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Invited Review

Olefin metathesis over supported rhenium oxide catalysts

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Abstract

Supported rhenium oxide has attracted much attention as solid catalyst for the olefin metathesis reaction because of practical applications. These catalysts are composed of rhenium oxide dispersed over a high surface-area support, such as alumina or silica–alumina. They have a high activity and high selectivity at temperatures of 0–100°C, while they bring about the metathesis of functionally substituted olefins when promoted with a suitable organometallic compound. The interaction of rhenium oxide with the support has been studied by a number of characterisation techniques, resulting in a detailed picture of the structure of the supported rhenium oxide. In this paper an overview is given of the current knowledge about rhenium-based metathesis catalysts, in particular the industrially used Re_2O_7/Al_2O_3 catalyst. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Alumina; Silica–alumina; Metathesis catalysts; Olefin metathesis; Rhenium oxide

1. Introduction

Olefin metathesis is a conversion process that can adapt the availability of olefins to the demand. In addition, it offers a unique path for producing important intermediates and end products from olefins, for example in the field of speciality chemicals and polymers [1]. For normal olefins, this catalytic reaction can be represented by reaction (1):

$$2\,\mathrm{R{-}CH{=}CH{-}R'} \rightleftharpoons \mathrm{R{-}CH{=}CH{-}R} + \mathrm{R'{-}CH{=}CH{-}R'} \qquad (1)$$

where R and R′ are alkyl groups or hydrogen. A simple example is the metathesis of propene into ethene and but-2-ene (R=H, $R'=CH_3$). This was the first industrial application of olefin metathesis as a means of converting surplus propene into useful products (the Phillips Triolefin Process) [2]. In fact, many olefinic substrates can undergo metathesis in the presence of a suitable catalyst, resulting in a wide variety of possible products [1].

For acyclic olefins the metathesis process is essentially thermoneutral, a statistical distribution of reactant and product molecules eventually results. This means that in the case of reaction (1), if both metathesis products remain in the reaction medium, the equilibrium mixture consists of reactant and products in the approximate molar ratio of 2:1:1.

The metathesis reaction is catalysed both in heterogeneous and homogeneous phases. A wide variety of transition metal compounds will catalyse the reaction and the most successful are based on W, Mo and Re. Heterogeneous catalysts generally consist of a transi-

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tion metal oxide, or an organometallic complex, deposited on a high-surface-area support (an inorganic oxide). Examples are Re_2O_7/Al_2O_3, MoO_3/SiO_2, WO_3/SiO_2, and $(\pi\text{-}C_4H_7)_4W/SiO_2$. Sometimes an organometallic compound of a non-transition metal is used as a promoter (cocatalyst), e.g. R_4Sn (R=alkyl), to increase the activity of the catalyst.

At the moment there are various commercial applications of olefin metathesis. The Triolefin Process for the production of high-purity ethene and but-2-ene from propene started to operate in 1966. The reaction takes place in a fixed-bed reactor with a WO_3/SiO_2 catalyst, doped with sodium to prevent double-bond shift reactions, at a reaction temperature of 350–425°C. A change in the economic climate and an increase in demand for propene led to the closure of the plant in 1972. Nowadays it is more attractive to use the Triolefin Process in the reverse direction as strong global demand for propene outpaces supply from conventional sources. Since the end of 1985 the Lyondell Petrochemical has already been operating a 136 000 t/a plant in Channelview, Texas (USA) for the production of propene via cross-metathesis between ethene and but-2-ene, the latter being obtained by dimerisation of part of the ethene [3]. Recently, BASF announced to build a large-scale steamcracker in the USA in a joint project with FINA, which will integrate Phillips metathesis technology to enhance the production of propene in relation to ethene [4]. Moreover, DEA announced that it is considering using Phillips metathesis technology to increase the propene capacity at its Karlsruhe refinery [5]. The Institut Français du Pétrole (IFP) and the Chinese Petroleum Corporation (Taiwan) have jointly developed a continuous process, called Meta-4, in which ethene and but-2-ene react with each other in the liquid phase in the presence of a Re_2O_7/Al_2O_3 catalyst at 35°C and 60 bar [6,7].

Since 1969 Phillips Petroleum has operated a 1400 t/a plant for the production of neohexene (3,3-dimethylbut-1-ene), an important intermediate in the manufacture of synthetic musks, via cross-metathesis of β-di-isobutene (2,4,4-trimethylpent-2-ene) with ethene (*ethenolysis*), again with a WO_3/SiO_2 metathesis catalyst, reaction (2) [8]:

$$(CH_3)_3CCH{=}C(CH_3)_2 + CH_2{=}CH_2 \rightleftharpoons (CH_3)_3CCH{=}CH_2 + CH_2{=}C(CH_3)_2 \qquad (2)$$

A large-scale industrial process incorporating olefin metathesis is the Shell Higher Olefins Process (SHOP) for converting ethene to detergent-range alkenes. In the first step of this three-stage process, ethene is oligomerised in the presence of a soluble Ni-phosphine catalyst to give a mixture of even-numbered linear alkenes ranging from C_4 to C_{40} with a Schultz–Flory distribution. The C_6 to C_{18} α-alkenes are separated from this mixture and can then be used for different purposes. In the second step the remaining lighter and heavier alkenes undergo double-bond isomerisation over a solid alkali-metal-based catalyst to an equilibrium mixture of internal alkenes. This mixture is then passed over a solid metathesis catalyst in the third step, resulting in a statistical distribution of linear internal alkenes with both odd and even numbers of carbon atoms. The desired detergent-range internal alkenes (C_{11}–C_{14}) (10–15% per pass) are subsequently separated by normal distillation; the remaining lower and higher alkenes are recycled. The metathesis step takes place at 100–125°C and 10 bar on an Al_2O_3-supported molybdate catalyst [1,9,10].

