



## Comparison of olefin metathesis by rhenium-containing $\gamma$ -alumina or silica–aluminas and by some mesoporous analogues

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### ABSTRACT

Oxide materials with rhenium(V) oxochloro complexes highly dispersed on the surface were prepared by grafting Re(V) alkoxochloro complexes onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, chlorinated alumina, 25 and 75 wt% SiO<sub>2</sub> silica–aluminas, mesoporous alumina with high specific surface area (685 m<sup>2</sup> g<sup>-1</sup>) and mesoporous silica–alumina (950 m<sup>2</sup> g<sup>-1</sup>). The activities of these catalysts for 1-octene metathesis at room temperature are compared in the presence of a promoter: Bu<sub>4</sub>Sn or Ph<sub>2</sub>SiH<sub>2</sub>. Systems consisting of pure alumina and chlorinated alumina supports with rhenium species and Bu<sub>4</sub>Sn lead to selective formation of 7-tetradecene and ethylene at 90–100% conversion. There is a dramatic change of selectivities with Bu<sub>4</sub>Sn and silica–alumina or with Ph<sub>2</sub>SiH<sub>2</sub> and aluminas. The difference is attributed to the formation of hydrido and carbene rhenium surface species which promote at the same time isomerization, self- and cross-metathesis. Mesostructured oxides do not show any clear advantage over commercial supports. Interestingly, modifying  $\gamma$ -alumina with hydrogen chloride increases the catalytic activity even at low rhenium loading (ca. 0.7 wt%).

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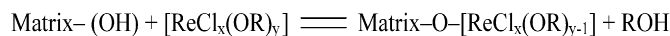
### 1. Introduction

Since the pioneering work of many groups [1–4], alkene metathesis is now widely used in large-scale industrial processes for the synthesis of linear olefins, polymeric materials and pharmaceutical intermediates. It is now extensively used in various kinds of reactions, such as ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM), acyclic diene metathesis polymerization (ADMET), and cross-metathesis (CM or XMET) [1–4]. Many homogeneous catalysts or precursors, containing transition metal complexes, mainly with Mo, W, Re and Ru [1], have served in olefin disproportionation. Among rhenium complexes, methyltrioxorhenium(VII), [CH<sub>3</sub>ReO<sub>3</sub>], denoted MTO [5,6], requires activation by a co-catalyst, a Lewis acid and an alkylating promoter (AlR<sub>n</sub>X<sub>3-n</sub> for homogeneous systems), unless it is grafted onto an acidic support. Alkyl-alkylidene-alkylidyne rhenium complexes such as [Re(C-*t*-Bu)(CH-*t*-Bu)(CH<sub>2</sub>-*t*-Bu)(CH<sub>3</sub>CN)(OTf)] metathesize *cis*-2-pentene, without the need for a co-catalyst, but they are not long-lived [7,8]. Interestingly, also without the help of any co-catalyst, [{O<sub>3</sub>ReO–Al(OAr)}<sub>2</sub>O] species and parent analogues, homogeneous models of rhenium oxide-on-alumina catalysts, show fairly high activity also with 2-pentene at 25 °C, tentatively re-

lated to the presence of Al–O–Al linkages which should induce a strong bidentate Lewis acidity [9–11]. The best heterogeneous catalysts involve supported Mo(VI), W(VI) or Re(VII) on aluminas or silicas: MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> or MoO<sub>3</sub>/SiO<sub>2</sub> from 100 to 200 °C, WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> at 150 °C; WO<sub>3</sub>/SiO<sub>2</sub> at 400 °C and Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub> which exhibits high activity and selectivity at temperatures below 100 °C [1]. These rhenium-based catalysts were thoroughly investigated because of their high performance even near room temperature, either in heterogeneous or in homogeneous systems [12]. The improvement in the catalytic activity of rhenium-containing materials has been attributed to Brønsted and/or Lewis acid sites; aluminas and silica–aluminas which contain these two types of acid sites are then better supports than pure siliceous materials with rather weak Brønsted centers. Thus, ≡Si–O–ReO<sub>3</sub> moieties may be regarded as completely inactive or weakly active rhenium species at room temperature in olefin metathesis (on standard amorphous silica [13] or mesoporous materials [14]). The surface complex ≡Si–O–[Re(C-*t*-Bu)(CH-*t*-Bu)(CH<sub>2</sub>-*t*-Bu)] supported on silica is an active metathesis catalyst or precursor [15], even for functionalized olefins [16]; this is certainly due to its well defined preformed complex with the key alkylidene ligand (vide supra and [7,8]), and not to the acid properties of the silica aerosil. Thus, even if several studies conclude that the acidity of the support is one of the key parameters in promoting the activity, preferential formation and site isolation of =Al–O–ReO<sub>3</sub> linkages with high rhenium dispersion are certainly important. Estimation of the

