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RHENIUM OXIDE-CONTAINING METATHESIS CATALYSTS: A STUDY OF TEMPERATURE PROGRAMMED REDUCTION AND THERMAL ANALYSIS

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ABSTRACT

Temperature-programmed reduction (TPR) measurements and thermal analysis were performed on various rhenium-containing metathesis catalysts, viz. Re_2O_7/Al_2O_3, $Re_2O_7/SiO_2 \cdot Al_2O_3$, $Re_2O_7/Al_2O_3 \cdot B_2O_3$ and $M_xO_y \cdot Re_2O_7/Al_2O_3$ ($M_xO_y = MoO_3$, WO_3 or V_2O_5). Of these the rhenium species of the $Re_2O_7/SiO_2 \cdot Al_2O_3$ and $M_xO_y \cdot Re_2O_7/Al_2O_3$ ($M_xO_y = WO_3$ or V_2O_5) catalysts show different redox properties. The addition of V_2O_5, WO_3 or MoO_3 lowers the thermal stability of rhenium species in the Re_2O_7/Al_2O_3 catalysts. The thermal stability of rhenium species decreases in the following order of catalysts: $Re_2O_7/Al_2O_3 > Re_2O_7/SiO_2 \cdot Al_2O_3 > Re_2O_7/Al_2O_3 \cdot B_2O_3$. The different activities of these catalysts can be ascribed neither to the reducibility of rhenium species and/or a possible steric hindrance of the rheniacyclobutane complexes, nor to the thermal stability of rhenium species of the catalysts.

INTRODUCTION

Alkene metathesis is a reaction in which new compounds are formed via an exchange of alkylidene fragments of alkene molecules (eqn. 1)

$$\begin{matrix} R_1R_2C{=}CR_3R_4 \\ + \\ R_5R_6C{=}CR_7R_8 \end{matrix} \rightleftharpoons \begin{matrix} R_1R_2C \\ \| \\ R_5R_6C \end{matrix} + \begin{matrix} CR_3R_4 \\ \| \\ CR_7R_8 \end{matrix} \tag{1}$$

Alkene metathesis, especially the metathesis of functionalized alkenes, is a reaction with many important potential applications [1–4].

Since its discovery [5], many homogeneous and heterogeneous catalyst systems have been found active in the metathesis of normal alkenes [1]. The first homogeneous catalyst system reported for the metathesis of functionalized alkenes was WCl_6–$SnMe_4$ [6]. Later a heterogeneous catalyst system, Re_2O_7/Al_2O_3–$SnMe_4$ [7,8], was also developed for this reaction.

Heterogeneous catalyst systems are more attractive than their homogeneous counterparts. However there are some drawbacks, e.g. the high cost of

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rhenium compounds and the low activity of catalysts with low Re_2O_7 loadings. Recently new catalyst systems, viz. $M_xO_y \cdot Re_2O_7/Al_2O_3$ ($M_xO_y = MoO_3$, WO_3 or V_2O_5) [9], $Re_2O_7/SiO_2 \cdot Al_2O_3$ [10] and $Re_2O_7/Al_2O_3 \cdot B_2O_3$ [11], with a suitable co-catalyst (SnR_4 or PbR_4, R = alkyl), have been developed. These catalyst systems show much higher activity at low Re_2O_7 loadings for the metathesis of functionalized alkenes than the corresponding Re_2O_7/Al_2O_3 systems.

The new catalysts were studied by techniques such as TPR and thermal analysis in order to gain a better understanding of the reason for their higher activity. The results are discussed with reference to their activity in metathesis.

EXPERIMENTAL

All the catalysts were prepared as described earlier, by impregnation of γ-Al_2O_3 (Ketjen, CK 300) [7], $SiO_2 \cdot Al_2O_3$ (SA) (Ketjen, HA, 374 $m^2\ g^{-1}$, 24.3 wt% Al_2O_3) [10] and $Al_2O_3 \cdot B_2O_3$ (AB) (10–20 wt% B_2O_3) [11] with an aqueous solution of NH_4ReO_4 (Drijfhout, > 99%). The $M_xO_y \cdot Re_2O_7/Al_2O_3$ ($M_xO_y = MoO_3$, WO_3 or V_2O_5) catalysts were prepared by first impregnating γ-Al_2O_3 with an aqueous solution of NH_4ReO_4, followed by a second impregnation with an aqueous solution of $(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$, NH_4VO_3 or $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (BDH), respectively [9], after drying at 383 K and calcination in air at 823 K.

