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Formation of the Active Form of Re_2O_7/SiO_2 Catalyst in Olefin Metathesis

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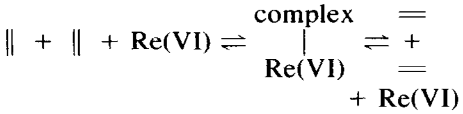
The formation, structure, and catalytic activity of Re_2O_7/SiO_2 in olefin metathesis in the low-temperature range (25–220°C) has been investigated. It has been established that in precatalysis conditions two different oxide structures are formed. A mixed surface rhenium oxide–perrhenate phase, viz. $ReO_x \cdot Re^{VII}O_4$, containing Re(VII)(T_d), Re(VI), and Re(IV) is formed upon air-calcining. A mesoperrhenate structure, viz. $ReO_x \cdot Re^{VII}O_5$, is formed on heating the dried samples in an inert gas flow. Electron Spin Resonance studies reveal that the activation (inert gas or vacuum treatment) leads to formation of anionic vacancies (F-centers) in the perrhenate phase. The catalytic activity in 1-butene metathesis has been investigated. The presence of a Re(VI)–mesoperrhenate structure has been found at the conditions of the maximum catalytic activity. The SiO_2 support exerts no stabilizing effect on this structure. Hence, it is unstable to moisture and easily reducible, which causes rapid catalyst deactivation. A complex active form including Re(VI), Re(VII), and an F-center (anionic vacancy) is suggested.

INTRODUCTION

Studies of the Re_2O_7/Al_2O_3 system used as a catalyst in the reaction of olefin metathesis in the temperature range 25–220°C revealed that the active form has a complex structure (*1*). This structure is formed during the various steps of catalyst treatment: (a) calcining in air at 450–550°C, which leads to the formation of a surface aluminum mesoperrhenate layer; (b) activation of the surface by treating the calcined samples in an inert gas flow or under vacuum, leading to dehydration and formation of oxygen-vacancy defects (F-centers); (c) partial reduction of Re(VII) by olefins, leading to an optimum Re(VII)/Re(VI) ratio. The simultaneous presence of these elements at the conditions of the maximum activity allows one to suggest the following mechanism:



$$\| + \| + \mathrm{Re(VI)} \rightleftharpoons \begin{array}{c}\text{complex}\\ | \\ \mathrm{Re(VI)}\end{array} \rightleftharpoons \begin{array}{c} = \\ + \\ = \end{array} + \mathrm{Re(VI)} \qquad (1)$$

$$\mathrm{Re(VI)} + \square \rightleftharpoons \mathrm{Re(VII)} + \mathrm{F} \qquad (2)$$

where □ denotes an anion vacancy in alumina. According to this mechanism the activation of the olefin molecule proceeds via formation of a Re(VI) complex. The electron transfer between Re(VII) and F-centers ensures high mobility of the Re(VI) ion in the layer of aluminum mesoperrhenate on the surface of the carrier. Hence the effective number of active sites is increased.

It was interesting to study the validity of these conclusions for catalytic systems having supports with properties and structure different from those of Al_2O_3 because of the important role of supports in the formation of the active form.

It was established that when MgO (an oxide with more ionic character of the metal–oxygen bond than that of Al_2O_3, i.e., more basic than Al_2O_3) is used as a support, the catalyst is not active in olefin metathesis unless metallic rhenium is formed (*2*). In the light of the above-mentioned considerations concerning the structure and properties of the catalytically active form, this lack of activity was explained as follows: (*3*): (a) bulk magnesium mesoperrhenate, $Mg_3(ReO_5)_2$, is formed and no electron

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transfer between it and the support occurs; (b) the electrons are localized on the anion vacancies due to the high ionicity of the MgO lattice and their mobility is reduced. These two factors impede the electron hopping on the surface, i.e., there is no interaction between the elements of the complex active form. This makes the Re_2O_7/MgO system inactive in the olefin metathesis in the range 25–220°C.