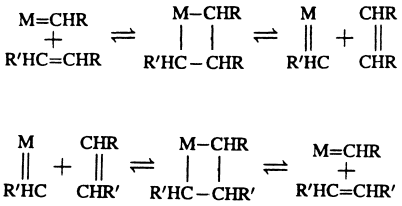
When the metathesis reaction is applied to cycloalkenes, linear unsaturated polymers are obtained, so-called polyalkenamers. This ring-opening metathesis polymerisation (ROMP) is driven by the release of ring strain in the starting material. Several interesting polymeric materials are commercially produced via the ROMP of different types of unsaturated cyclic monomers such as cyclooctene, norbornene and dicyclopentadiene, using homogeneous catalyst systems [1].

Cross-metathesis between a cyclic and an acyclic olefin provides a convenient route to certain polyunsaturated compounds for the speciality chemical market. Shell developed a process, called FEAST, for the manufacture of α,ω-dienes by ethenolysis of cycloalkenes using a Bu_4Sn-promoted Re_2O_7/Al_2O_3 catalyst (at 0–20°C and 1–2 bar), e.g. for the production of hexa-1,5-diene via ethenolysis of cycloocta-1,5-diene [11]. A commercial plant (3000 t/a) was opened in 1987 in France, but is now no longer in operation.

The fact that many commercially attractive applications of the metathesis of unsaturated hydrocarbons can be envisaged has been the incentive for much research into satisfactory catalysts. In this respect, heterogeneous rhenium-based metathesis catalysts have attracted much attention because of their high potential for practical applications. In this review, after a short introduction into the reaction mechanism, an overview is given of the current knowledge about rhenium-based metathesis catalysts, in particular the industrially used Re_2O_7/Al_2O_3 catalyst.[1]

2. Reaction mechanism

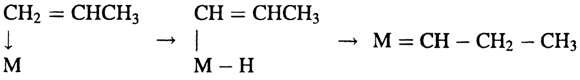
Metathesis is a transalkylidenation reaction and it is generally accepted that the reaction proceeds via the so-called metal carbene mechanism. The propagation reaction involves a transition-metal carbene as the active species with a vacant co-ordination site at the transition metal. The alkene co-ordinates at this vacant site, and subsequently a metallacyclobutane intermediate is formed. The metallacycle is unstable and cleaves to form a new metal carbene complex and a new alkene, reaction (3):



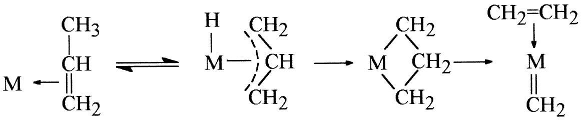
$$\begin{matrix} \mathrm{M{=}CHR} & & \mathrm{M{-}CHR} & & \mathrm{M} & & \mathrm{CHR} \\ + & \rightleftharpoons & |\quad| & \rightleftharpoons & \| & + & \| \\ \mathrm{R'HC{=}CHR} & & \mathrm{R'HC{-}CHR} & & \mathrm{R'HC} & & \mathrm{CHR} \end{matrix}$$

$$\begin{matrix} \mathrm{M} & & \mathrm{CHR} & & \mathrm{M{-}CHR} & & \mathrm{M{=}CHR} \\ \| & + & \| & \rightleftharpoons & |\quad| & \rightleftharpoons & + \\ \mathrm{R'HC} & & \mathrm{CHR'} & & \mathrm{R'HC{-}CHR'} & & \mathrm{R'HC{=}CHR'} \end{matrix} \qquad (3)$$

In heterogeneous metathesis the initial metal carbene can be formed by a reaction between the catalyst and the promoter, if present, or by interaction of the substrate alkene with the transition metal centre. In the latter case more than one initiation mechanism has been devised on the basis of experimental evidence. The most accepted routes to the first metal carbene include the formation of a π-complex between the reacting alkene and the transition metal, followed by either a 1,2-hydrogen shift mechanism, reaction (4), or a hydride transfer to form successively a π-allyl complex, a metallacyclobutane, and the metal carbene reaction (5):



$$\begin{matrix} \mathrm{CH_2 = CHCH_3} & & \mathrm{CH = CHCH_3} & & \\ \downarrow & \rightarrow & | & \rightarrow & \mathrm{M = CH - CH_2 - CH_3} \\ \mathrm{M} & & \mathrm{M - H} & & \end{matrix} \qquad (4)$$



(5)

3. Rhenium-based metathesis catalysts

Rhenium-based metathesis catalysts are composed of rhenium oxide dispersed over a high-surface-area oxide support, such as alumina or silica–alumina. They have a high activity and high selectivity at low temperatures (20–100°C), while they are also active for the metathesis of functionally substituted olefins when promoted with a tetraalkyltin or- lead compound [12].

