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The Effect of the Calcination Temperature on the Activity of Re_2O_7/γ-Al_2O_3 Catalysts for the Metathesis of Propene

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The activity of Re_2O_7/γ-Al_2O_3 catalysts for the metathesis of propene could be increased by using a higher calcination temperature than normally employed. The optimal calcination temperature depends upon the wt% Re_2O_7 in the catalyst and lies between 1100 and 1200 K. The lower the wt% Re_2O_7, the higher the optimal calcination temperature. The largest increase in activity was found in low-loaded catalysts (e.g., 3 wt% Re_2O_7). The improvement is explained in terms of redistribution of ReO_4 groups over the alumina surface, for which spectroscopic evidence is presented. A catalyst that was calcined at a high temperature could be regenerated after deactivation at the normal calcination temperature (823 K) without substantial loss of its previously gained increase in activity. The results presented in this study underpin a previously proposed theory on the role of the support in the formation of an active site. © 1993 Academic Press, Inc.

INTRODUCTION

Re_2O_7/γ-Al_2O_3 is an attractive catalyst for the metathesis of alkenes because of its high activity and selectivity under very mild reaction conditions. This is reflected in the two commercial applications in which this catalyst is used (*1*, *2*).

Until now, the activity of the original heterogeneous Re_2O_7/γ-Al_2O_3 catalyst (*3*) has been improved in three different ways: (1) by phosphating the alumina support (*4*), (2) by adding a third metal oxide such as MoO_3, V_2O_5, or WO_3 (*5*, *6*), and (3) by using other supports than γ-alumina, for instance, silica–alumina (*7*, *8*) or alumina-bora (*9*). However, side reactions, such as double-bond isomerization, can sometimes undo the latter way of improvement by decreasing the selectivity of the catalyst. The catalytic activity of supported rhenium oxide catalysts can also be improved considerably by adding a tetra-alkyltin promoter (*8*, *10*).

Important factors for the choice of a catalyst, besides its activity and selectivity, are its stability and regenerability. Both aspects were studied in previous papers (*11*, *12*). The stability of the catalyst depends on the reaction conditions, but supported rhenium oxide catalysts will probably always deactivate. The regenerability of metathesis catalysts depends on the choice between an unpromoted catalyst and a promoted catalyst. The former can be regenerated many times without any loss of activity, while the latter has a limited cycle-life.

Most of the alterations made to the original Re_2O_7/γ-Al_2O_3 catalyst were empirical findings, mainly because there still was no unifying theory that could explain the differences in activity of all supported rhenium-based catalysts. Laverty *et al.* (*13*) were the first to propose that protons from acidic hydroxyl groups on the surface of the catalyst are involved in the creation of active sites (metal carbenes). Xu *et al.* (*14*) found that the metathesis activity of supported rhenium oxide catalysts was proportional to their Brønsted acidity (measured by *in situ* FTIR using pyridine adsorption), support-

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ing the ideas of Laverty *et al.* This explanation, however, is not completely satisfactory. For instance, the addition of cesium to metathesis catalysts decreases their Brønsted acidity, which results in a more selective catalyst; the activity of these catalysts, however, is not affected by the cesium treatment (*15*). Recently we have proposed a theory that can satisfactorily explain the differences in activity of a number of rhenium-based catalysts (*11, 16*). Brønsted acid hydroxyl groups do play a role in this theory, but in an indirect manner. The theory is based on the acidity of the different types of hydroxyl groups on the support and on the distribution of ReO_4 groups over the support after the calcination procedure. Spectroscopic evidence for the validity of this theory has recently been presented (*17*).

Typically, supported rhenium oxide catalysts are prepared by impregnation of the support with an aqueous solution of NH_4ReO_4, followed by drying at 383 K and calcination at a temperature of 773–873 K (*3, 15, 18, 19*). During calcination decomposition of NH_4ReO_4 occurs and the supported rhenium oxide is obtained.

This rhenium oxide phase consists of monomeric surface ReO_4 groups. In low-loaded Re_2O_7/γ-Al_2O_3 catalysts ReO_4^- ions have unevenly replaced the five different types of hydroxyl groups on the surface of γ-alumina; most of the rhenium has preferentially replaced basic hydroxyls or is adsorbed on coordinatively unsaturated (cus) Al^{3+} surface sites (Lewis acid sites) (*17*). This results in a low number of active sites, because these rhenium centres are too electron-rich to allow, for instance, the complexation of the carbon–carbon double bond of an alkene during metathesis. Increasing the rhenium content leads to a more effective replacement of acidic alumina hydroxyl groups. These electron-deficient Re centres will more easily accept the complexation of a carbon–carbon double bond. This leads to an almost exponential increase in activity as a function of the rhenium loading.

If it were possible to achieve a "better" distribution of rhenium over the support, ideally in such a way that the rhenium has preferentially replaced the acidic hydroxyl groups, the activity of the catalyst would be higher. Based on this idea, we have tried to improve the standard Re_2O_7/γ-Al_2O_3 catalyst by changing the calcination procedure, because this is the stage in the catalyst preparation in which the rhenium oxide is formed and distributed over the alumina surface. The catalysts were tested for the metathesis of propene,

$$2\,CH_2{=}CH{-}CH_3 \rightleftharpoons CH_2{=}CH_2 + CH_3{-}CH{=}CH{-}CH_3,$$

and characterized by BET measurements, temperature-programmed reduction, temperature-programmed dehydroxylation, infrared spectroscopy, and pyridine adsorption.