In the present paper the Re_2O_7/SiO_2 system is studied in order to clarify the effect of a support which is more covalent than Al_2O_3.

The catalytic activity of Re_2O_7/SiO_2 was first reported by Heckelsberg *et al.* (*4*) who carried out their investigations within the temperature range 300–500°C. Then Lin *et al.* (*5*) found that 10% Re_2O_7/SiO_2 exhibited no measurable activity up to 180°C. At this temperature Nakamura *et al.* (*6*) established low catalytic activity of 3.5% Re_2O_7/SiO_2. However, we observed a considerable initial activity in the temperature range 75–220°C (*7*). The structure of this system has been studied very little (*8–10*).

These incomplete and contradictory data prompted us to carry out a comprehensive study of the formation of the catalyst and its properties and structure under different precatalysis conditions. The catalyst activity for 1-butene metathesis in the 25–220°C range, its poisoning, and regeneration have also been investigated. The changes in rhenium state on the surface have been examined by means of various physical methods. A complex structure of the active form is suggested.

EXPERIMENTAL

The samples were obtained by impregnation of the carrier SiO_2 (Degussa, surface area 420 m^2/g) with an aqueous solution of NH_4ReO_4 (Fluka, puriss.). The initial rhenium loading was in the concentration range 1–13 wt% Re_2O_7/SiO_2. After 24 h storage the suspension was dried at 105°C for 2 h. The carriers were precalcined in air at 600°C for 6 h. Chemical analysis, as well as the apparatus and experimental details for thermal analysis, X-ray, diffuse reflectance spectroscopy, and infrared spectroscopy have been described elsewhere (*11*).

The catalytic activity of the samples was estimated at atmospheric pressure in a flow system in a quartz reactor. Catalyst 1.5–3 g of particle size 0.150–0.300 mm (40–90 mesh) was used. The absence of diffusion limitations, both external and internal, was verified by a number of tests.

Prior to the catalytic activity measurements the dry samples were calcined *in situ* in a flow of dry air for 2 h at 450–580°C, followed by 1 h heating in an inert gas flow (N_2 or Ar) at the same temperature. After cooling to reaction temperature in an inert gas flow, olefins (propene or 1-butene) were passed at a rate of 250–1100°C cm^3/h. In most experiments a rate of 270 cm^3/h was used. The temperature was controlled (±2°C) by a thermocouple placed in the catalyst bed. The reaction products were analyzed by GLC.

Quartz reaction vessels were used for thermal and vacuum treatments of the samples in the spectroscopic studies, allowing gas and vapor dosage.

RESULTS

Thermal Decomposition of NH_4ReO_4/SiO_2 in Air

The white, dry samples turn grey above 200°C and then blacken. Above 340°C the color grows pale, passes into brown, then beige-brown, and above 420°C, into white with a light lilac tint.

The calcining of the samples containing more than 7% Re_2O_7/SiO_2 is accompanied by sublimate deposition on the cold parts of the reactor as pale yellow (Re_2O_7), dark blue or red brown (ReO_3) crystallites. Quantitative analysis shows that only 6.2 wt% of rhenium, calculated as R_2O_7, remains on the support surface after the calcining of 13% Re_2O_7/SiO_2.

These visible changes are examined by means of different physical methods.

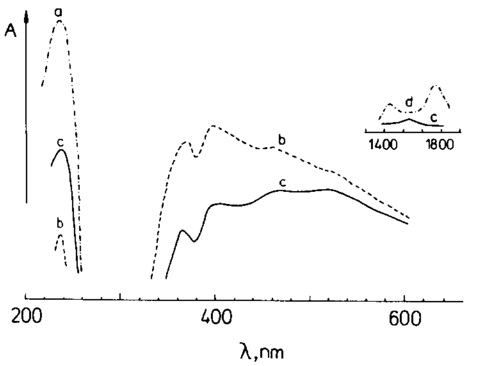

FIG. 1. Diffuse reflectance spectra of 6.2 wt% Re_2O_7/SiO_2 samples: (a) dried at 105°C for 2 h; (b) calcined in air at 350°C for 2 h; (c) calcined in air at 450°C for 2 h; (d) the pure carrier after storage in the presence of moisture.