Temperature programmed reduction (TPR) experiments were carried out in a TPR apparatus in a flow of a H_2/Ar mixture (67% H_2) with a flow rate of 20 ml min^{-1} (STP) at a heating rate of 10 K min^{-1} (unless otherwise stated) as described earlier [12]. For calculation of the activation energy for reduction (E_a, J mol^{-1}), additional measurements at a different heating rate (1 or 5 K min^{-1}) were obtained and E_a values were calculated using eqn. 2, by plotting $\ln(\phi/T_{max}^2)$ versus $1/T_{max}$ as described in ref. 13.

$$\ln(\phi/T_{max}^2) = -(E_a/RT_{max}) + \ln(AR/E_a) + C \qquad (2)$$

Here, ϕ is the heating rate (K s^{-1}), T_{max} (K) is the position of the TPR peak maximum, A (s^{-1}) is the Arrhenius constant, R (J mol^{-1} K^{-1}) is the gas constant and C is a term which depends on the mechanism of reduction and which under certain circumstances can be considered as a constant [13]. The catalysts were measured after having been dried at 383 K, followed by calcination in air at 823 K for 2 h.

Thermal analysis was carried out with commercial equipment (Mettler No. 206 thermobalance) in a flow of dry air (80 ml min^{-1}, STP) at a heating rate of 10 K min^{-1}. Differential thermal gravimetry (DTG) measurements and differential thermal analysis (DTA) were carried out simultaneously. An empty alumina sample holder was used as reference. The temperature was measured by a Rh–Pt (10% Pt) thermocouple. In these experiments the catalysts were used after drying at 383 K.

Surface areas of a series of $MoO_3 \cdot Re_2O_7/Al_2O_3$ catalysts were measured by means of commercial equipment (Sorptomatic 1800, Carlo Erba) according to the BET method [14,15]. The samples were measured after being pretreated in vacuo at 473 K for 1 h with nitrogen as the absorbate.

RESULTS

Figure 1 shows TPR patterns (1 K min^{-1}) of 12 wt% Re_2O_7 on γ-Al_2O_3 or on $SiO_2 \cdot Al_2O_3$ (SA) and of 18 wt% Re_2O_7/SA. The TPR peak for rhenium reduction appears at ca. 530 K for a 12 wt% Re_2O_7/Al_2O_3 catalyst and at ca. 480 K for the SA-based catalysts. The TPR peaks of the SA-based catalysts show small shoulders, which is not observed for the γ-Al_2O_3-based catalyst.

Figure 2 shows TPR patterns (10 K min^{-1}) of a series of $MoO_3 \cdot Re_2O_7/Al_2O_3$ catalysts with various Mo : Re atomic ratios and of 18 wt% MoO_3/Al_2O_3. It appears that the addition of MoO_3 to a 6 wt% Re_2O_7/Al_2O_3 catalyst hardly affects the peak position for rhenium reduction.

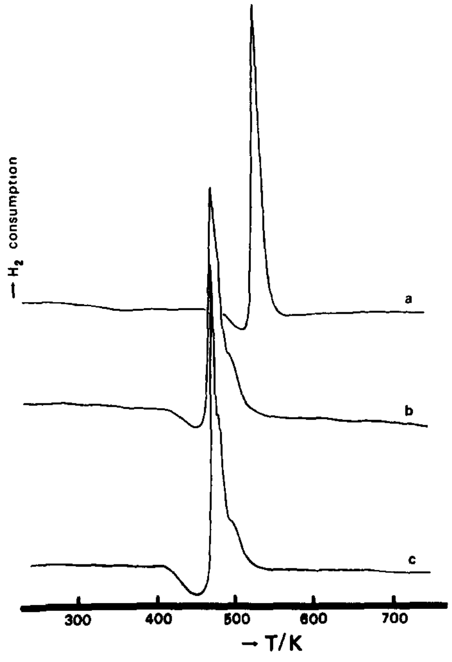

Fig. 1. TPR patterns (1 K min^{-1}) of: (a) 12 wt% Re_2O_7/Al_2O_3; (b) 12 wt% Re_2O_7/SA; (c) 18 wt% Re_2O_7/SA.

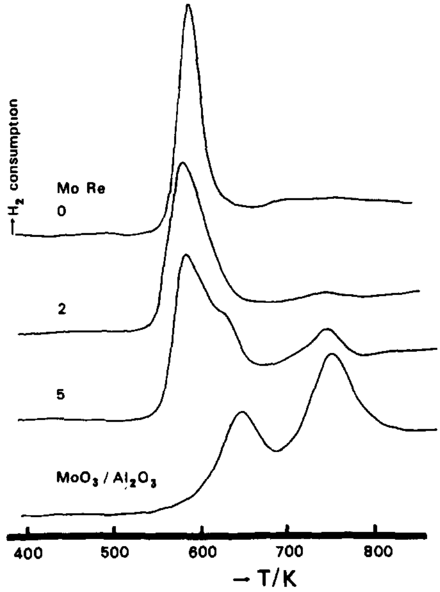

Fig. 2. TPR patterns (10 K min^{-1}) of $MoO_3 \cdot Re_2O_7/Al_2O_3$ catalysts with various Mo:Re atomic ratios (Re:Al = 1:74 (at)) and of an 18 wt% MoO_3/Al_2O_3 catalyst.