METHODS

Catalysts and Pretreatments

All catalysts were prepared by pore-volume impregnation of the support with calculated amounts of an aqueous solution of ammonium perrhenate (Johnson Matthey, JMC 836 Specpure), followed by overnight drying in air at 383 K. The support used was γ-alumina (Ketjen CK 300, S (BET, N_2) = 208 m^2/g). It was ground and sieved and the 180–250 μm fraction was used. The catalyst samples were calcined *in situ*.

Activity Measurements

The metathesis reactions were carried out in a conventional microcatalytic fixed-bed flow reactor. The reactor was a quartz tube (10 mm I.D.) that could be placed in a vertical oven. The standard calcination procedure consisted of heating 200 mg of the catalyst sample in an oxygen stream (3.5×10^{-5} mol/s) for 2 h at temperatures between 823 K and 1273 K (heating rate 10 K/min), followed by a nitrogen purge for 15 min at the calcination temperature.

The reactor was subsequently taken out of the oven and cooled to room temperature in 5 to 10 min. Next, the catalyst was left under flowing nitrogen for about one hour at room temperature. Standard reaction conditions were a contact time (W/F) of 11.55 kg(cat) · s/mol, a pressure of 1.5 bar and a reaction temperature of 353 K. The propene (Matheson, C.P.) was purified by means of purification beds containing γ-alumina, 3A molecular sieves and Cu/Al_2O_3, respectively.

The reaction products were analysed online by an Intersmat gas chromatograph, using a 30% bis(2(2-methoxy, ethoxy) ethyl)ether on Chromosorb P (180–250 μm) column (3.6 m × 3.2 mm O.D.) and a flame ionization detector. The GC signals were processed by a Milton Roy CI-10 integrator.

BET Measurements

The specific surface area, the pore volume and the pore radius of the supports and the catalysts were determined by the BET method on a Carlo Erba Sorptomatic 1800. Measurements were performed with nitrogen as the adsorbate at 77 K, after pretreating the samples at 473 K under vacuum for 1 h.

Temperature-Programmed Reduction

Temperature-programmed reduction (TPR) of the catalysts was carried out with a hydrogen–argon mixture (2 : 1) at atmospheric pressure in a conventional TPR setup. The gas mixture (13.8 μmol/s) was passed over approximately 75 mg of the oxidic sample placed in a quartz tube (4 mm I.D.). The temperature of the sample was increased linearly at a rate of 10 K/min. Water formed during the reduction was trapped by 3A molecular sieves. The hydrogen concentration was continuously monitored by a thermal conductivity detector and evaluated by a Shimadzu C-R3A electronic integrator. Calibration of the TPR was performed with CuO. The position of the peak maxima could be determined with an accuracy of ±5 K.

Temperature-Programmed Dehydroxylation

Temperature-programmed dehydroxylation (TPDH) was carried out under flowing air using two P_2O_5-coated platinum wires as a detector. A certain voltage is applied over the wires and the current changes when water is adsorbed and electrolyzed. This signal is proportional to the amount of water or hydroxyl groups that have left the surface of the catalyst. Calibration was performed with $BaCl_2 \cdot 2H_2O$. In a typical experiment ca. 40 mg of catalyst was held at 393 K for 2 h under flowing air (3.5×10^{-5} mol/s). Water loss had by then decreased to zero. The samples were then heated at a rate of 10 K/min up to 1273 K.

Infrared Measurements

Before the IR spectra were recorded the catalysts were calcined in oxygen (3.5×10^{-5} mol/s) at the desired temperature for 2 h (heating rate 0.167 K/s), cooled under nitrogen to 550 K, and subsequently exposed to air for further cooling. IR spectra were recorded on a Mattson Polaris spectrometer, using self-supporting disks of a 20-mg sample (approx. 8 mg cm^{-2}). Before a spectrum was recorded, the sample was evacuated at T = 723 K, in order to obtain well resolved spectra.

Pyridine Adsorption Measurements

Pyridine adsorption was effected in an *in situ* cell, using self-supporting wafers as before. After evacuation at 723 K, and cooling to 423 K, 10 Torr pyridine was admitted. The adsorption time was about half an hour and the sample was then evacuated again (while still at 423 K). The IR spectrum was determined at room temperature on a Mattson Galaxy spectrometer.