X-Ray analysis. The dried samples of 5–13 wt% Re_2O_7/SiO_2 reveal the presence of seven diffraction lines at d = 5.30, 3.46, 2.92, 2.57, 2.23, 2.18, and 1.78 Å. With increasing calcination temperature their intensity decreases and no new lines are detected. The samples calcined at 400–800°C are X-ray amorphous.

Thermal analysis. The thermal analysis curves (TG, DTG, and DTA) of the samples containing 5 wt% Re_2O_7/SiO_2 are similar to those of the pure carrier. With increasing temperature an endothermic effect is observed on the DTA curve at 180°C attributed to elimination of the physically adsorbed water. A plateau in the range 300–700°C is ascribed to further surface dexydroxylation and some slight structural changes. The thermal analysis curves of the samples containing 13 wt% Re_2O_7/SiO_2 show decomposition of NH_4ReO_4 in the range 360–400°C. The 60% weight losses after heating at 750°C registered by the TG curve indicate rhenium sublimation.

Diffuse reflectance spectra (DRS). The freshly calcined SiO_2 carrier is optically inactive in the whole wavelength region under study. After storage in air, intensive absorption bands appear at 1450 and 1950 nm in the near infrared region (Fig. 1d). They are always registered in the catalyst exposed to moisture.

The white, dry, 13 wt% Re_2O_7/SiO_2 sample displays an absorption band at 235 nm (Fig. 1a). After calcining up to 350°C new bands appear at 365, 400, 460, and 530 nm, the band at 400 being dominant (Fig. 1b). In a sample calcined at 450°C, bands at 235, 365, 400, 470, 520, and 1670 nm are registered (Fig. 1c). The band at 520 nm is the most intense one. The variation in the amount of supported rhenium from 1 to 5 and 13 wt% Re_2O_7 leads to no changes in the position and number of the bands.

Upon heating the dried samples in an inert gas flow (N_2, Ar) to 450°C for 2 h, besides bands at 230, 365, 400, 520, and 1750 nm, new absorption bands at 245 and 330 nm are observed (Fig. 2a). Large amounts of sublimation products, mainly ReO_3 and less Re_2O_7 are deposited on the cold parts of the reactor. The samples turn from pale pink into greenish in air and their spectra are drastically modified (Fig. 2b). The bands at 245, 330, and 520 nm disappear and new bands appear at 235, 450, and 570 nm. The band at 1750 nm in the near-IR region broadens and new bands, attributed to the water vapor adsorption on the carrier, appear at 1450 and 1950 nm (*12*).

It is an interesting fact that if $HReO_4$ is used instead of NH_4ReO_4, the dried samples of $HReO_4/SiO_2$ show no bands until calcining at 230°C. Above this temperature

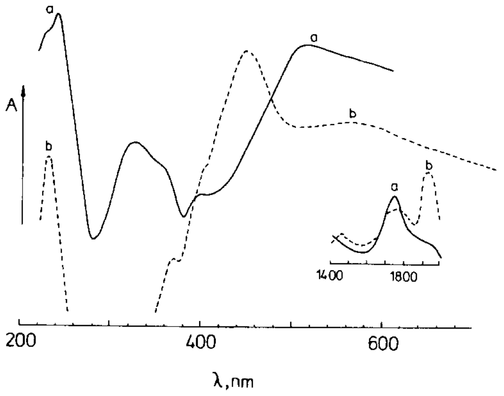

FIG. 2. Diffuse reflectance spectra of dried samples of 6.2 wt% Re_2O_7/SiO_2 heated in an inert gas atmosphere: (a) heated at 450°C for 2 h; (b) the heated samples after contact with air.

bands at 365, 400, and 460 nm arise. At 330°C the samples are greyish pink and bands at 520 and 1700 nm are present. Further calcining at higher temperatures leads to a spectrum similar to that of Fig. 1c. The same spectrum is obtained if one starts from ReO_3/SiO_2 or ReO_2/SiO_2.