Figure 3 show TPR patterns (10 K min^{-1}) of some 3 wt% Re_2O_7 catalysts on various $Al_2O_3 \cdot B_2O_3$ (AB) carriers containing 10 wt%, 15 wt% and 20 wt% B_2O_3, and of an AB (10 wt% B_2O_3) carrier. The peak due to the reduction of rhenium oxide becomes smaller with an increasing boria content, while the peak positions are about the same. The AB carrier does not show a peak in TPR.

Table 1 lists the T_{max} values for rhenium reduction for some 6 wt% Re_2O_7 catalysts and for some catalysts based on 6 wt% Re_2O_7/Al_2O_3.

TABLE 1

T_{max} values for the reduction of rhenium species of some catalysts, measured at a heating rate of 10 K min^{-1} and their E_a values

Catalyst	T_{max} (K)	E_a (J mol^{-1})
Re_2O_7/Al_2O_3 [a]	591	100
Re_2O_7/SA [a]	561	91
Re_2O_7/AB [a]	586	110
$MoO_3 \cdot Re_2O_7/Al_2O_3$ [b]	593	114
$WO_3 \cdot Re_2O_7/Al_2O_3$ [b]	553	–
$V_2O_5 \cdot Re_2O_7/Al_2O_3$ [b]	633	–

[a] containing 6 wt% Re_2O_7. [b] M:Re (at) = 4:1 (M = V, Mo or W), based on a 6 wt% Re_2O_7/Al_2O_3 catalyst.

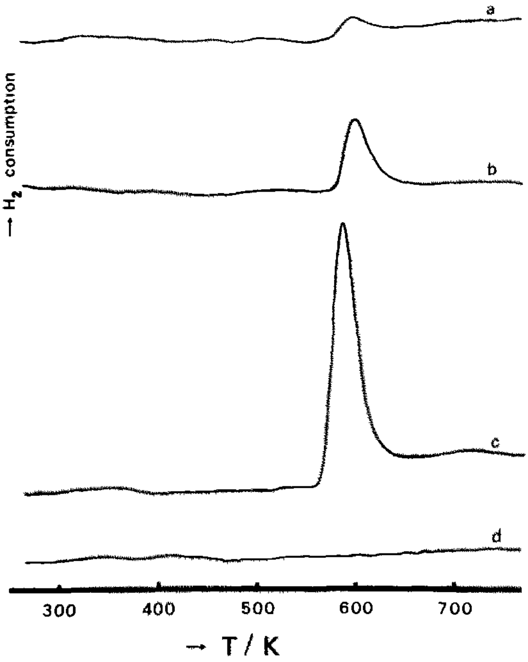

Fig. 3. TPR patterns (10 K min^{-1}) of 3 wt% Re_2O_7/AB catalysts, with the AB carriers containing: (a) 20 wt% B_2O_3; (b) 15 wt% B_2O_3; (c) 10 wt% B_2O_3; (d) an AB (10 wt% B_2O_3) carrier.

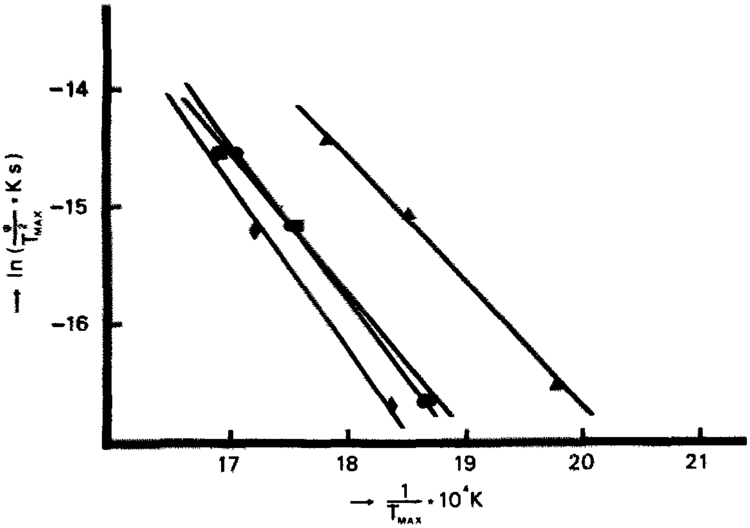

Fig. 4. Arrhenius plots for the reduction of rhenium species of several 6 wt% Re_2O_7 catalysts and a catalyst based on 6 wt% Re_2O_7/Al_2O_3: (■) Re_2O_7/Al_2O_3; (▲) Re_2O_7/SA; (◆) Re_2O_7/AB (10 wt% B_2O_3); (●) $MoO_3 \cdot Re_2O_7/Al_2O_3$ (Mo : Re : Al = 4 : 1 : 74 (at)).