RESULTS

Activity Measurements

Experiments to study the effect of the calcination temperature on the catalytic activity were carried out with 3, 6, and 12 wt%

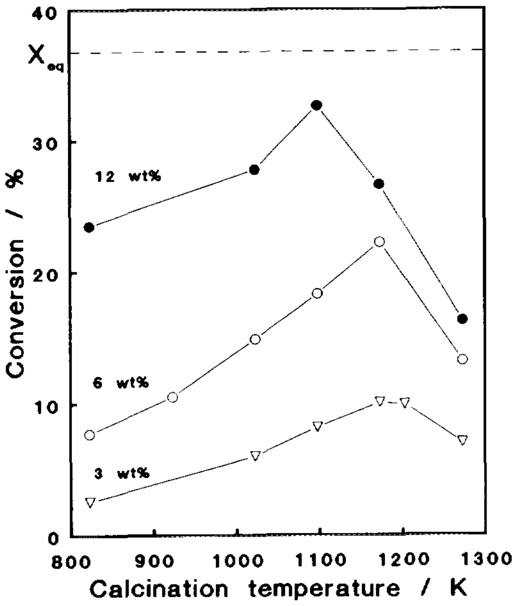


FIG. 1. Propene conversion (measured after 0.5 h) as a function of calcination temperature for 3, 6, and 12 wt% Re_2O_7/γ-Al_2O_3 catalysts. Reaction temperature, 353 K; W/F = 11.55 kg(cat) · s/mol; X_{eq} = equilibrium conversion. All catalysts were calcined for 2 h under oxygen (3.5×10^{-5} mol/s) (heating rate 10 K/min); the calcination temperature was varied between 823 and 1273 K.

Re_2O_7/γ-Al_2O_3 catalysts. Figure 1 shows the conversions obtained with these catalysts after 0.5 h process time as a function of the calcination temperature. The activity of all three catalysts increased with increasing calcination temperature, with a maximum in activity between 1100 and 1200 K. The optimal calcination temperature tends to increase with decreasing rhenium oxide content.

Normally, a rhenium deposition could be detected on the colder parts of the quartz reactor tube after calcination of the catalysts at 1273 K. Apparently, the rhenium oxide is very mobile at this temperature; the Re–O–Al bonds are easily broken and rhenium oxide can migrate out of the catalyst bed. The loss of rhenium was confirmed by TPR measurements (vide infra).

To prove that in the optimal calcination-temperature range 1100–1200 K rhenium oxide is also mobile, a 6 wt% catalyst mixed with an equal amount of support material was calcined at 1173 K. After the calcination, the catalyst and the admixed support material were separated, which was possible because different sieve fractions for the original catalyst and the admixed support were used. An analysis of the two fractions by means of inductively coupled plasma–atom emission spectrometry showed that nearly half of the rhenium originally present on the catalyst had moved to the support material, despite the fact that with an undiluted 6 wt% catalyst all rhenium oxide remained in the sample at this calcination temperature.

Additional experiments with a 6 wt% catalyst showed that variation of the calcination time at the optimal calcination temperature of 1173 K between 0 h (calcination stopped after a temperature of 1173 K was reached) and 3 h did not substantially influence the activity or stability.

BET Measurements

One has to consider that the structure of γ-alumina changes when it is exposed to high temperatures. Therefore, we obtained information on the texture of the catalysts from BET measurements of 6 wt% catalysts calcined between 823 and 1273 K. Characterization in terms of surface area, pore volume and pore radius (Table 1) showed that

TABLE 1

Surface Area, Pore Volume, and Pore Radius for γ-Al_2O_3 and 6 wt% Re_2O_7/γ-Al_2O_3 Catalysts Calcined between 823 and 1273 K (Calcination Time, 2 h)

Sample	Calcination temperature (K)	Surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Pore radius (nm)
6 wt% Re_2O_7/γ-Al_2O_3	823	191	0.47	4.0
6 wt% Re_2O_7/γ-Al_2O_3	923	189	0.45	4.0
6 wt% Re_2O_7/γ-Al_2O_3	1023	194	0.48	4.0
6 wt% Re_2O_7/γ-Al_2O_3	1098	162	0.44	4.8
6 wt% Re_2O_7/γ-Al_2O_3	1173	147	0.46	—
6 wt% Re_2O_7/γ-Al_2O_3	1203	99	0.43	6.7
6 wt% Re_2O_7/γ-Al_2O_3	1273	83	0.44	8.5
γ-Al_2O_3	823	208	0.51	4.2
γ-Al_2O_3	1173	183	0.49	4.2

TABLE 2

Average wt% Re_2O_7 as a Function of Calcination Temperature as Determined by Hydrogen Consumption in TPR for 6 wt% $Re_2O_7/\gamma\text{-}Al_2O_3$ Catalysts Calcined between 823 and 1273 K

Calcination temperature (K)	Rhenium oxide (wt%)
823	6.0
923	6.3
1023	6.1
1173	5.9
1273	3.3

calcination temperatures higher than 1023 K induce a reduction in surface area, accompanied by an enlargement of the mean pore radius, while the pore volume remained virtually constant.

TPR Measurements

The 6 wt% catalysts calcined at different temperatures were analyzed by means of TPR. All spectra showed one single reduction peak with a peak maximum at about 605 K.

The total hydrogen consumption in TPR is equivalent to the amount of rhenium present in the catalyst. The weight percentage Re_2O_7 as determined by TPR still present in the catalysts after calcination at different temperatures is shown in Table 2. It can be clearly seen that the amount of rhenium strongly decreased above a calcination temperature of 1173 K.