Physicochemical Properties of the Calcined Samples

Further investigations have been carried out to clarify the physicochemial properties of the surface obtained upon calcining up to 450°C.

Thermal stability. No change in the position and number of the bands occurs within the range 450–700°C of calcination temperatures. Only a slight increase in intensity is observed in the diffuse reflectance spectra of the samples. After calcining at 750°C the bands disappear, which corresponds to the thermal analysis data for rhenium sublimation at the same temperature.

Water solubility. On treatment of the calcined samples containing 6.2 wt% Re_2O_7/SiO_2 with boiling water, 92% of rhenium is extracted as ReO_4^-.

Reducibility. If the air-calcined 6.2 wt% Re_2O_7/SiO_2 samples are treated in an inert gas flow and then flushed with H_2 in the temperature range 140–550°C for 1–3 h, diffraction lines of metallic rhenium (d = 2.36, 2.23, 2.11 Å) (JCPDS File No. 5-702) appear. It is only at lower reduction temperatures (3 h at 100°C) that they are not registered.

The initial structure is completely recovered after oxidation regeneration, as the reflectance spectra indicate. No diffraction lines are recorded.

Activation of the Catalyst

Evolution of water is observed upon inert gas or vacuum treatment after air-calcining of the samples. In the diffuse reflectance spectra only an increase of the band intensity is detected.

However, a symmetrical ESR signal arises at $g = 2.004$ with $\Delta H = 6.9$ G. The signal disappears on air contact and reappears after activation.

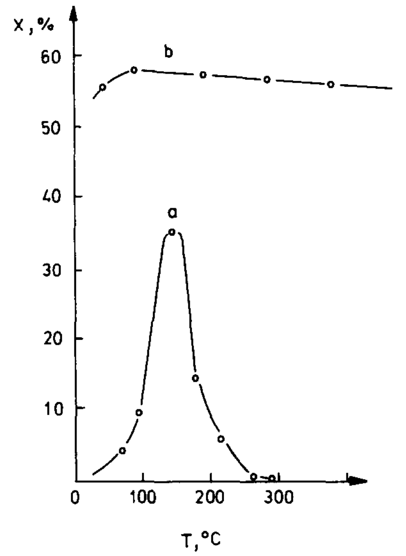

FIG. 3. Conversion of 1-butene vs temperature: (a) on a 6.2 wt% Re_2O_7/SiO_2 catalyst; (b) thermodynamic equilibrium curve, according to Ref. (*30*). The sample was analyzed 20 min after start of the reaction.

A similar treatment applied to the pure carrier does not cause the appearance of paramagnetic centers.

Catalytic Activity

The conversion of 1-butene at different temperatures in the 25–220°C range is presented in Fig. 3a. One can note that catalytic activity is displayed at about 75°C, reaches a maximum at 150°C and decreases with further increase of temperature.

The dependence of 1-butene conversion on time at various temperatures is shown in Fig. 4.

It is evident that at lower temperatures the conversion, although insignificant, remains constant with time (Fig. 4a). The initial degree of conversion is also increased, then it sharply decreases with the increasing of temperature (Figs. 4b,c). It should be noted that even at temperatures as low as 75°C only propene and pentenes are observed. No ethene and hexenes are detected as metathesis products. This indi-

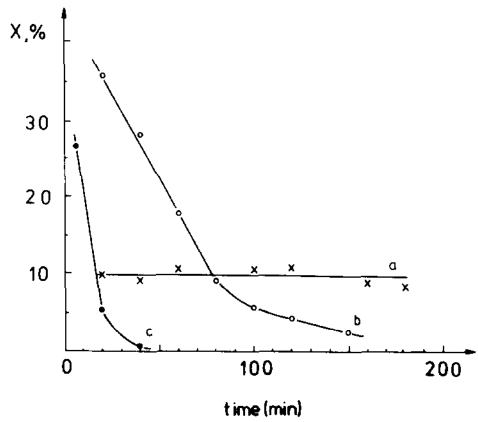

FIG. 4. Conversion of 1-butene vs reaction time over 6.2 wt% Re_2O_7/SiO_2 catalyst: (a) at 110°C; (b) at 150°C; (c) at 220°C.

cates that the metathesis occurs between 1-butene and *cis*- or *trans*-2-butenes.