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**Scheme 1.** Grafting of alkoxochlororhenium complexes on oxides.

number of active sites present in conventional  $\text{ReO}_x/\gamma\text{-Al}_2\text{O}_3$  (prepared with  $\text{NH}_4^+$ ,  $\text{ReO}_4^-$  or  $\text{H}^+$ ,  $\text{ReO}_4^-$ ) catalysts by energy dispersive X-ray analysis (EDX) suggested that a very low percentage (less than 1%) of the rhenium was really involved in the metathesis reaction [17]. This proposal led to the design of novel heterogeneous catalysts obtained by grafting alkoxochlororhenium species,  $[\text{ReCl}_x(\text{OEt})_y]_n$ , onto  $\gamma$ -alumina [17]. The surface reaction is represented in Scheme 1 where Matrix-(OH) denotes bare Brønsted sites, preferentially  $=\text{Al}-\text{O}-\text{H}$ .

After thermal treatment, the activity of the resulting pre-catalyst with ca. 1.5 wt% Re [18] exceeds that of known  $\text{ReO}_x/\text{Al}_2\text{O}_3$  prepared by the conventional method (capillary or dry impregnation with  $\text{NH}_4\text{ReO}_4$  or perhenic acid involving 7.5 wt% Re). These results suggest that carbene rhenium surface species represent only a small part of the rhenium deposited by “dry impregnation” of  $\gamma$ -alumina. An improvement in the catalytic activities was already claimed (vide infra) when active phases were supported on mesostructured materials, by comparison with conventional  $\gamma$ - $\text{Al}_2\text{O}_3$ - or  $\text{SiO}_2$ -based catalysts. However, are mesoporous materials containing aluminum oxide really more promising than classical industrial supports, to develop rhenium alkylidene intermediates involved in the propagation of the catalysis cycle?

Since the early 1990s and the advent of mesoporous silica [19, 20], several transition metal species, particularly with molybdenum [14,21,22], tungsten [14,23,24], rhenium [14,25–31] and ruthenium [32–35], have been grafted onto or inserted into mesoporous materials. Great efforts have been devoted to improving the incorporation of Al(III) into mesoporous silica in relation with: (i) the synthesis of classical silica–alumina analogues; (ii) the supposed easy substitution of Si by Al, and (iii) the creation of Lewis acid sites and an increase in Brønsted acidity and ion exchange capacity (vide supra). Few rhenium-containing mesoporous materials with aluminum oxide have been reported, probably because mesoporous alumina or well defined aluminum-containing mesoporous silica is more difficult to synthesize than the corresponding pure siliceous materials. Rhenium oxide supported on ordered mesoporous aluminas has been claimed as more active and selective than  $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$  for alkene metathesis, but high optimum loadings of 6–15% are considered [25,27,29–31] and isomerization occurring on Brønsted acid sites can also occur [25,29,30]. The catalysts were prepared with ammonium perhenate, perhenic acid (incipient wetness impregnation, thermal spreading, etc.) or grafting of MTO [26,28,36–38]. A second question can be raised: are the low rhenium contents in the range of those proposed for the grafting of alkoxochlororhenium species onto  $\gamma$ -alumina [17] likely to work with alumina-based mesoporous materials?

Keeping in mind these two questions, the present paper considers the objective of preparing low-loaded precursors (0.5–2 wt% Re) via a route involving the grafting (Scheme 1) of  $[\text{ReCl}_x(\text{OR})_y]$ , previously synthesized from  $[\text{Re}_2\text{Cl}_{10}]/\text{anhydrous ethanol}$  [17],  $\gamma$ -alumina, silica–aluminas (25 and 75 wt%  $\text{SiO}_2$ ), and mesoporous alumina or silica–alumina. We observed that promotion by chlorination is particularly effective in alkene metathesis, this leads us to use chlorinated alumina as a support of chlororhenium species.