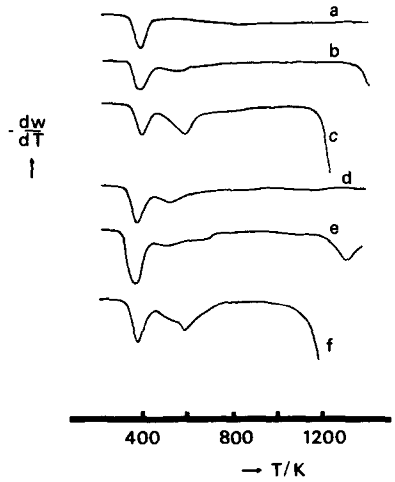

Fig. 5. DTG patterns of: (a) γ-Al_2O_3; (b) 12 wt% Re_2O_7/Al_2O_3; (c) 18 wt% Re_2O_7/Al_2O_3; (d) SA carrier; (e) 12 wt% Re_2O_7/SA; (f) 18 wt% Re_2O_7/SA. The measurements were carried out in air at a heating rate of 10 K min^{-1}.

Figure 4 shows Arrhenius plots for various Re_2O_7-containing catalysts. The activation energies calculated for the reduction of rhenium species are 100, 91, 110 and 114 kJ mol^{-1} respectively for the 6 wt% Re_2O_7/Al_2O_3, 6 wt% Re_2O_7/SA, 6 wt% Re_2O_7/AB catalysts and a $MoO_3 \cdot Re_2O_7/Al_2O_3$ (Mo : Re : Al = 4 : 1 : 74 (at)) catalyst.

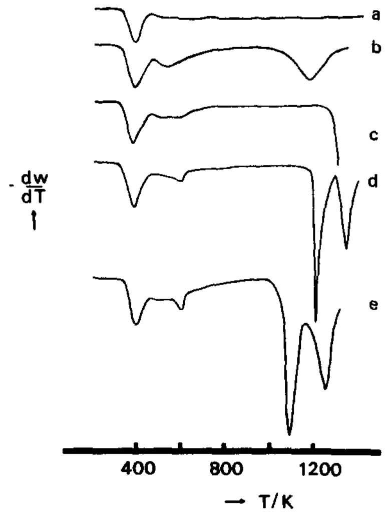

Fig 6. DTG patterns of: (a) 6 wt% Re_2O_7/Al_2O_3; (b) $WO_3 \cdot Re_2O_7/Al_2O_3$ (W : Re : Al = 4 : 1 : 74 (at)); (c)–(e) $MoO_3 \cdot Re_2O_7/Al_2O_3$ catalysts with various Mo : Re atomic ratios (Re : Al = 1 : 74). (c) Mo : Re = 1 : 1; (d) Mo : Re = 2 : 1; (e) Mo : Re = 4 : 1. The measurements were carried out in air at a heating rate of 10 K min^{-1}.

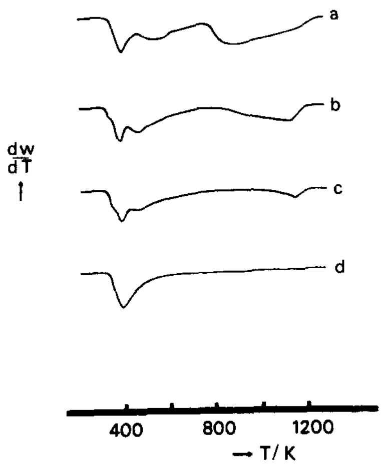

Fig. 7. DTG patterns of Re_2O_7/AB (10 wt% B_2O_3) catalysts with: (a) 9 wt% Re_2O_7; (b) 6 wt% Re_2O_7; (c) 3 wt% Re_2O_7 and of the AB carrier (d). The measurements were carried out in air at a heating rate of 10 K min^{-1}.

Figure 5 shows DTG patterns of catalysts with 0, 12 and 18 wt% Re_2O_7 on both γ-Al_2O_3 and SA. All the samples show a peak at ca. 390 K. Silica–alumina and the SA-supported catalysts show an additional small peak at ca. 530 K. For catalysts with 12 and 18 wt% Re_2O_7, additional peaks appear at ca. 590 K and at a higher temperature.