The activity is completely regenerated on air-calcining at 580°C. It was found that after 54 reaction–regeneration cycles the catalyst contains 4.4 wt% Re_2O_7 as compared to the initially deposited amount of 6.2 wt% Re_2O_7. However, no decrease of the conversion is observed.

The pure SiO_2 carrier displays no activity for metathesis. However, it starts to isomerize 1-butene into *cis*- and *trans*-2-butenes even at 50°C, reaching 52% conversion at 75°C. This accounts for the lack of ethene and hexenes among the reaction products.

Olefin Treatment of the Samples

The olefin interaction with an air-calcined and activated catalyst is followed by diffuse reflectance spectroscopic study of the samples.

No absorption bands are detected on the pure carrier after treatment with 1-butene up to 250°C.

When 1-butene traces reach the catalyst surface at room temperature, rapid color changes are observed: the pale lilac sample turns into violet, having a spectrum shown in Fig. 5a. Bands at 365 and 400 nm are registered, as well as an intense band at 520 nm. The sample becomes yellow-greenish on exposure to air and new bands at 235, 450, and a shoulder at 570 nm appear. The bands at 365 and 400 nm remain, while the intense peak at 520 nm transforms into a shoulder (Fig. 5a′).

If the passing of 1-butene continues for 20 min the sample turns from light lilac into green–brown, and a spectrum (Fig. 5b) similar in the absorption band position to that in Fig. 2b is observed. The sample becomes grey blue on air contact and its spectrum is shown in Fig. 5b′. The relative band intensity is changed: the peak at 450 nm is transformed into a shoulder, and the shoulder at 570 nm into a peak. After 10 days storage in air, the samples become white and low-intensity bands at 235 and 400 nm are observed (Fig. 5c).

Various color changes are also observed after treatment with 1-butene at the temperature of maximum activity, i.e., 150°C (Fig. 6). On treatment for 20 min the sample becomes greyish lilac and bands at 325, 395 nm with a broad maximum at 520 nm are detected (Fig. 6a). The sample becomes green immediately on air contact. The broad maximum in the visible region disappears, and bands at 450 nm with a shoulder at 570 nm develop (Fig. 6b). After 70 days

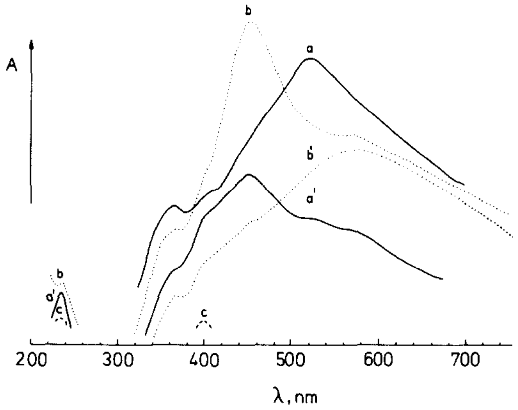

FIG. 5. Diffuse reflectance spectra of 6.2 wt% Re_2O_7/SiO_2 treated with 1-butene at 25°C: (a) treated with 1-butene traces; (a′) sample (a) after air contact; (b) treated with 1-butene for 20 min; (b′) sample (b) after air contact; (c) sample (b) after 10 days storage in air.