TPDH Measurements

It is well known that calcination of γ-alumina results in the loss of hydroxyl groups on the surface. We obtained a quantification of the extent of dehydroxylation by means of temperature-programmed dehydroxylation (TPDH). Figure 2 shows the result of such an experiment with a 6 wt% $Re_2O_7/\gamma\text{-}Al_2O_3$ catalyst. The area under the curve of Fig. 2 corresponds to 4.5 mmol OH/g of catalyst. Using a value for the surface area of 191 m^2/g (Table 1), this corresponds to a loss of 14 OH/nm^2.

Regenerability

An important aspect of these catalysts is their regenerability. Figure 3 shows the conversion after 0.5 h process time of a 6 wt% catalyst as a function of the number of times it was regenerated. The catalyst was first calcined at 1173 K; this resulted in a decrease in surface area from 191 to 147 m^2/g. After 17 h of propene metathesis at 353 K the catalyst had lost more than half of its activity. It was

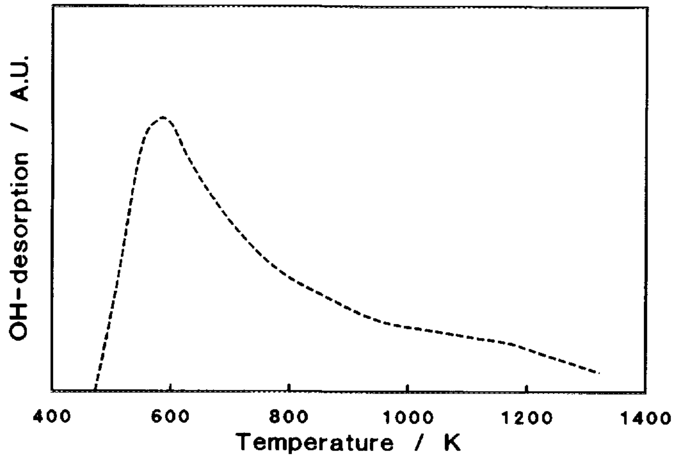


FIG. 2. Temperature-programmed dehydroxylation of a 6 wt% $Re_2O_7/\gamma\text{-}Al_2O_3$ catalyst.

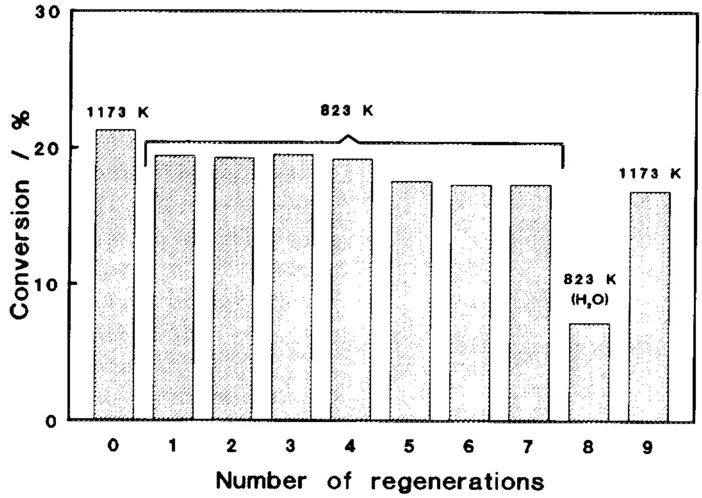


FIG. 3. Propene conversion (measured after 0.5 h process time) as a function of the number of regenerations (6 wt% $Re_2O_7/\gamma\text{-}Al_2O_3$ catalyst calcined at 1173 K and regenerated at 823 K).

then regenerated at 823 K in flowing oxygen, followed by another deactivation experiment. This cycle was repeated several times. The catalyst was exposed to moist air before each regeneration. The conversion after 0.5 h of process time dropped somewhat after the successive regenerations but seemed to stabilize at a lower level. After the seventh regeneration experiment the catalyst was exposed to excess water; all pores were filled with water. Next, it was again regenerated at 823 K. The level of activity had dropped to that of a fresh catalyst calcined at 823 K (see Fig. 3). When the catalyst was then again calcined at 1173 K, the conversion had almost returned to that of the previous experiments. This second high-temperature calcination was, however, accompanied by another substantial loss of surface area (S (BET, N_2) = 112 m^2/g, V_p = 0.432 cm^3/g, r_p = 5.5 nm).

Infrared and Pyridine Adsorption Measurements

In principle it is possible to follow changes in ReO_4 distribution over the various alumina surface sites through FTIR spectroscopy (*17*). Thus, the OH region of the IR spectrum was compared for the following samples: (a) the alumina support, calcined at 1173 K, (b) 6 wt% $Re_2O_7/\gamma\text{-}Al_2O_3$, calcined at 1173 K, and (c) the previous sample, rehydrated through pore-filling with water, and calcined at 823 K. The spectra are shown in Fig. 4, and the absorbances of the three types of hydroxyl groups are collected in Table 3. It is clear that some of the rhenium is bonded to (former) Al–OH sites after calcination at 1173 K and that rehydration leads to a rhenium movement away from those sites.