How an activating agent or promoter forms active sites is still a subject of interest. One of the first model complexes for the activation of silanes,  $[\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8]$ , probably has an agostic  $\text{Si}-\text{H} \cdots \text{Re}$  interaction [39]; this led us to use  $\text{Ph}_2\text{SiH}_2$  to modify the surface of rhenium deposits on aluminum oxide and to generate hydrido- and/or even carbene rhenium species [18]. It is well known that  $\text{Si}-\text{H}$  bonds represent a particularly interesting case because the interaction can be strong enough for  $\eta^2\text{-SiH}_2\text{R}_2$  com-

plexes to exist. Thus, comparison of  $\text{Ph}_2\text{SiH}_2$  and  $\text{Bu}_4\text{Sn}$  will be considered in conjunction with the role of the support (aluminas and silica–aluminas, and some mesoporous analogues).

The solid samples were characterized by elemental analysis, X-ray powder diffraction, transmission electron microscopy (TEM) and EDX analysis, dinitrogen adsorption–desorption at 77 K, and solid state  $^{27}\text{Al}$  and  $^1\text{H}$  MAS-NMR spectroscopies. The activities of these catalysts for 1-octene metathesis at room temperature are compared.

## 2. Experimental

### 2.1. Reagents

1-Propanol (Rectapur), sodium silicate solution (27 wt%  $\text{SiO}_2$ , 8 wt%  $\text{Na}_2\text{O}$ , Rectapur),  $\text{C}_6\text{H}_5\text{Cl}$  (PhCl, 99.6%) and 4 Å molecular sieves were purchased from Prolabo. Aluminum tri-sec-butoxide (97%)  $[\text{Al}(\text{OCH}(\text{CH}_3)(\text{C}_2\text{H}_5))_3]$ , aluminum isopropoxide (98%)  $[\text{Al}(\text{OCH}(\text{CH}_3)_2)_3]$ , dry hexane (99%), lauric acid (99%)  $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$  and  $[\text{Re}_2\text{Cl}_{10}]$  were obtained from Aldrich.  $\text{Bu}_4\text{Sn}$  (98%), 1-octene (99%) (without peroxides, stored under dry dinitrogen), and tetradecyltrimethylammonium bromide ( $\text{C}_{14}\text{TMABr}$ , 98%) were purchased from Fluka,  $\text{Ph}_2\text{SiH}_2$   $[(\text{C}_6\text{H}_5)_2\text{SiH}_2]$  from Merck, and  $\text{H}_2\text{SO}_4$  and  $\text{C}_2\text{H}_5\text{OH}$  (anhydrous, 99.9%) from Carlo Erba. Perhenic acid  $[\text{HReO}_4]$  in aqueous solution was prepared by slow addition of finely powdered samples of metallic rhenium to hydrogen peroxide (30 wt% aqueous  $\text{H}_2\text{O}_2$ , stabilizer: stannate); it was neutralized by aqueous ammonia and concentrated to get white crystalline ammonium perhenate,  $\text{NH}_4\text{ReO}_4$  [40]. CAUTION: self-heating can rapidly increase the decomposition rate of destabilized hydrogen peroxide. Carry out the reaction on a small scale. Tetrabutylstannate ( $\text{Bu}_4\text{Sn}$ ) is a highly toxic flammable liquid. Appropriate safety precautions and procedures should be employed during all stages of the handling and disposal of this compound.  $\gamma$ -Alumina and silica–aluminas with 25 or 75 wt%  $\text{SiO}_2$  were commercial products (Rhodia) with surface areas of 224, 280 and 330  $\text{m}^2\text{g}^{-1}$ , and pore volumes of 0.53, 0.80 and 0.80  $\text{cm}^3\text{g}^{-1}$ , respectively. Elemental analysis did not reveal the presence of any impurity. Chlorinated alumina ( $\gamma\text{-Al}_2\text{O}_3\text{-Cl}$ ) was obtained by interaction of  $\text{HCl}(\text{g})/\text{H}_2$  (2/1) with  $\gamma$ -alumina (surface area: 206  $\text{m}^2\text{g}^{-1}$ , pore volume: 0.46  $\text{cm}^3\text{g}^{-1}$ ) [41,42] (see Section 2.3.4).