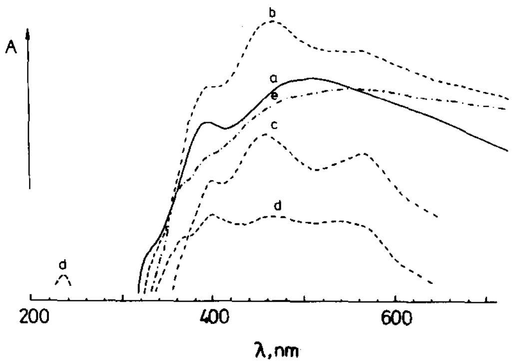

FIG. 6. Diffuse reflectance spectra of 6.2 wt% Re_2O_7/SiO_2 sample treated with 1-butene at 150°C: (a) for 20 min; (b) sample (a) after air contact; (c) sample (a) after 24 h air exposure; (d) sample (a) after 70 days storage in air; (e) after 60-min treatment with 1-butene.

storage in air, the sample becomes light pink, and the intensity of the bands at 370, 400, 460, and 570 nm is considerably lowered. A band at 235 nm is also detected (Fig. 6d).

Greyish-black samples are obtained on prolonged treatment (60 min) with 1-butene at 150°C or at a higher temperature (220°C, 20 min). Bands at 365 and 395 nm and a strong plateau in the visible region are observed in their spectra (Fig. 6e). The spectra do not change immediately on air contact. After 70 days storage the samples become dark violet, and bands at 460 and 530 nm are registered in the visible region. In contrast to the calcined catalyst, the band at 460 nm is dominant.

The initial spectrum is completely recovered on regeneration in air at 580°C for 2 h in all cases.

The ESR signal disappears after treatment of the calcined samples with olefin at 25°C. No paramagnetic centers are detected upon increasing temperature up to 150°C.

DISCUSSION

Catalyst Structure after Calcining

On the basis of the X-ray data it may be assumed that rhenium in the dried catalyst is present as the NH_4ReO_4 phase (*13*). The latter decomposes on calcining in air into ReO_2, ReO_3, and Re_2O_7 (*14*). Their presence is not detected by X-ray analysis but it is proved by the bands in the diffuse reflectance spectra (Fig. 1b): Re(VII)(T_d) at 235 nm, Re(VI) at 520 and 1700 nm, and Re(IV) at 365, 400, and 460 nm (*11, 15*). The relative intensity of the first three bands increases after calcining above 400°C (Fig. 1c). (The IR spectra do not show significant structural differences between the dried and calcined samples.)

This means that the structure formed contains rhenium in different valence states. The structure is independent of the initial valence state of rhenium. The lack of diffraction patterns indicates that it is either amorphous or finely dispersed. It remains unchanged on increasing the rhenium loading, in contrast to the data reported for the systems MoO_3 or WO_3 on SiO_2 (*16*). As the thermal analysis results indicate, the surface is saturated with rhenium at approx. 7% deposition of NH_4ReO_4. The rest of the rhenium sublimes.

The low-temperature reduction by H_2 (140°C) of the calcined samples to metallic rhenium is analogous to that of pure rhenium oxides (*17*). It suggests that the obtained structure resembles an oxide phase. However, the thermal stability of the structure formed rejects the idea of the presence of Re_2O_7, ReO_3, and ReO_2 on the surface as free oxides. Its high water solubility as ReO_4^- is one more evidence in support of this, since ReO_2 and ReO_3 are insoluble (*18*). An assumption can be made that a surface silico-rhenium acid is formed. However, this idea is not consistent since rhenium manifested no tendency to iso- or heteropoly-acid formation, in contrast to Mo and W (*19*). On the other hand, rhenium silicides are formed at high temperature and pressures (*20*).

There are some data in the literature referring to air-stable oxide structures, in which rhenium exists in mixed valence states, e.g., $BiRe^{V,VI}O_6$ (*21*), or participating both as cation and anion in $Re^VO_2 \cdot en_2 \cdot$

$Re^{VII}O_4$ (*22*). These data encouraged us to suppose that the structure formed is represented by a mixed rhenium oxide–perrhenate surface, $ReO_x.Re^{VII}O_4/SiO_2$.