The number of (free) Lewis acid (cus) sites can be gauged through pyridine (py) adsorption coupled with IR spectroscopy. From the integrated absorbance of the band at 1455 cm^{-1}, the number of adsorbed pyridine molecules can be determined (*20*). The alumina support, after calcination at 823 K, was found to adsorb 225 μmol py/g. A 6 wt% $Re_2O_7/\gamma\text{-}Al_2O_3$ sample, after calcination at the same temperature, was found to adsorb 130 μmol py/g, i.e., 95 μmol/g less than the bare carrier.

DISCUSSION

Activity Measurements

It is evident that a change in the calcination procedure can change the performance of a $Re_2O_7/\gamma\text{-}Al_2O_3$ metathesis catalyst.

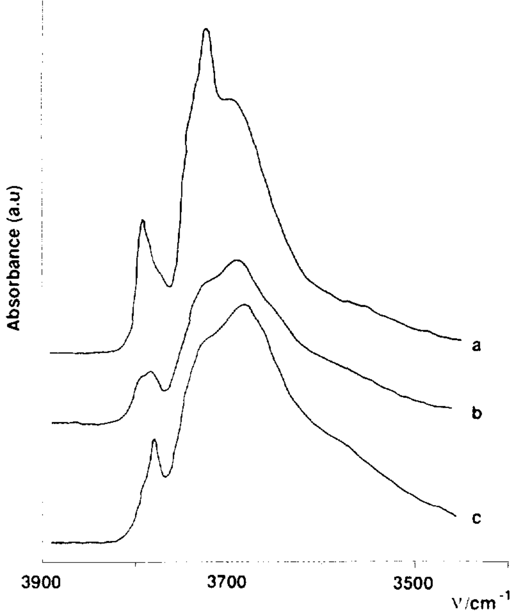


FIG. 4. FTIR spectra in the OH stretching region of $Re_2O_7/\gamma\text{-}Al_2O_3$ catalysts: (a) $\gamma\text{-}Al_2O_3$ calcined at 1173 K, (b) 6 wt% $Re_2O_7/\gamma\text{-}Al_2O_3$ calcined at 1173 K, and (c) previous sample after rehydration and calcination at 823 K.

These results indicate that anchoring of the rhenium oxide occurs during the calcination of the catalyst and not during the impregnation step. This is not surprising since TPR and Raman measurements indicate that in dried catalysts before calcination rhenium is still present as NH_4ReO_4 (*10*).

The normal calcination temperature still used by many authors is 773–823 K (*15, 18, 19*). The choice of this temperature range probably stems from the early days of heterogeneous metathesis and was never changed because it was high enough to decompose the rhenium oxide precursor NH_4ReO_4 (*10*).

At 823 K rhenium oxide remains firmly bonded to the alumina surface; this was the first indication of the fact that the rhenium is not simply present as Re_2O_7 on the support, because Re_2O_7 already sublimes at 475 K (9). This immobility of rhenium oxide on alumina is in contrast to its behaviour on silica–alumina in which rhenium oxide was shown to migrate already at 823 K (*16*).

Increasing the calcination temperature to the point where the rhenium oxide on γ-alumina becomes mobile might affect the distribution of the rhenium over the support. It was shown that rhenium oxide is indeed very mobile at the optimum calcination temperature for a 6 wt% catalyst of 1173 K, since it spread over extra support material that was added. The activity of $Re_2O_7/\gamma\text{-}Al_2O_3$ catalysts increased with increasing calcination temperature; a high-temperature treatment gave a catalyst containing 3 wt% Re_2O_7 that performed better than a standard catalyst containing 6 wt% Re_2O_7 (Fig. 1). Our recently proposed theory (*11, 16, 17*) predicts the improvements that were achieved. In catalysts containing 3 wt% Re_2O_7 the ReO_4^- ions do not replace many hydroxyl groups of the alumina during calcination, but show a strong preference for adsorption on coordinatively unsaturated (cus) Al^{3+} surface sites (Lewis acid sites). These rhenium centres will not form active sites (metal carbenes); consequently, low-loaded catalysts will only have a very low activity. Since rhenium oxide is mobile at higher calcination temperatures, the Re distribution will change, apparently in such a way that the number of active sites increases, resulting in an increase of the conversion by a factor of 4 (Fig. 1). It will be argued later on that a nearly random distri-

TABLE 3

IR Absorbances for the Absorption Bands of the Three Types of Hydroxyl Groups for 6 wt% Re_2O_7 on $\gamma\text{-}Al_2O_3$

Sample	Calcination temperature (K)	Absorbance		
		3780 cm^{-1} (basic)	3730 cm^{-1} (neutral)	3690 cm^{-1} (acidic)
$\gamma\text{-}Al_2O_3$	1173[a]	0.036	0.087	0.068
$Re_2O_7/\gamma\text{-}Al_2O_3$	1173[a]	0.014	0.035	0.042
$Re_2O_7/\gamma\text{-}Al_2O_3$[b]	823	0.028	0.052	0.062

[a] Cooled to 823 K in nitrogen, followed by cooling to room temperature in ambient air.