Figure 6 shows DTG patterns of several $M_xO_y \cdot Re_2O_7/Al_2O_3$ (M_xO_y = MoO_3 or WO_3) catalysts based on 6 wt% Re_2O_7/Al_2O_3 [and of a 6 wt% Re_2O_7/Al_2O_3] catalyst. All the samples show a peak at ca. 390 K. Additional peaks appear at ca. 500–600 K and at higher temperatures.

Figure 7 shows DTG patterns of catalysts with 0, 3, 6 and 9 wt% Re_2O_7 on AB (10 wt% B_2O_3). The peak at ca. 400 K is present in all the samples.

TABLE 2

Surface area (BET) results from a series of $MoO_3 \cdot Re_2O_7/Al_2O_3$ catalysts based on a 6 wt% Re_2O_7/Al_2O_3 and of the alumina carrier

Sample Mo:Re	S_a (m^2g^{-1})	V_p (cm^3g^{-1})	r_p (nm)
0.5:1	210	0.479	4
1:1	192	–	–
2:1	194	–	–
3:1	193	0.424	4
4:1	181	0.400	4
5:1	186	0.400	4
γ-Al_2O_3	208	0.510	0–6

S_a, V_p and r_p are the specific surface area, pore volume and pore radius of the samples, respectively.

For the 3, 6 and 9 wt% Re_2O_7/AB catalysts, peaks at 490–560 K and at a higher temperature are also present.

Table 2 gives some surface area (BET) results for a series of $MoO_3 \cdot Re_2O_7/Al_2O_3$ catalysts with various Mo : Re atomic ratios and the alumina carrier.

DISCUSSION

Metal–carbene and metallacyclobutane species are currently accepted as the reaction intermediates in alkene metathesis [1]. After calcination, rhenium is in its highest oxidation state (7 +). To initiate an active rhenium carbene, a partial reduction of rhenium species is necessary [16]. A TPR study can give information about the reduction parameters, such as T_{max} and E_a, of reducible species. Although H_2 is not a selective reducing agent, the reducibility of rhenium species of the different catalysts can be studied.

In the TPR patterns of most of the catalysts studied, it appears that rhenium species show only a single reduction peak. One exception is shown in Fig. 1, in the TPR patterns of the 18 wt% Re_2O_7/SA catalyst, where two small shoulders for reduction of rhenium species are observed. In the TPR patterns of SA catalysts with a lower wt% of Re_2O_7, only one shoulder is observed. A TPR measurement (1 K min^{-1}) of a 12 wt% Re_2O_7/SA catalyst which was calcined for 18 h, gave a result similar to that shown in Fig. 1, which was calcined for 2 h. This excludes the possibility that these shoulders are due to reduction of incompletely decomposed NH_4ReO_4. Also, in the TPR pattern of the 12 wt% Re_2O_7/Al_2O_3 catalyst in Fig. 1 which was obtained using the same sample amount as the corresponding SA catalyst, rhenium species are reduced as a single peak. This excludes the possibility that these shoulders are due to a mass transfer limitation of H_2. The rhenium TPR peak position of SA-supported catalysts appears at a lower temperature than that of the Al_2O_3-supported catalysts. Therefore, it is conceivable that most of the rhenium species on SA catalysts resides on the silicium sites, since it is known [17] that silica has a weaker support interaction with rhenium than alumina. A tentative interpretation is that the shoulders are due to the reduction of rhenium residing on the aluminium sites. Although the rhenium species on aluminium sites are reduced at a higher temperature, on SA catalysts this reduction could be catalysed by the reduced rhenium species on the silicium sites (since rhenium reduction is an autocatalytic process) which would make reduction easier. Another possibility is the reduction of rhenium oxide clusters which might be present due to the high Re_2O_7 loading. This could explain why at lower Re_2O_7 loadings one of the shoulders disappeared. For 1 K min^{-1} measurements, a desorption process appears in our system, at a temperature just below the T_{max} of rhenium reduction.