It is interesting that bands at 245 and 330 nm are detected after calcining the dry samples in an inert gas flow (Fig. 2a). A band at 240 nm is observed in the spectrum of $Re^VOCl_5^{2-}$ in 10 *M* HCl (*23*), and band at 330 nm in the diffuse reflectance spectra of $Ba_3(Re^{VII}O_5)_2$ (*24*) where Re(VII) has C_{4v} coordination (*25*). This suggests the idea that instead of rhenium oxide–perrhenate, a rhenium oxide–mesoperrhenate structure, $ReO_x \cdot Re^{VII}O_5/SiO_2$, is formed. The assumption is further supported by the behavior of the samples on air exposure (Fig. 2b): a color change is observed, accompanied by disappearance of the bands of Re (VII) mesoperrhenate (330 nm), Re(VI) at 520 and 1700 nm, and appearance of the bands of Re(VII)(T_d) at 235 nm and Re(IV) at 450 and 570 nm. It is known (*23, 26*) that Re(VI) and Re(V) oxochlorides under air-moisture conditions disproportionate into Re(VII) and Re(IV). The same is observed in Fig. 2b. This again suggests that a rhenium oxide–mesoperrhenate structure is formed upon heating of the dried NH_4ReO_4/SiO_2 samples in an inert gas flow.

Catalyst Structure after Activation

In the case of an alumina support, a partial dehydration of the Al_2O_3 surface occurs upon activation and anionic vacancies are formed (*1*). In contrast, the SiO_2 carrier, being more a covalent oxide, has a broad forbidden band gap and such defects cannot be formed under the mild experimental conditions applied in the present study. Anionic vacancies appear in SiO_2 only after γ-radiation (*27*).

For this reason we suggest that the weak ESR signal, which arises after rhenium deposition, may be ascribed to an F-center formed in the mixed rhenium oxide–perrhenate phase on the surface.

Signals with similar parameters (g = 2.002–2.0019 and ΔH = 6.7–7.8 G) and behavior are observed in transition metal oxides, such as MoO_3, WO_3, V_2O_5, and Ta_2O_5 after thermovacuum treatment for 1 h at 450°C. No signals appear in the absence of such a treatment. They disappear reversibly on air contact (*28*).

Therefore, the following mechanism of F-center formation may be suggested: the narrow forbidden gap of the rhenium oxide phase (1.2 eV for $Re^{IV}O_2$ (*29*)) provides the possibility of an easy anionic vacancy formation evolution of oxygen from the rhenium phase. Upon interaction between the vacancy and a neighboring Re(VI) ion an F-center is formed similar to Eq. (2)

$$\mathrm{Re(VI)} + \square \rightleftharpoons \mathrm{Re(VII)} + \mathrm{F}$$

Here □ denotes an anionic vacancy in the rhenium oxide–perrhenate phase. The electrons captured by the anionic vacancies have high mobility because of the narrow forbidden gap of rhenium oxides. This results in a low F-center concentration and a weak signal intensity.

It may be concluded that after-air calcining and inert gas or vacuum activation, a defect rhenium oxide–perrhenate phase is formed on the surface, containing Re(VII), Re(VI) ions, and F-centers.

Catalyst Structure upon Olefin Treatment

The rich color spectrum which is observed upon olefin treatment of the samples indicates that various rhenium compounds are formed at the surface.

The diffuse reflectance spectra show (Figs. 1c, 5a, and 6a) that the intensities of the Re(VI) band at 520 nm and of the Re(IV) bands at 365 and 400 nm are increased. This indicates that reduction of the calcined and activated catalyst has taken place.

The color, and hence the spectra, of the olefin-treated samples change upon contact with air (Figs. 5a–a′ and 6a–d). The band of Re(VI) at 520 nm gradually disappears, while the band of Re(VII)(T_d) at 235 nm appears. The bands of Re(IV) at 365, 400, 460, and 570 nm undergo different changes, some of them disappear completely (Fig. 6d). These experimental data are in agreement with the already mentioned (Fig. 2a,b) property of Re(VI) and Re(V) salts to disproportionate upon hydrolysis to Re(IV) and Re(VII). In this case atmospheric water vapor is the hydrolyzing agent.