### 2.2. Characterizations

X-ray diffraction patterns were recorded on a Bruker D8 diffractometer using  $\text{Cu K}\alpha$  radiation (1.54 Å) with  $0.02^\circ$  ( $2\theta$ ) step size and 6 s step time in the range  $2 < 2\theta < 10^\circ$ . Adsorption and desorption isotherms for nitrogen were obtained at 77 K using a Micromeritics ASAP 2010. The samples were outgassed at 393 K and 0.3 Pa for 4 h before measurements. Elemental analyses were carried out at the Service Central d'Analyse (CNRS-Lyon) by inductive coupling plasma-atomic emission spectroscopy (ICP-AES) after alkaline fusion with  $\text{Li}_2\text{B}_4\text{O}_7$ . TEM and EDX analyses were performed using a JEOL JEM 2010 transmission electron microscope operating at 200 kV, equipped with a PGT Imix-PC system. The X-ray peaks ( $\text{Si K}\alpha$  at 1.75 keV,  $\text{Al K}\alpha$  at 1.487 keV,  $\text{Cl K}\alpha$  at 2.62 keV,  $\text{Re L}\alpha$  at 8.652 keV,  $\text{Re L}\beta_1$  at 10.009 keV,  $\text{Re L}\beta_2$  at 10.273 keV and  $\text{Re L}\gamma_1$  at 11.684 keV) emitted from a part of the bulk and/or from the surface (spot beam analysis) were recorded in the 0–15 keV range. Data do not include oxygen composition because the instrument is not sensitive to oxygen. The samples were dispersed in cyclohexane by sonication and placed on carbon-covered copper grids and dried in dry air. Room-temperature solid-state magic-angle spinning nuclear magnetic resonance (MAS NMR) experiments were performed on a Bruker AVANCE400 spectrometer at 9.4 T in 4 mm

zirconia rotors.  $^{27}\text{Al}$  one-pulse experiments (aqueous solution of  $\text{Al}(\text{NO}_3)_3$  as reference) were performed by spinning at 12 kHz with a selective pulse ( $<\pi/6$ ) duration of 1  $\mu\text{s}$ , recycle time 1 s and 2048 acquisitions. The triple quantum MAS (3QMAS) spectra were acquired with Z-filtering [43] and hypercomplex (States) phase detection. The pulse durations were set empirically to 4 and 1.5  $\mu\text{s}$  for the first and the second pulses, respectively ( $\Omega_1/2\pi = 90$  kHz), and to 8.5  $\mu\text{s}$  for the third selective pulse ( $\Omega_1/2\pi = 10$  kHz). These values maximized the observed signal. 32  $t_1$  increments of 31  $\mu\text{s}$  were acquired in the first dimension. A total of 2000 scans was accumulated with a recycle time of 1 s. Data processing including shearing and scaling according to the  $\bar{C}_z$  convention [44] was performed using the xfshear “au” NMR program. Room-temperature single-pulse  $^1\text{H}$  experiments at 400 MHz (TMS as reference) were performed with a  $90^\circ$  pulse duration of 2  $\mu\text{s}$  and a recycle delay of 40 s (8 scans). The MAS equipment for rotation (14 kHz) was carefully cleaned to avoid spurious proton signals. The probe signal was subtracted from the total FID. For the experiments with  $\text{Ph}_2\text{SiH}_2$  and mesoporous alumina, the samples were treated in vacuum (below 1 Pa) at temperatures between 300 and 550 K.  $\text{Ph}_2\text{SiH}_2$  (10  $\mu\text{L}$ ) was introduced with a micro-syringe under reduced pressure.

### 2.3. Catalyst preparation

#### 2.3.1. Mesoporous alumina ( $\text{Al}_2\text{O}_3/\text{meso}$ )

Mesoporous alumina was synthesized according to a slightly modified procedure described by Čejka et al. [45], with anionic surfactant. Typically, to a solution of 3.4 g (0.015 mol) of lauric acid in 100 mL (1.2 mol) of 1-propanol and 3.1 mL (0.172 mol) of  $\text{H}_2\text{O}$ , stirred for 30 min at room temperature, 13.7 g (0.05 mol) of aluminum tri-sec-butoxide was added and the reaction mixture stirred for 20 min. The gel was aged in a static Teflon-coated stainless steel autoclave and held at  $100^\circ\text{C}$  for 50 h. The molar composition of the synthesis gel was: 1 Al/3.44  $\text{H}_2\text{O}$ /0.3 lauric acid/24  $\text{C}_3\text{H}_7\text{OH}$ . After cooling to room temperature, the resulting mixture was suction-filtered, the recovered solid treated with  $\text{C}_2\text{H}_5\text{OH}$  and dried overnight over  $\text{P}_4\text{O}_{10}$ . Before grafting with the solution of Re(V) chloroalkoxides, solids were calcined for 2 h in dinitrogen 99.99% ( $2.5\text{ cm}^3\text{ s}^{-1}$ ) at  $410^\circ\text{C}$  ( $30^\circ\text{C h}^{-1}$ ) and in air ( $2.5\text{ cm}^3\text{ s}^{-1}$ ) at  $420^\circ\text{C}$  for 9 h ( $30^\circ\text{C h}^{-1}$ ).