[b] Previous sample, rehydrated.

bution of ReO_4 units over all types of sites has occurred.

The conversion of a catalyst containing 6 wt% Re_2O_7 increased by nearly a factor of 3 when increasing the calcination temperature, while the conversion of a catalyst containing 12 wt% Re_2O_7 roughly increased by a factor 1.5. However, the latter factor is strongly influenced by the fact that thermodynamic equilibrium conversion is almost reached. The explanation for the fact that "highly" loaded catalysts are less affected by a high temperature calcination should be sought in the fact that the higher the rhenium oxide loading of γ-alumina-supported catalysts the lower the fraction of ReO_4 groups that are adsorbed on cus Al^{3+} sites or have replaced the basic hydroxyl groups of the alumina, i.e., the lower the fraction of ReO_4 groups that will not become active sites. Therefore, the effect of a redistribution is smaller at higher loading.

The fact that calcination of catalysts containing 3, 6, or 12 wt% Re_2O_7 at 1273 K results in a decrease in activity is ascribed to a loss of rhenium oxide (Table 2). It can be seen in Fig. 1 that the optimal calcination temperature is lower if the wt% Re_2O_7 in the catalyst is higher. One can imagine that the loss of rhenium is caused by a recombination reaction of surface rhenia monomers in which Re_2O_7 is formed, followed by gas-phase transport out of the catalyst bed. It is not surprising that this reaction proceeds faster at high rhenium oxide surface concentrations. It follows from Fig. 1 and Table 2 that the propene conversion per gram Re_2O_7 still left behind on the (6 wt%) catalyst is nearly equal for a catalyst calcined at 1173 or 1273 K.

To verify if this loss of rhenium is the only reason for a decrease in activity at too elevated calcination temperatures, a 6 wt% catalyst was calcined at 1273 K with an extra bed of alumina downstream of the catalyst bed, so that gas-phase rhenium oxide could be trapped on this extra alumina. No loss of rhenium was detected in this combination. The same activity was obtained as with a catalyst containing 6 wt% Re_2O_7 calcined at 1173 K.

BET Measurements

Not only does rhenium oxide become mobile during calcination at high temperatures, but the alumina also undergoes textural changes, such as loss of surface area (Table 1). The extent to which the surface area reduces is determined by the kinetic parameters of the transformation, i.e., the calcination temperature and the calcination time. Moreover, eventually γ-alumina will also undergo phase transformations and change into its thermodynamically most stable phase of α-alumina, by following the sequence $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$-alumina (*21–23*). For the system Re_2O_7/γ-Al_2O_3 the formation of θ-alumina after calcination at 1225 K for 16 h was indicated by the appearance of an extra Raman band at 252 cm^{-1} (*24*).

We found, however, no correlation between the surface area and the catalytic activity: the surface area remained constant in the temperature range 823–1023 K (Table 1), while the catalytic activity increased in this temperature range (Fig. 1). The regeneration experiments (vide infra) suggest that the textural changes of the alumina that occur during calcination at high temperatures do not affect the performance of the catalyst.

The bare support calcined at 1173 K had a lower surface area than the support calcined at 873 K (Table 1), but this decrease is somewhat less than that shown by the rhenium-containing catalyst (88 vs 77% of the initial surface area left). Apparently, rhenium accelerates the collapse of surface area. It is known that some metals catalyze such transformations, whereas others slow them down (*21*, *22*).

TPR Measurements

The fact that in all of the TPR measurements of the catalysts containing 6 wt% Re_2O_7 calcined at different temperatures only one peak is observed (corresponding to the reduction of Re^{7+} to metallic rhenium

(*25*)), and the fact that the total amount of rhenium, calculated from this hydrogen consumption, remains virtually constant up to 1173 K indicates that rhenium does not react with the support material at temperatures up to 1273 K, but remains present as stabilized surface-coordinated ReO_4 groups. This is in contrast with the system WO_3/Al_2O_3 in which $Al_2(WO_4)_3$ is formed after calcination at high temperatures (*26*). Laser-Raman measurements by Hardcastle *et al.* (*24*) also indicate that even after prolonged calcination at 1223 K the rhenium oxide on alumina is still present as adsorbed surface ReO_4 species.

Arnoldy *et al.* (*25*) found a relationship between the reducibility and the rhenium content of $Re_2O_7/\gamma\text{-}Al_2O_3$ metathesis catalysts. Since there is also a relationship between the rhenium content and the activity, they postulate a possible relationship between activity and reducibility. Since the activity of our catalysts increased tremendously with increasing calcination temperature and the reducibility did not change (no shift of T_{max} in TPR), we conclude that a relationship between activity and reducibility does not exist. The decrease in TPR-peak maximum with increasing rhenium content that was found by Arnoldy *et al.* is probably caused by autocatalysis effects and is not related to metathesis activity.

ReO_4 Distribution over the Various Alumina Surface Sites

From the above discussion it is apparent that the distribution of ReO_4 units over the various alumina surface sites should be the main parameter determining the eventual metathesis activity of a catalyst. To actually determine that distribution we rely on IR measurements, where we have taken the 6 wt% Re_2O_7/alumina catalyst series as an example.