Many studies have been devoted to the structure of the catalyst precursor before and after calcination, as well as the structure of the catalyst during reaction. The most significant parameters governing catalytic activity include the oxidation state of the rhenium ion, the nature and number of the ligands, and the geometry of the active complex.

3.1. Re_2O_7/Al_2O_3

3.1.1. Catalyst synthesis

Typically, a Re_2O_7/Al_2O_3 metathesis catalyst is prepared by impregnation of a γ-alumina support (surface area 180–200 $m^2\ g^{-1}$) with an aqueous solution of a rhenium salt such as NH_4ReO_4 or perrhenic acid ($HReO_4$), followed by drying at 110–120°C and calcination at 500°C or 550°C in flowing air. During calcination, decomposition of this salt occurs and formally Re_2O_7/Al_2O_3 is obtained, which should be referred to as the catalyst precursor. After introduction of the reactant, the initiation reaction leads to reduction of the Re^{7+} ions and formation of the metal carbene complexes, the active sites in metathesis.

3.1.2. Catalyst characterisation

The molecular surface structure of the Re_2O_7/Al_2O_3 catalyst precursor after calcination has been extensively investigated by a number of characterisation techniques, including diffuse reflectance spectroscopy (DRS) [13–16], electron spin resonance (ESR) [17,18], extended X-ray absorption fine structure (EXAFS) [19,20], fast-atom bombardment-mass spec-

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[1] For an earlier review see [50].

trometry (FABMS) [21,22], ^1H magic-angle spinning nuclear magnetic resonance (MAS NMR) [23], infrared spectroscopy (IR) [24–30], laser Raman spectroscopy (LRS) [26,28,31–34], temperature-programmed reduction (TPR) [18,28,35–37], X-ray absorption near-edge spectroscopy (XANES) [20,32], X-ray diffraction (XRD) [19,38–40] and X-ray photoelectron spectroscopy (XPS) [18,41–44]. An overview of these techniques, and the potential and limitations of each characterisation technique can be found in the literature [45,46]. Here we will summarise the more relevant findings obtained by these techniques with respect to the actual rhenium oxide catalyst.

TPR experiments showed that rhenium oxide on alumina is present as a surface phase [36], which is in agreement with IR studies which revealed that the alumina surface hydroxyl groups are removed by the supported rhenium oxide phase [24]. The system is generally described as a monolayer catalyst, as was indicated by XPS studies [18,41,42]. Re_2O_7 forms a monolayer up to a surface coverage of about one Re atom per 0.35 nm^2 ($\sim$18 wt% Re_2O_7).

Detailed information about the molecular structure of the rhenium oxide on the alumina support was obtained from Raman studies. These studies revealed that under ambient conditions supported rhenium oxide on alumina is present as monomeric surface ReO_4^- species, possessing C_{3v} symmetry, consistent with the presence of three equivalent terminal Re=O bonds and one Re–O–Al linkage to the support, independent of the rhenium loading [26,28,31,32]. This conclusion was confirmed by XANES measurements under ambient conditions [32].

Fig. 1 presents the Raman spectra of Re_2O_7/Al_2O_3 catalysts under dehydrated conditions as a function of rhenium oxide surface coverage [28]. The spectra suggest that two monomeric surface rhenium oxide species (ReO_4) are present on alumina under dehydrated conditions, and their ratio is a function of surface coverage. One surface species, observed at all coverages, possesses Raman bands at 1004, 890 and 340 cm^{-1} (with a shoulder at $\sim$310 cm^{-1}), which are assigned to the symmetric stretching, antisymmetric stretching and bending mode, respectively. A second surface species is observed at higher loadings with Raman bands at 1015 cm^{-1} (symmetric stretching mode) 980 cm^{-1} (antisymmetric stretching mode) and 340 cm^{-1} (with a shoulder at 310 cm^{-1}) [28].

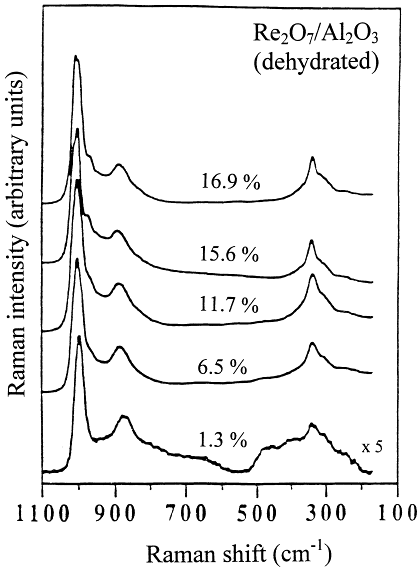


Fig. 1. In situ Raman spectra of Re_2O_7/Al_2O_3 as a function of rhenium oxide loading [28].