Our attention was attracted by the band at 320 nm (Fig. 6a). This band appears also in the spectrum of the sample which has been dried and then heated in a nitrogen flow NH_4ReO_4/SiO_2 (Fig. 2a). Similar to the latter sample, the band gradually disappears upon contact with atmospheric moisture, while the bands of Re(IV) and Re(VII)(T_d) (Figs. 6b–d) appear. The similarity of the bands in Figs. 2 and 6 allows us to ascribe the band at 320 nm to Re(VII) (C_{4v}) in the mesoperrhenate ion ReO_5^{3-} of the surface $Re^{VI}O_x \cdot Re^{VII}O_5$ phase.

The disappearance of the Re(VII) bands and the transformation of the Re(VI) and Re(IV) bands of the grey–black samples into an intense plateau after a relatively short treatment with olefins at 140°C or higher temperatures can be related to the more advanced reduction of the surface, since no deposition of coke is observed.

Structure of the Catalytically Active Form

Other authors have also established that the system is not catalytically active at room temperature (*5*). The diffuse reflectance spectra provide an explanation of this fact. Figure 5a shows that immediately after the first portions of olefin pass over the surface of the sample the amount of Re(VI)–520 nm on the surface is increased. However, after that (Fig. 5b) Re(VI) disappears, while Re(IV) is increased and the appearance of Re(VII)(T_d) is registered, i.e., the rhenium species comes into contact with water vapor. In this case this is the water released by the olefin reduction of the surface. This water cannot be removed from the system at room temperature and its causes the already mentioned disproportionation of Re(VI) to Re(IV) and Re(VII)(T_d). Apparently, the combination of Re(VII) and Re(IV) cannot condition catalytic activity. The same fact was established for the Re_2O_7/Al_2O_3 system, when the dried samples were calcined in an inert gas flow. In this case Re(IV) together with Re(VII) (C_{4v}) prevails over Re(VI), which strongly decreases the catalytic activity (*1*).

The system becomes catalytically active (Fig. 4a) with the increase of the reaction temperature since the "reduction" water can be easily removed.

The simultaneous presence of Re(VI)-520 nm and Re(VII) (C_{4v})–325 nm (Fig. 6a) can be detected in the diffuse reflectance spectra of the samples treated by 1-butene under the conditions of maximum catalytic activity (after a 20-min run at 150°C—Fig. 3a). The further reduction of the surface at the same temperature leads to the disappearance of Re(VII) (Fig. 6e) and the activity is decreased (Fig. 4b). Therefore, the Re(VI) and Re(IV) ions do not contribute to the catalytic activity.

The rapid decrease of the activity at higher temperatures (Fig. 4c) is connected with the further reduction of the surface, since no Re(VI) and Re(IV) bands are registered any more. Since no products of olefin decomposition are observed, one can conclude that the decrease in the activity is indeed caused by the reduction of the active forms, and not by coke deposition.

In addition, the ESR signal disappearance in the presence of 1-butene allows us to suggest that the F-center interacts with the olefin.

Therefore, one can conclude that the active form has a complex structure and consists of Re(VI), Re(VII) (C_{4v}), and an F-center.

Apparently, favorable conditions exist in the defect rhenium oxide–perrhenate phase for electron transfer on the surface. In other words, under our experimental conditions, interaction between the elements of the active form takes place (similar to that in the Re_2O_7/Al_2O_3 system), which ensures the catalytic activity in olefin metathesis.

However, the specific properties of SiO_2 lead to some differences, when compared to Al_2O_3- or MgO-supported catalysts.

(a) Upon calcining in air not a mesoperrhenate, but a mixed rhenium oxide phase is formed. This phase is relatively stable to high-temperature treatment, but is unstable to moisture and is easily reduced.

(b) The mesopherrhenate phase is formed under reaction conditions, but SiO_2 does not manifest a stabilizing effect on it. Its lack of stability to moisture is the reason for observing no catalytic activity at room temperature, while its easy reducibility leads to a rapid decrease of the activity at higher temperatures. The regeneration in air recovers completely the oxide structure and its catalytic activity.

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