First, it seemed necessary to substantiate the claim that in catalysts calcined at 823 K, about 3 wt% Re_2O_7 is sitting on the cus Al(3+) sites (*17*). This amount of Re_2O_7 corresponds to 124 μmol/g. The difference in the amount of free cus sites between the carrier and 6 wt% Re_2O_7/alumina, as determined by pyridine adsorption/IR, turns out to be 95 μmol/g, in reasonable agreement with expectation.

Then, the attempt was made to derive the distribution of ReO_4 units over the various hydroxyl groups from the changes in IR absorbance of those groups. For a fully quantitative determination one would need the molar extinction coefficients, which are bound to vary from one band to another. Since these are not available, the simplifying assumption is made that all OH groups have the same extinction coefficient, and we derive from our previous work (*17*) that reacting 1 wt% Re_2O_7 with OH groups leads to a decrease in absorbance of 0.020 (normalized to a wafer weight of 22 mg). To be able to proceed, a further simplifying assumption is needed, viz., that the alumina surface after calcination at 1173 K is the same regardless of whether Re_2O_7 was present during the calcination or not, so that we can use the latter as the reference material. In view of these assumptions, the following treatment is only semi-quantitative at best.

From the numbers collected in Table 3 one can, with the help of the two assumptions discussed above, calculate the amount of Re_2O_7 that is present on (former) hydroxyl sites after calcination at 1173 K, and the number of Re_2O_7/cus sites is then obtained by difference. The derived distribution of ReO_4 units over cus sites, total OH, and acidic OH, the latter being the putative precursors to the active metathesis sites, is given in Table 4. This distribution is compared with the random one, and with the distribution derived for the same catalyst but after calcination at 823 K. It is clear from Table 4 that increasing the calcination temperature from 823 K to 1173 K changes the ReO_4 distribution from one heavily skewed towards ReO_4/cus sites and with very few ReO_4/OH(acidic) sites, towards a more or less random one, leading to an increase in ReO_4/OH(acidic) sites by a factor of 4 to 5. That is, there is a clear shift from

TABLE 4

Calculated Distribution of ReO_4 Units over the Various Alumina Surface Sites in 6 wt% Re_2O_7/γ-Al_2O_3 Catalysts

Sample pretreatment	ReO_4/cus (wt%)	ReO_4/OH(total) (wt%)	ReO_4/OH(acidic) (wt%)
Calcined at 1173 K	1.0	5.0	1.2
Do., theoretical[a]	1.4	4.6	1.6
Do., rehydrated and calcined at 823 K	3.5	2.5	~0.3
Calcined at 823 K	3.0	3.0	~0.25

[a] Assuming random distribution of ReO_4 units.

ReO_4/cus sites in the 823 K calcined catalyst towards ReO_4/OH sites in the 1173 K calcined catalyst, particularly increasing the number of ReO_4 sites replacing acidic hydroxyls.

The present IR data, then, are fully consistent with the model proposed above to explain (a) the increase in activity of conventional Re_2O_7/γ-Al_2O_3 catalysts with increasing Re loading and (b) the increase in activity upon increasing the calcination temperature from 823 to 1173 K (cf. "Activity Measurements").

TPDH Measurements

From the TPDH measurements it was calculated that a total of 14 OH/nm^2 leave the surface of a 6 wt% Re_2O_7/γ-Al_2O_3 catalyst upon heating to 1273 K. Comparison of this value with a value of 12–16 OH/nm^2 for fully hydroxylated bare alumina (*23, 27*) suggests that the surface of the catalyst is totally dehydroxylated after the TPDH experiment. This means that calcination of a 6 wt% Re_2O_7/γ-Al_2O_3 catalyst at 1173 K for 2 h should result in a nearly total dehydroxylation of the surface. It thus follows that the catalytic activity increases with increasing calcination temperature, whereas the number of hydroxyl groups decreases. Therefore, the catalytic activity is almost inversely proportional to the number of hydroxyl groups on the surface. Moreover, we showed that on Re_2O_7/γ-Al_2O_3 catalysts the number of surface hydroxyl groups strongly decreases with increasing rhenium content, whereas the catalytic activity increases (*17*). Therefore, previously proposed initiation reactions in which metal carbenes are formed by means of a proton transfer from Brønsted acid hydroxyl groups on the surface of the catalyst to reduced metal ions (*13, 14*) are contradicted by our present results.