These findings are supported by in situ infrared spectroscopy [26,28]. The two monomeric surface rhenium oxide species at high loadings both possess three terminal Re=O bonds and one bridging Re–O–Al bond [26,28,30,34]. However, the terminal Re=O bonds are slightly different for both surface species, and this is caused by the difference in the bridging Re–O-support bond strength. It was deduced from Raman, IR and TPR studies that the second type of rhenium oxide species, present at higher coverage, has a weaker Re–O–Al bond strength [28]. The weaker Re–O-support bond strength of the second rhenium oxide is further supported by Brönsted acidity measurements [47]. These measurements showed that a Re_2O_7/Al_2O_3 catalyst having more than 6 wt% Re_2O_7 possesses Brönsted acid sites, the number of which increases with increasing rhenium oxide coverage, which suggests that the Brönsted acid proton is associated with the second surface rhenium oxide species. Vuurman et al. [28] propose that the surface Brönsted acid site is located at the bridging Re–O–Al bond, the presence of which decreases the Re–O–Al bond strength, but direct spectroscopic evidence is not available. Recently, Schekler-Nahama et al. [48] concluded from IR measurements that Lewis acidity plays a more important role for a good processing of the metathesis reaction.

Even at high rhenium loadings the surface rhenium oxide species do not possess Raman signals due to polymerised surface species; they remain isolated at all surface coverages. However, certain authors conclude from spectroscopic (IR) and activity studies that dimeric Re–O–Re species are also present at higher loadings [17,18,21,25,44], in spite of the fact that two coupled surface rhenium monomers have very similar structure to that of Re_2O_7, which is volatile above 300°C. Also, XRD of catalysts with a Re_2O_7 content of up to 18 wt% indicated the absence of Re_2O_7 crystals on the Re_2O_7/Al_2O_3 catalyst surface [36,38].

It is difficult to draw any definite conclusions with respect to the oxidation state of the rhenium under reaction conditions, although partial reduction of Re^{7+} to Re^{6+} , Re^{4+} and Re^{3+} has been observed by XPS studies [43,44]. It has been shown that pretreatment in H_2 or CO at 500°C followed by exposure to oxygen at room temperature enhances the activity of low-loaded catalysts. This treatment presumably brings the surface compound into the most favoured oxidation state for the formation of the initial metal carbene [17]. Pretreatment first with propene at 450°C and then with O_2 at 80°C gives the same result [18]. γ-irradiation of Re_2O_7/Al_2O_3 in a reducing atmosphere gives an increase in reaction rate of at least a factor 10 [49].

Poisoning experiments with NO, kinetic studies and chemical counting indicate that the number of rhenium sites that are active is only a small fraction of the total number of rhenium atoms present (<1%) [50–52]. This implies that one should be cautious in deriving a picture of the active site from information about the bulk structure of the catalyst.

3.1.3. Catalytic activity

A remarkable dependence of the rate of propene metathesis over a Re_2O_7/Al_2O_3 catalyst on the percentage of Re_2O_7 was observed (Fig. 2). At low rhenium content the catalytic activity is extremely low, but the activity increases exponentially above a Re_2O_7 loading of about 6 wt% Re_2O_7, the highest activity is reached at ~18 wt% Re_2O_7 [38]. The catalytic activity is probably only limited by the maximum amount of rhenium oxide that can be anchored on the alumina surface. Indeed, it has been shown that there is a maximum loading (14–18 wt% Re_2O_7), which depends on the type of alumina used (viz. surface area and pore volume) [28,53].

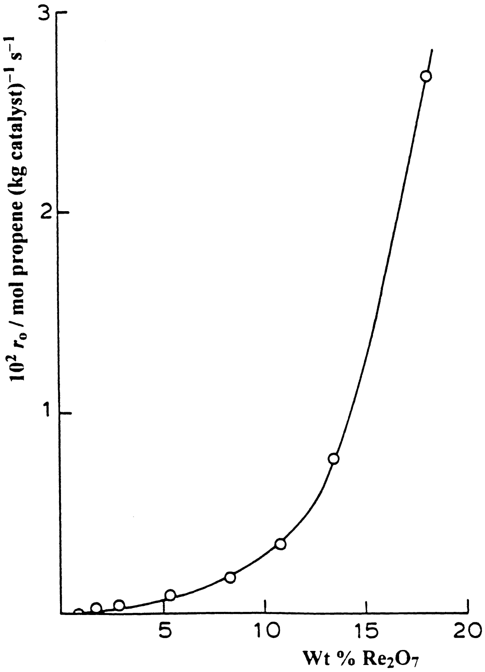


Fig. 2. Initial rate of propene metathesis (r_0) on Re_2O_7/Al_2O_3 at 50°C as a function of Re_2O_7 loading [38].