Arnoldy et al. [18] explained the high metathesis activity of Re_2O_7/Al_2O_3 catalysts with high Re_2O_7 loadings by a higher reducibility and/or by less steric hindrance of the metallacyclobutane complexes. Our TPR measurements of $M_xO_y \cdot Re_2O_7/Al_2O_3$ ($M_xO_y = MoO_3$, WO_3 or V_2O_5), Re_2O_7/SA and Re_2O_7/AB catalysts, which are very active at low Re_2O_7 loadings, do not confirm this suggestion. For different $MoO_3 \cdot Re_2O_7/Al_2O_3$ catalysts, the TPR peak position for rhenium reduction is about the same as that of the corresponding Re_2O_7/Al_2O_3 catalyst (Fig. 2 and Table 1). It appears that the reduction of rhenium species is not influenced by the addition of MoO_3 to the Re_2O_7/Al_2O_3 catalysts. Under TPR conditions, the reduction of molybdenum species also takes place, and this also is not influenced by the reduction of rhenium species. It appears that the reduction of rhenium and molybdenum species on $MoO_3 \cdot Re_2O_7/Al_2O_3$ catalysts resembles the reduction of a physical mixture of MoO_3/Al_2O_3 and Re_2O_7/Al_2O_3. Although the T_{max} values are about the same, the catalytic activity varies considerably with a varying Mo : Re : Al atomic ratio. The highest activity of these catalysts is obtained with an atomic ratio Mo : Re : Al = 4 : 1 : 74 [19,20]. For this catalyst, the activation energy (E_a) for the reduction of rhenium species is calculated as 114 kJ mol^{-1}. This value is slightly higher than that for the corresponding Re_2O_7/Al_2O_3 catalyst (100 kJ mol^{-1}). For $WO_3 \cdot Re_2O_7/Al_2O_3$ (W : Re : Al = 4 : 1 : 74 (at)) and $V_2O_5 \cdot Re_2O_7/Al_2O_3$ (V : Re : Al = 4 : 1 : 74 (at)) catalysts, T_{max} values of 553 K and 633 K respectively were observed (Table 1), and the TPR patterns showed also a single peak for rhenium reduction. These catalysts are both much more active than the corresponding Re_2O_7/Al_2O_3 catalyst [19,20]. In contrast to the $MoO_3 \cdot Re_2O_7/Al_2O_3$ (Mo : Re : Al = 4 : 1 : 74 (at)) and the 6 wt% Re_2O_7/Al_2O_3 catalysts, in $WO_3 \cdot Re_2O_7/Al_2O_3$ (W : Re : Al = 4 : 1 : 74 (at)) and $V_2O_5 \cdot Re_2O_7/Al_2O_3$ (V : Re : Al = 4 : 1 : 74 (at)) catalysts it seems that the reduction of the rhenium species is influenced by the addition of WO_3 or V_2O_5 (Table 1). However, $MoO_3 \cdot Re_2O_7/Al_2O_3$ (Mo : Re : Al = 4 : 1 : 74 (at)) is about as active as the $WO_3 \cdot Re_2O_7/Al_2O_3$ (W : Re : Al = 4 : 1 : 74 (at)) catalyst. From these results of T_{max} and E_a values, it appears that a general correlation between easier reduction of rhenium species, i.e. lower T_{max} and E_a values, and higher activity of the catalysts does not exist.

Another indication that a high reducibility of rhenium species is not of primary importance for the metathesis activity of rhenium-containing catalysts, comes from TPR measurements of Re_2O_7/AB catalysts. These AB catalysts are much more active even at low Re_2O_7 loadings than the corresponding Al_2O_3-based catalysts [11,19,20]. However, the TPR patterns of both types of catalysts and the T_{max} values are about the same, indicating a similar reducibility of the rhenium species on these catalysts (Fig. 3 and Table 1). That the rhenium reduction peak became smaller with an increasing boria loading indicates that less of the rhenium species is available for the reduction. This is ascribed to the formation of a solid solution of rhenium oxide with boria [11]. The activation energy (E_a) for reduction of the rhenium species of a 6 wt% Re_2O_7/AB catalyst (110 KJ mol^{-1}), is slightly higher than that of the corresponding Re_2O_7/Al_2O_3 catalyst (100 kJ mol^{-1}). Again it appears that there is no general relationship between the easier reduction of rhenium species and higher activity of the catalysts.

As already observed from Fig. 1 and according to Table 1, SA catalysts show a higher reducibility for rhenium species than Al_2O_3 catalysts: the T_{max} values are lower and the calculated E_a value for reduction of rhenium of a 6 wt% Re_2O_7/SA catalyst is slightly lower than that of a 6 wt% Re_2O_7/Al_2O_3.

Although SA-based catalysts showed a higher reducibility, it appears from the results obtained from Re_2O_7/AB and $M_xO_y \cdot Re_2O_7/Al_2O_3$ catalysts that a high reducibility of rhenium species does not necessarily lead to a higher metathesis activity of the catalysts. The apparent differing behaviour of rhenium species on SA catalysts for example indicates even more strongly that as long as the carrier material stabilizes rhenium species to a certain degree, there must be other factors causing the high activity of these catalysts.