#### 2.3.2. MCM-41 mesoporous silica ( $\text{SiO}_2/\text{meso}$ ) [46]

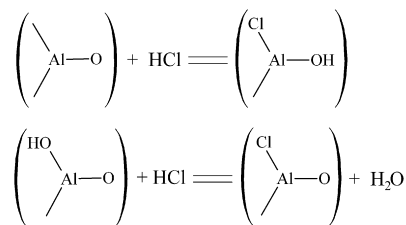
9.9 g (0.0408 mol) of sodium silicate solution were diluted with 30 mL (1.66 mol) of water and slowly added to a mixture of 7.5 g (0.022 mol) of  $\text{C}_{14}\text{TMABr}$  in 80 mL (4.4 mol) of  $\text{H}_2\text{O}$ . After stirring for 30 min at room temperature, the pH of the gel was adjusted to 10 with 2 M  $\text{H}_2\text{SO}_4$ , the solution was stirred for 30 min more and aged in a stainless steel autoclave and held at  $100^\circ\text{C}$  for two days. The solid was suction-filtered and dried over  $\text{P}_4\text{O}_{10}$ , and then calcined for 6 h in air ( $2.5\text{ cm}^3\text{ s}^{-1}$ ) at  $550^\circ\text{C}$ .

#### 2.3.3. Aluminum grafting onto MCM-41 silica ( $\text{SiO}_2\text{-Al}_2\text{O}_3/\text{meso}$ ) [47,48]

A solution of 1.4 g (0.006 mol) of aluminum isopropoxide in dry hexane (150 mL) was added to a suspension of 2.0 g of all-silica MCM-41, synthesized according to Section 2.3.2, in 50 mL of dry hexane. The mixture was stirred for 10 min and aged for 30 h at room temperature, the rest of the synthesis being identical with that for mesoporous silica (see Section 2.3.2).

#### 2.3.4. $\gamma$ -Alumina chlorinated with hydrogen chloride ( $\text{Al}_2\text{O}_3\text{-Cl}$ )

Hydrogen chloride is known to react with the hydroxyl groups of  $\gamma$ -alumina from 280 to  $730^\circ\text{C}$ . The reaction is thought to occur via two dissociative pathways (Scheme 2), the latter playing a minor role. The main step generates initially  $\text{Cl-Al}(\text{OH})$  sites; some of them are dehydroxylated at  $580^\circ\text{C}$ . Infrared data provide evidence



Scheme 2. Synthesis of chlorinated alumina: initiation steps.

for the replacement of some surface hydroxyl groups by chlorine and the formation of water and  $=\text{Al-Cl}$  surface species. Detailed analyses of the dehydroxylation process cannot determine the coordination of the last OH groups after thermo-evacuation.

The material, shaped in ball form, was a  $\gamma$ -alumina from Akzo (Ketjen CK-300) with BET area  $206\text{ m}^2\text{ g}^{-1}$ , and pore volume  $0.46\text{ cm}^3\text{ g}^{-1}$ . This solid (1.5 g) was first dehydrated at  $350^\circ\text{C}$  (12 h) in a silica glass reactor freed of grease. Chlorination was then carried out at atmospheric pressure and  $580^\circ\text{C}$ , with a gas flow ( $0.5\text{ cm}^3\text{ s}^{-1}$ ) containing  $\text{HCl}/\text{H}_2$  (2/1) for 4 h. The pre-catalyst thus obtained was quickly cooled to  $60^\circ\text{C}$  in a reduced flow of the chlorination gas and dry dinitrogen 99.99% to  $20^\circ\text{C}$ . The chlorine content was in the range 1.90–2.10 wt%.