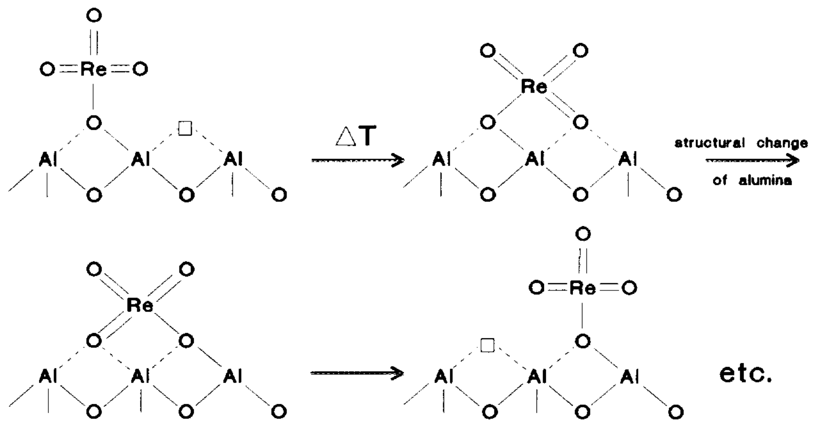
Regeneration Experiments

Although a small decrease in activity is observed after regeneration at 823 K of a catalyst containing 6 wt% Re_2O_7 which was initially calcined at 1173 K (Fig. 3), it appears that this catalyst needs to be calcined at 1173 K only once in order to maintain this increased activity. However, the regeneration experiments also clearly indicated that the activity increase of the catalyst induced by calcination at 1173 K can be reversed upon treatment with excess water. This can be explained as follows. When there is enough water present, the Re–O–Al bond can be easily hydrolyzed, an observation also made by Hardcastle *et al.* (*24*). The net result of such a hydrolysis is that the rhenium will be redistributed again, apparently in approximately the same way as after the very first impregnation with an aqueous solution of NH_4ReO_4. A semiquantitative measure of this redistribution can be deduced from IR measurements (OH stretch region), under the same assumptions as applied above in the previous section but one. The ReO_4 distribution so obtained for the rehydrated catalyst is included in Table 4. It is clearly consistent with the idea that upon rehydrating a catalyst precalcined at 1173 K, and calcining it at 823 K, more or less the same ReO_4 distribution is obtained as for a fresh, 823 K calcined, catalyst. The surface area has changed in the meantime, but its surface structure has been modified only slightly, which means that the changes of the alumina that occur during high temperature calcination are not relevant to the metathesis activity. The initial distribution is an unfavourable situation, which leads to a low activity. Calcination at 1173 K after the water treatment brings back the favourable situation. The fact that the surface area is again strongly reduced after the second high-temperature calcination obviously suggests that the number of calcinations at 1173 K is limited.

Mechanism by Which Rhenium Oxide Moves across the Surface

The question that remains is to ask what is the mechanism by which the rhenium moves across the surface. The spreading of one oxide over the surface of another oxide is up until now mainly discussed phenomenologically: the type of support and the structural properties of the metal oxide seem to play an important role (*28*). Recently, Leyrer *et al.* (*29*) concluded that spreading of MoO_3 over Al_2O_3 for a mechanical mixture is solely due to a solid–solid wetting process, in which the decrease in surface free energy is to be considered as the dominant driving force. In our study, however, rhenium oxide is present as monomers, the surface of the alumina is already wetted by the rhenium oxide. Movement of rhenium oxide will therefore not result in a decrease in surface free energy. Our system is probably best described by a temperature-induced random motion of ReO_4 groups over the surface. It seems likely that at best a random distribution of ReO_4 groups over all types of sites on the alumina surface, previously covered by basic, neutral, and acidic hydroxyl groups, has occurred. This means that in principle the activity of this catalyst can be further improved; other methods for selective anchoring of rhenium in places formerly bearing acidic hydroxyl groups should then be employed.

One can schematically visualize the mechanism by which rhenium is redistributed as is shown in Scheme 1. The reaction depicted in this scheme can only take place when there is enough energy available to break Re–O–Al bonds and when there are vacancies on the surface of the alumina. Both demands are satisfied at high calcination temperatures. Surface defects (anion vacancies) which are created by the dehydroxylation process can be annihilated by an attack of one of the oxygen atoms attached to rhenium on this vacancy. Movement of this rhenium has to be accompanied by a structural change of the alumina in order to maintain electroneutrality. This might explain the acceleration of the collapse of surface area in rhenium-containing catalysts, relative to bare alumina.



SCHEME 1

CONCLUSIONS

The activity of Re_2O_7/γ-Al_2O_3 metathesis catalysts strongly depends on the calcination procedure. Calcination between 1100 and 1200 K (heating rate of 10 K/min) for up to 3 h gives an optimal result. The improvement is explained in terms of redistribution of ReO_4 groups over the alumina surface. Rhenium that is anchored to the alumina sites previously covered by Brønsted acid hydroxyl groups has a low electron density and is thought to be mainly responsible for the metathesis activity. However, in low-loaded catalysts the ReO_4 groups are mainly not anchored to those sites. A high-temperature calcination results in a nearly random distribution of ReO_4 groups over all types of sites on the alumina surface, thus increasing the activity.

The structural changes of the γ-alumina, such as loss of surface area, that have occurred after calcination at 1173 K have no influence on the metathesis activity.

Catalysts which have undergone a high-temperature calcination can be regenerated at 823 K in oxygen, after metathesis, without substantial loss of their previously gained increase in activity. The catalyst can be brought back to its original state by a treatment with excess water before regeneration at 823 K. A high-temperature calcination after that returned the catalyst to its most active form again. This process points out the reversibility of the changes.

The results from this study are completely in agreement with our previously proposed theory on the prerequisite for an active site.

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