One of the possible factors is a change in the activation entropy ΔS (J mol^{-1} K^{-1}), as suggested by Arnoldy et al. [18]. A change in the activation entropy can be calculated with the Eyring equation (eqn. 3)

$$\Delta S/R = \ln A - \Delta n - \ln(kT/h) \qquad (3)$$

In this equation Δn stands for the change in the number of molecules when the activated complex involved in the reduction of Re–O bonds is formed, T (K) is the temperature, k (J K^{-1}) is Boltzmann's constant and h (J s) is Planck's constant. A variation of the intercept in the Arrhenius plots, which is equal to $\ln(AR/E_a) + C$, suggests a change in the Arrhenius constant A. If we assume that, as changes in E_a are relatively small, rhenium reduction takes place via the same reduction mechanism for all the catalysts studied, C can be taken as a constant [17,18]. Using the E_a values calculated, a change in the Arrhenius constant A with respect to 6 wt% Re_2O_7/Al_2O_3 by a factor of 0.5 for 6 wt% Re_2O_7/SA, 10 for 6 wt% Re_2O_7/AB and 15 for $MoO_3 \cdot Re_2O_7/Al_2O_3$ (Mo : Re : Al = 4 : 1 : 74 (at)) was obtained. From eqn. 3, it can be shown that these changes in the Arrhenius constant are equivalent to changes in ΔS (relative to that of a 6 wt% Re_2O_7/Al_2O_3 catalyst) of: −7, 19 and 23 J mol^{-1} K^{-1} for 6 wt% Re_2O_7/SA, 6 wt% Re_2O_7/AB and a $MoO_3 \cdot Re_2O_7/Al_2O_3$ catalyst (Mo : Re : Al = 4 : 1 : 74 (at)), respectively.

Arnoldy et al. [18] reported changes in ΔS of 25–40 J mol^{-1} K^{-1} for Re_2O_7/Al_2O_3 catalysts with different Re_2O_7 loadings. Compared with these results, the values that we obtained are relatively small. It appears that no general correlation can be obtained between a change of ΔS to a higher value, and higher activity of the catalysts. We must therefore conclude that a change in the activation entropy ΔS is also not of major influence on the high activity of the catalysts. This is even more unlikely when we consider the method used to prepare the $M_xO_y \cdot Re_2O_7/Al_2O_3$ catalysts. They were made by deposition of M_xO_y on a calcined Re_2O_7/Al_2O_3 catalyst. It is inconceivable that this gives the activated rhenium complexes a higher activation entropy, or a higher freedom of rotation, leading to a less steric hindrance of these complexes and of the extended metathesis, activated rheniacyclobutane complexes.

With thermal analysis another interesting feature can be observed, i.e. the thermal stability of rhenium species on the different catalysts. In addition, processes occurring during calcination can be investigated. For example, with DTG, the decomposition of NH_4ReO_4 (eqn. 4) on Al_2O_3 can be observed.

$$2\,NH_4ReO_4 \rightarrow 2\,NH_3 + Re_2O_7 + H_2O \qquad (4)$$

From a simultaneously recorded DTA pattern, a small endothermic effect was observed when the rhenium loading was higher than ca. 12 wt%.

It is known [21] that sublimation of Re_2O_7 takes place at a temperature of ca. 630 K. In the catalysts, however, rhenium is bound to the support in an oxidic form. It would be expected that sublimation of the rhenium species takes place at a higher temperature due to stabilization by the support. For the different catalysts, it appears that the supports strongly influence the thermal stability of the rhenium species.

The DTG patterns in Figs. 5–7 were all obtained after correction for the buoyancy effect, by control runs in the absence of samples. All these samples show a peak at ca. 390 K, probably due to the desorption of physisorbed water. This peak in DTG was accompanied by an endothermic effect, observed in DTA.

In Fig. 5, the peak at ca. 590 K is ascribed to the decomposition of NH_4ReO_4 (eqn. 4). It is known [21,22] that at about this temperature, decomposition of pure NH_4ReO_4 takes place. At high Re_2O_7 loadings, loss of chemisorbed water might contribute also to the weight loss that takes place during decomposition of NH_4ReO_4, due to extended coverage of aluminium sites with rhenium species. This could lead to extra loss of surface OH groups as water. This would explain why the weight loss at ca. 590 K for the catalysts in Fig. 5 is not proportional to the Re_2O_7 loading. For Re_2O_7/SA catalysts, a small additional peak at ca. 530 K is observed, which is probably due to a second dehydration step. The peak at higher temperature ($>$ 1100 K) is ascribed to the sublimation of rhenium species. For both alumina- or SA-supported catalysts with a higher Re_2O_7 loading, this peak shifts to a lower temperature. Also, for SA catalysts this peak is at a lower temperature than that of the corresponding γ-Al_2O_3 catalysts, indicating a lower thermal stability of rhenium species on SA than on Al_2O_3 catalysts. Facile loss of rhenium, especially during the activation is unfavourable to the activity of the catalysts. For both Re_2O_7/Al_2O_3 and Re_2O_7/SA catalysts, no obvious loss of rhenium is observed at the activation temperature we used (823 K). Obviously, the high activity of SA catalysts cannot be due to a higher thermal stability of rhenium species of these catalysts.

