.e., one-third of the tetrahedral ( $T_d$ ) sites remain unoccupied (42). They may be occupied by rhenium ions, which have similar ionic radii to  $\text{Al}^{3+}$ ;  $\text{Re}(\text{VII})(T_d) = 0.54 \text{ \AA}$ ;  $\text{Al}^{3+}(T_d) = 0.53 \text{ \AA}$ ;  $\text{Re}^{7+}(O_h) = 0.71 \text{ \AA}$ ;  $\text{Al}^{3+}(O_h) = 0.67 \text{ \AA}$  (43).

However, the results from the X-ray analysis did not confirm this assumption, since no change in the position of the carrier diffraction line was observed with increasing rhenium content, i.e., there was no change in the parameter of the host lattice (43). The insertion of rhenium in the lattice seems to be strongly hampered because of the high positive charge of the Re(VII) cation. An eventual insertion of Re(IV) ions is much more probable.

Re(VII) insertion is also at variance with other experimental data (44). If one starts from other crystal structures as carriers (white, optically clear substances), e.g., Ga or Zr oxides or salts, it is observed that on thermal treatment in air they interacted with  $\text{NH}_4\text{ReO}_4$  or  $\text{HReO}_4$  in a manner similar to that of aluminum oxides and salts: pale-yellow products are obtained, which

are thermally stable up to 800°C and their DR spectra resemble those of  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  (Fig. 3d). On water treatment a part of the rhenium is extracted, while another remains, as shown by the DR spectrum. This suggests that the formation of surface mesoperrhenate structures is not a characteristic feature of aluminum oxides and salts only, but it may be typical of other elements as well.

Samples active for metathesis were obtained after calcining in conditions favorable for the surface mesoperrhenate structure formation (Table 1). The catalytic activity is enhanced (5) with increasing Re content, which reveals the necessity of completing the monolayer on the surface.

If the structure is a bulky one, e.g., magnesium mesoperrhenate,  $\text{Mg}_3(\text{ReO}_5)$ , the catalyst displays no activity for olefin metathesis at low temperatures (25–220°C) (25). Probably, the formation of a polymeric monolayer on the catalyst surface in oxidative conditions is a common property of the three oxides used for olefin metathesis, namely  $\text{MoO}_3/\text{Al}_2\text{O}_3$  (29a),  $\text{WO}_3/\text{Al}_2\text{O}_3$  (29b), and  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ .

#### CONCLUSIONS

Therefore, the conclusion may be drawn that upon air calcining an oxidic Re(VII) structure is formed on the carrier. From the spectral and chemical data mentioned above, it is suggested that the structure represents predominantly a monolayer of surface aluminum mesoperrhenate ("AlReO<sub>5</sub>") rejecting  $\text{Re}_2\text{O}_7$  or  $\text{ReO}_4^-$  structures as less probable. Some accommodation of Re(IV) and Re(VI) ions is not excluded.

#### ACKNOWLEDGMENT

The authors are grateful to Dr. E. S. Shpiro of the Zelinsky Institute of Organic Chemistry, USSR Academy of Sciences, Moscow, USSR for recording the X-ray photoelectron spectra.

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