Based on an examination of the surface OH groups by FTIR, the following explanation for this activity behaviour can be given. The alumina support contains five different types of surface hydroxyl groups – two types with a basic character, one neutral type and two types with an acidic character – with IR bands between 3400 and 3800 cm^{-1} [54]. The bands at the highest frequency in the OH stretch region of the IR spectrum (3775 cm^{-1}) have been assigned to the most basic surface hydroxyl groups, bands at 3730 cm^{-1} to neutral OH groups, and those with the lowest frequency (3690 cm^{-1}) to acidic OH groups. During catalyst preparation ReO_4^- ions react with the surface OH groups. Fig. 3 shows the IR spectra of Re_2O_7/γ-Al_2O_3 catalysts with Re_2O_7 loadings of 0, 3, 6, 12 and 18 wt%, respectively. The spectra show that at very low Re_2O_7 loadings the absorbances of all type of OH groups increase slightly with increasing rhenium loading. This indicates that ReO_4^- ions probably do not react with OH groups in the first instance, but are adsorbed on coordinatively unsaturated (cus) Al^{3+} surface sites (Lewis acid sites). This adsorption of ReO_4^- ions on cus Al^{3+} sites might result in the formation of new OH groups attached to these

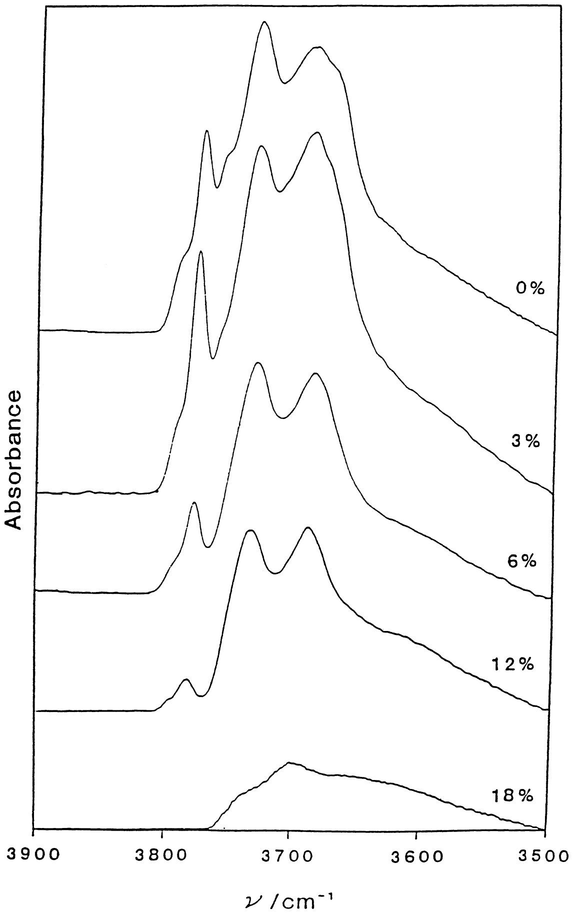


Fig. 3. FTIR spectra in the OH stretching region of Re_2O_7/γ-Al_2O_3 catalysts with varying Re_2O_7 loadings [27].

adsorbed Re centres, which could explain the slight increase in absorbance at low Re loadings. After this slight increase, the IR bands all decrease with increasing rhenium loading, suggesting that ReO_4 groups have replaced the surface OH groups. The consumption of these surface hydroxyls proceeds in a sequential way. At the lower rhenium loadings ReO_4^- ions have reacted predominantly with the more basic alumina OH groups, while at higher rhenium loadings subsequently the neutral and more acidic OH groups have also reacted, the latter resulting in the most active sites. These rhenium centres will be relatively electron-poor and therefore they will easily accept the complexation of an electron-rich carbon–carbon double bond of the alkene, which is necessary for the propagation of the metathesis reaction [27]. The surface rhenium oxide species is formed up to monolayer coverage, i.e. when all the reactive surface hydroxyls of the support have been titrated. Thus, at a 18 wt% Re_2O_7 loading nearly all surface hydroxyls have reacted with ReO_4^- ions [27]. The selective consumption of the alumina hydroxyl groups with increasing surface rhenium oxide coverage has been confirmed by others [29]. From the above it follows that it is important to obtain information about the concentration and properties of surface hydroxyls and their interaction with the rhenium oxide overlayer.

Combining the above-mentioned findings with the Raman and IR data under dehydrated conditions suggests that the first type of rhenium oxide species (see Section 3.1.2) is associated with the replacement of the basic hydroxyl groups while the second type of rhenium oxide species is associated with the replacement of the neutral and acidic hydroxyl groups of alumina. So, it is conceivable that the second surface rhenium oxide species is the precursor of the catalytic active site [28].

The catalytic activity of a Re_2O_7/Al_2O_3 catalyst can be increased by treating alumina first with an acid capable of reacting with the basic OH groups of the alumina, such as HCl or HF [23]. The activity of the Re_2O_7/Al_2O_3 catalyst – in particular a low-loaded catalyst – can also be increased by using a higher calcination temperature than that normally employed. The optimum calcination temperature depends on the rhenium content of the catalyst and lies between 825°C and 925°C. The increase in activity is explained in terms of redistribution of ReO_4 groups over the alumina surface (from basic or cus Al sites to alumina sites previously covered by acid hydroxyl groups), for which spectroscopic evidence (FTIR) was presented [55].

3.1.4. *Selectivity*

Because of the mild conditions under which the Re_2O_7/Al_2O_3 catalyst is active the possibility of side reactions such as isomerisation of the substrate or product olefins is very low, and the selectivity in metathesis is consequently high, viz. nearly 100%.