In Fig. 6, all the patterns again show a peak at ca. 390 K due to the desorption of physisorbed water. For the 6 wt% Re_2O_7/Al_2O_3 catalyst, the weight loss due to the decomposition of NH_4ReO_4 is too small to observe clearly. Also the peak due to the sublimation of rhenium species is not observed. It is likely that on Re_2O_7/Al_2O_3 catalysts with a relative low Re_2O_7 loading, the rhenium species is bound to the stronger interacting sites on the alumina. This suggests why the loss of rhenium species takes place at a relatively higher temperature. The DTG curve of $WO_3 \cdot Re_2O_7/Al_2O_3$ (curve b) shows, besides the dehydration peak, a peak at ca. 500 K due to the decomposition of $(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$. At ca. 1150 K, a peak due to the sublimation of rhenium species is observed. For $MoO_3 \cdot Re_2O_7/Al_2O_3$ catalysts, in addition to a dehydration peak, a peak at ca. 600 K due to the decomposition of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ is observed. For these catalysts also two peaks are observed at higher temperatures (curve d and e). The lower peak can be ascribed to the sublimation of rhenium species and the higher peak to the sublimation of molybdenum species. With a decreasing Mo:Re atomic ratio, these peaks shift towards higher temperatures. The assignment of the peaks at higher temperatures for the catalysts in Fig. 6 is based on the melting points of the corresponding unsupported metal oxides, which are 570, 1068 and 1746 K for Re_2O_7, MoO_3 and WO_3, respectively [23]. It appears that the addition of MoO_3 or WO_3 to a Re_2O_7/Al_2O_3 catalyst lowers the thermal stability of the rhenium species. However, no obvious loss of rhenium species is observed at the activation temperature (823 K).

For Re_2O_7/AB catalysts, similar DTG patterns are obtained (Fig. 7). The peak observed at ca. 400 K can be ascribed to the conversion of orthoboric acid to metaboric acid [11] and also to desorption of physisorbed water. The peak at ca. 500 K is ascribed to the decomposition of NH_4ReO_4 and the conversion of metaboric acid to boria [11], and the peak at the higher temperature to the sublimation of the rhenium species. With an increasing Re_2O_7 loading, the peak at higher temperature shifts to successively lower temperatures. For the 9 wt% Re_2O_7/AB catalysts, a loss of rhenium species was observed at the activation temperature (823 K). Indeed this has led to a lower activity in this case [19]. For AB catalysts with a lower wt% Re_2O_7, however, no loss of rhenium was observed at the activation temperature.

It follows from Table 2 that the pore radii hardly change with the addition of MoO_3 to a 6 wt% Re_2O_7/Al_2O_3 catalyst, while the pore volumes and the specific surface areas gradually decrease. This can be explained by a gradually filling of the pores and the blocking of the pore mouths, as more MoO_3 is added. It implies that the higher activity of $MoO_3 \cdot Re_2O_7/Al_2O_3$ catalysts compared with the corresponding Re_2O_7/Al_2O_3 catalyst cannot be ascribed to a higher surface area.

Until now, the only property of the Re_2O_7-containing catalysts we have found to have a general correlation with the metathesis activity, is the Brönsted acidity of the catalysts [19,20]. We have proposed a model which can explain the role of Brönsted acid sites in the reaction [19]. The results from TPR measurements and thermal analysis of the catalysts, support this model in that they show that high metathesis activity is correlated neither to the redox properties of rhenium species of these catalysts nor to their thermal stability.

From the present study, it thus appears that for rhenium-containing metathesis catalysts, a relatively higher reducibility of rhenium species does not determine a higher metathesis activity and neither does a high freedom of rotation of the rheniacyclobutane complexes. The addition of M_xO_y ($M_xO_y = MoO_3$ or WO_3) to Re_2O_7/Al_2O_3 catalysts lowers the thermal stability of the rhenium species. The thermal stability of rhenium species decreases with carriers in the order $Al_2O_3 > SA > AB$. However, a higher or lower thermal stability of rhenium surface species is not the cause of a high metathesis activity.

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