3.2. *Modified Re_2O_7/Al_2O_3 catalysts*

The catalytic performance of Re_2O_7/Al_2O_3 in the region of lower rhenium loadings (<10 wt% Re_2O_7)

can be greatly improved by (i) the incorporation of a third metal oxide such as V_2O_5, MoO_3 or WO_3 [40,56,57]; (ii) the use of a mixed support, e.g. SiO_2–Al_2O_3 [58,59] or Al_2O_3–B_2O_3 [60,61]; or (iii) the use of phosphated alumina [27].

Several explanations can be envisaged. FTIR spectra of pyridine adsorbed on various supported Re_2O_7 catalysts indicate a positive correlation between the catalyst activity and the Brönsted acidity of both the supports and their corresponding catalysts [46,62]. Indeed, infrared spectroscopy showed that in the case of Re_2O_7 supported on phosphated alumina already at low rhenium loadings acidic OH groups, either bonded to P or Al, are substituted by ReO_4 groups, resulting in a catalyst with a higher activity than the corresponding alumina-supported catalyst [27]. It is also possible that by modification the support better stabilises the Re species in the oxidation state which is most favourable for the formation of the initial rhenium carbene complex [61].

The structure of the rhenium oxide phase present on SiO_2–Al_2O_3 has been studied less than the structure on alumina. An XPS study showed that at least up to a 3 wt% Re_2O_7 loading, the rhenium oxide supported on SiO_2–Al_2O_3 ($\sim$25 wt% Al_2O_3) has predominantly a monomeric structure; at higher loadings it is also present in three-dimensional clusters [41], which was confirmed by transmission electron microscopy [63]. Since cluster formation does not occur on γ-alumina, it seems likely that the clusters reside on the silica component of the silica–alumina. It could well be that during calcination the rhenium oxide on the silica part of the silica–alumina coalesces because of the weak interaction between rhenium oxide and silica.

In contrast to what has been observed for the Re_2O_7/Al_2O_3 catalyst, the specific catalytic activity (turnover frequency) decreases with increasing rhenium content when SiO_2–Al_2O_3 is used as the support [64]. A high activity is obtained for a silica–alumina-supported catalyst with an alumina content of about 25 wt% alumina, which has the highest Brönsted acidity. This Brönsted acidity is due to two types of hydroxyl groups: hydroxyl groups attached to a Si atom and bridging hydroxyl groups attached to both a Si and an Al atom. The latter type of hydroxyl groups is more electron-poor – more Brönsted acidic – than the silanol groups. At low rhenium loadings ReO_4^- ions react preferably with the Si–Al bridging surface hydroxyl groups during calcination, resulting in electron-poor rhenium centres (ReO_4 tetrahedra), the active site precursors. This might explain why Re_2O_7 supported on silica–alumina is already very active at low rhenium loadings. At higher rhenium loadings the hydroxyl groups attached to a Si atom are also replaced, resulting in inactive rhenium centres of the type $\equiv$Si–O–ReO_3 (or rhenium clusters), as it is known that Re_2O_7/SiO_2 has no activity in olefin metathesis [65]. The inactivity of Re_2O_7/SiO_2 might be due to the fact that SiO_2 does not stabilise the necessary intermediate oxidation state of rhenium.

This behaviour also explains the so-called dilution effect, which was observed in the metathesis of methyl oleate. Diluting a 3 wt% Re_2O_7/SiO_2–Al_2O_3 catalyst, with a silica–alumina support containing $\leq$25 wt% alumina, with extra support material before calcination resulted in a spectacular increase in its specific activity. Rhenium analysis by ICP–AES of the original catalyst and the admixed support revealed that during calcination part of the rhenium migrated from the original catalyst to the admixed support, leading to a "lower-loaded" catalyst, but with the same total amount of rhenium. For a diluted 3 wt% Re_2O_7/Al_2O_3 catalyst no rhenium transfer was observed during calcination, whereas in the case of a 3 wt% Re_2O_7/SiO_2 catalyst almost half of the rhenium migrated to the admixed support when the catalyst sample had been diluted with a same amount of silica. This supports the idea that in the case of the Re_2O_7/SiO_2–Al_2O_3 catalyst the rhenium had migrated from the silica of the original catalyst to the admixed support at places where Al atoms are present.

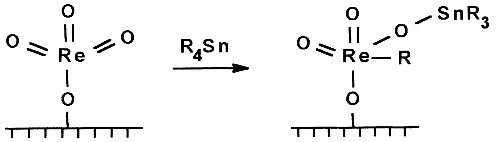
There is an apparent discrepancy in the hypothesis that the ReO_4^- ions react first with the acidic hydroxyl groups of the silica–alumina support, but with the Lewis acid and subsequently the basic hydroxyl groups of the alumina support. In fact, the ReO_4 species prefer to bind to aluminium containing sites, either during impregnation or during calcination, as inferred from the dilution experiments.

A further enhancement in activity of the rhenium-based catalyst by a factor 5–10 can still be obtained by adding a tetraalkyltin promoter [49,59,66]. When promoted with a small amount of a tetraalkyltin (R_4Sn, R=Me, Et or Bu) or a tetraalkyllead (R_4Sn, R=Et or Bu) compound all of these modified catalysts bring about the metathesis of alkenes containing functional groups (e.g. unsaturated carboxylic esters and nitriles) [67,68–70].

3.2.1. *Role of the promoter*

The active sites generated by R_4Sn may be intrinsically different from those present on the unpromoted catalyst [71,72]. That means that the nature of the active sites, which are presumably rhenium carbenes, depends on their mode of formation from the Re_2O_7/Al_2O_3 catalyst precursor and the activating agent employed, be it an alkene or tetraalkyltin. For Re_2O_7/Al_2O_3 it is assumed that the generation of the initiating Re-carbene occurs by the π-allyl mechanism (reaction (5)) [73]. The way in which an alkyltin (or alkyllead) compound forms active sites is still not well understood. Conceivable are reduction of the rhenium, modification of the active site (by addition of a tin ligand) and generation of new initiating metal-alkylidene species (via a double alkylation followed by an α-H-abstraction).

A few studies have been carried out concerning the nature of the interaction between the tin compound and the surface rhenium species [33,39,70,74–76]. It has been proposed that an organorhenium intermediate is formed upon treating the Re_2O_7/Al_2O_3 catalyst with a R_4Sn promoter, reaction (6), via a single alkylation of a rhenium site [71].



A

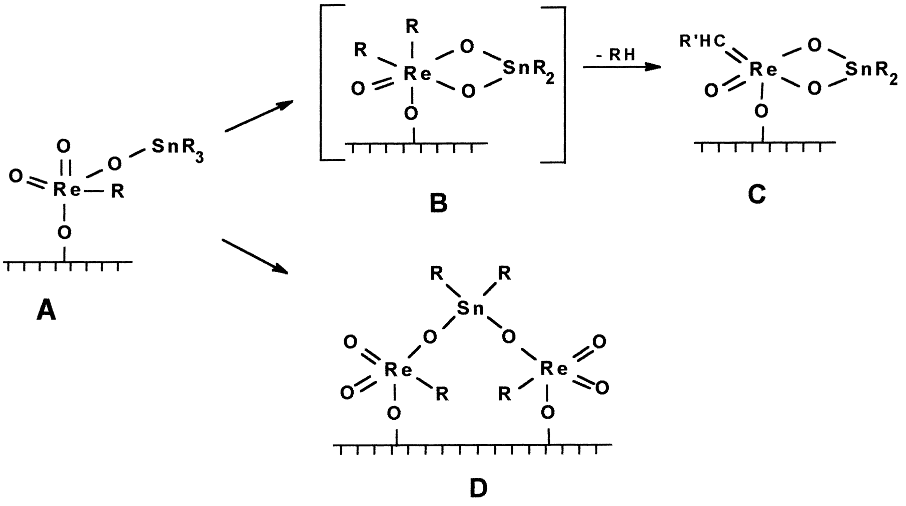
(6)

Williams and Harrison [33] reported evidence for the presence of Re–O–Sn bonds from in situ Raman spectroscopic studies of Re_2O_7/Al_2O_3 samples before and after addition of $(CH_3)_4Sn$. Their spectrum of activated Re_2O_7/Al_2O_3 treated with 1% v/v $(CH_3)_4Sn$ shows, apart from rhenium bands at 996, 884 and 338 cm^{-1}, respectively, three new bands at 520, 547 and 777 cm^{-1}. By comparison with Raman spectra obtained from $(CH_3)_4Sn$ itself, the bands at 520 and 547 cm^{-1} were assigned to tin–carbon vibrations in $(CH_3)_4Sn$. The extra band at 777 cm^{-1} was assigned to a new species formed by reaction of $(CH_3)_4Sn$ with the rhenium oxide, postulated to contain Re–O–Sn bonds, thereby creating new sites at which catalysis may occur. However, in a Raman study of the model compound $(CH_3)_3SnReO_3$, the 777 cm^{-1} band was not observed [77]. Moreover, a band at 777 cm^{-1} would be too high to be a Re–O–Sn vibration; it can be rather assigned to Sn–O vibrations. A band observed at 521 cm^{-1} with the model compound $(CH_3)_3SnReO_3$ was assigned to a Re–O–Sn vibration (symmetric stretching mode) [77]. Thus, the 520 cm^{-1} band observed by Williams and Harrison [33] was also probably due to Re–O–Sn vibrations.

Based on ^{119}Sn Mössbauer and ^{13}C and ^{119}Sn MAS NMR experiments with the catalyst system $Re_2O_7/SiO_2–Al_2O_3/R_4Sn$ ($\leq$6 wt% Re_2O_7), reactions as depicted in Scheme 1 have been proposed [75]. Both ^{119}Sn NMR and Mössbauer data accounted for the presence of species A. The R ligand on species A might undergo an electrophilic attack from a remaining OH^- group from the surface with release of an alkane. Mössbauer data suggest that higher rhenium loadings favour species D. A double alkylation involving two rhenium species (D) seems however highly improbable owing to the low density of such rhenium sites, but cannot be ruled out as the degree of dispersion of $Re_2O_7/SiO_2–Al_2O_3$ decreases strongly above 3 wt% Re_2O_7. If a double alkylation involving only one rhenium site took place, a coordinatively saturated species, B, would be formed. This species might undergo an α-H-abstraction, spontaneous or surface-induced, leading to a rhenium–alkylidene species, C. Although an alkylidene ligand in the rhenium co-ordination sphere could not be spectroscopically identified, chemical reactivity studies suggest its presence in minor amounts. While species A would predominate for $Re_2O_7/SiO_2–Al_2O_3/R_4Sn$ systems, in particular when R=Et, for the system $Re_2O_7/Al_2O_3/Bu_4Sn$ there would only be species C or D [75,76].

3.3. *Deactivated catalysts*

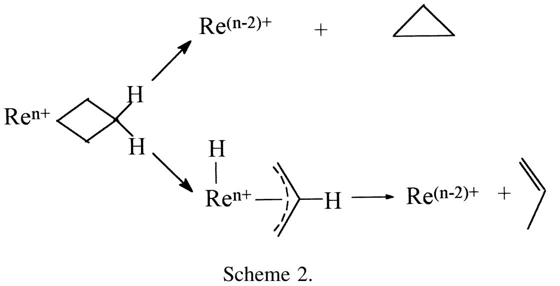
Catalyst deactivation is a serious drawback to exploiting alkene metathesis in industry. There are many routes for the deactivation of a rhenium-based catalyst. Polar compounds, such as H_2O, which might be present as an impurity in the reactant(s), are catalyst poisons [49,78]. Other possible routes for the deactivation of rhenium-based catalysts include (i) reduction



Scheme 1.

of the rhenium below its optimum oxidation state; (ii) adsorption of polymeric by-products on the surface of the catalyst, blocking the active sites; (iii) reductive elimination of the metallacyclobutane intermediate. Even when the greatest care is taken, deactivation of the rhenium catalyst cannot be avoided. Therefore, reductive elimination of the metallacyclobutane intermediate (to form cyclopropane, or β-elimination to an alkene; Scheme 2) – an intrinsic deactivation mechanism – is probably the main cause of deactivation and always seems operative [49,71,78].

Despite their relatively fast deactivation, supported rhenium oxide catalysts are preferred for practical applications because of their low operation temperature. Unpromoted Re_2O_7/Al_2O_3 catalysts can easily be regenerated by oxidation in an airflow at 550°C under atmospheric pressure without any loss of activity. In the Meta-4 process (see Section 1) the metathesis reactor (a fixed-bed, liquid-phase, up-flow reactor) operates in a regenerative mode. A small fraction of the catalyst is withdrawn periodically from the bottom of the metathesis reactor and transferred to the regenerator, while at the same time an equal amount of fully regenerated catalyst is returned to the top of the reactor [6,7].



Scheme 2.

Although a tetraalkyltin-promoted Re_2O_7/Al_2O_3 catalyst is much more active than an unpromoted catalyst, it deactivates more rapidly. The activity of a deactivated tetraalkyltin-promoted Re_2O_7/Al_2O_3 catalyst can only be partly restored by heating in a stream of oxygen or air, followed by further addition of promoter. The partial loss of activity is attributed to accumulation of tin on the catalyst surface [79].

3.4. Kinetics

Many kinetic studies have been devoted to the metathesis of alkenes over a Re_2O_7/Al_2O_3 catalyst. An extensive kinetic analysis of propene metathesis led to Eq. (7) for the initial reaction rate r_0

$$r_0 = kKp(1 + Kp) \tag{7}$$

where k is the reaction rate constant, K is the adsorption equilibrium constant for propene and p is the propene partial pressure. Further investigations of propene metathesis using mixtures of reactant and product molecules resulted in a rate expression derived from a kinetic model based on alkylidene complexes as intermediates, in which product-desorption processes are the rate-determining steps [51]. Another kinetic study concerns the liquid-phase metathesis of oct-1-ene at 9 bar over the Re_2O_7/Al_2O_3 catalyst [80]. The experimental data obtained are best interpreted in terms of a model in which either product desorption or interconversion of the alkene/alkylidene complex is rate-determining.

3.5. *Conclusions*

For decades catalytic alkene metathesis has become a well-established reaction in petrochemistry and organic synthesis. Heterogeneous catalysis is attractive in particular for the metathesis of acyclic alkenes. The catalyst Re_2O_7/Al_2O_3 has great potential because of its high activity and selectivity at low temperatures. The turnover frequency dramatically increases with the rhenium loading, which is explained by a selective consumption of the alumina hydroxyl groups with increasing surface rhenium coverage. The results of the various characterisation methods indicate that Re_2O_7/Al_2O_3 is a monolayer catalyst. Under dehydrated conditions, at higher loadings, two monomeric surface rhenium species are present on the alumina; both possess three terminal Re=O bonds and one bridging Re–O–Al bond (C_{3v} symmetry), the terminal Re=O bonds being slightly different for both surface rhenium oxide species.

Several ways of modifying of this system, including the addition of an alkyltin promoter, has led to much better performances. In the latter case more study is required to reveal the exact nature of the active site. Further improvement of the rhenium oxide catalyst could be sought in the selective anchoring of rhenium oxide species on acid hydroxyl groups of the support, and in the use of other mixed oxides as a support.

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