#### 2.3.5. Rhenium grafting onto $\gamma\text{-Al}_2\text{O}_3$ , silica–alumina and onto mesoporous supports

It is essential that the matrix material used for grafting be free of adsorbed water, as this would merely react with and destroy the rhenium(V) complex (it is known that  $[\text{Re}_2\text{Cl}_{10}]$  hydrolysis gives Re(IV) and Re(VII) species). 1 g of the support was evacuated at  $200^\circ\text{C}$  ( $35^\circ\text{C h}^{-1}$ ) for 2 h. The solid was then added to a solution of  $[\text{Re}_2\text{Cl}_{10}]$  (40 mg,  $1.1 \times 10^{-4}$  mol) and anhydrous  $\text{C}_2\text{H}_5\text{OH}$  (20 mL) under anaerobic conditions (dry dinitrogen). The mixture was refluxed for 6 h in  $\text{N}_2$  at  $65^\circ\text{C}$  and the solid dried overnight over  $\text{P}_4\text{O}_{10}$  after removing the solvent. The solid was calcined for 2 h in dry  $\text{N}_2$  ( $1\text{ cm}^3\text{ s}^{-1}$ ) at  $350^\circ\text{C}$  ( $120^\circ\text{C h}^{-1}$ ). It should be noted that the entire rhenium grafting procedure must be done in a dry atmosphere. As the solid thus obtained is highly moisture-sensitive, it is kept in a sealed container in dry dinitrogen.

#### 2.3.6. Rhenium oxide ( $\text{ReO}_x$ ) on $\gamma\text{-Al}_2\text{O}_3$ prepared by dry or incipient wetness impregnation, denoted $\text{Re-Al}_2\text{O}_3$ (reforming)

Extruded samples with Cl content lower than 200 ppm (1.5 g) were submitted to constant and gentle shaking, and an aqueous solution of a rhenium salt such as  $\text{NH}_4\text{ReO}_4$  or perrhenic acid was slowly added. The solid and the solution were placed in thermoregulated ( $50^\circ\text{C}$ ) Erlenmeyer flasks and graduated burettes, respectively. For the rhenium content of 7.0 wt%, three dry impregnation steps with  $\text{NH}_4\text{ReO}_4$  were necessary. Each step was followed by drying at  $110^\circ\text{C}$  and calcination at  $550^\circ\text{C}$  for 6 h in flowing air ( $1.7\text{ cm}^3\text{ s}^{-1}$ ).

### 2.4. Catalysis tests

Catalysts were tested in 1-octene metathesis at  $20^\circ\text{C}$  with a substrate/Re molar ratio of about 100. In a typical experiment, with stirring at room temperature and atmospheric pressure in a very slow flow of dry  $\text{N}_2$ , ca. 0.4 g of the catalyst was placed in a micro-reactor without solvent or with 2 mL of dry  $\text{PhCl}$  and 10  $\mu\text{L}$  of tetrabutyltin ( $\text{Bu}_4\text{Sn}$ ) or of diphenylsilane ( $\text{Ph}_2\text{SiH}_2$ ), active sites are generated quickly; then 0.7 mL of 1-octene (4 mmol) was added. Ethylene was continuously released from the reactor. The progress of the reaction was monitored by GC with 0.2  $\mu\text{L}$  of supernatant at given intervals (Delsi 30 gas chromatograph equipped with 0.25-mm-diameter 50 m OV-1701 capillary column and a

**Table 1**  
Elemental analysis and textural properties of initial supports and rhenium-containing catalysts

Entry	Pre-catalyst	Re (wt%)	Cl (wt%)	Cl/Re (mol/mol)	Si/Al (mol/mol)	Al/Re (mol/mol)	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_p^b$ ( $\text{cm}^3 \text{g}^{-1}$ )	$a_0$ (Å)	$d_p^c$ (Å)	$w^d$ (Å)
1	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> (75/25)	–	–	–	2.54 <sup>e</sup>	–	330	0.80	–	–	–
2	Re-SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> (75/25)	0.42	0.40	5.0	2.54	217 (45) <sup>a</sup>	329	0.78	–	–	–
3	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> (25/75)	–	–	–	0.28 <sup>f</sup>	–	280	0.80	–	–	–
4	Re-SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> (25/75)	1.11	0.80	3.8	0.28	246 (134) <sup>a</sup>	279	0.75	–	–	–
5	Al <sub>2</sub> O <sub>3</sub>	–	–	–	–	–	224	0.53	–	–	–
6	Re-Al <sub>2</sub> O <sub>3</sub>	2.18	0.90	2.2	–	164 (178) <sup>a</sup>	214	0.50	–	–	–
7	Al <sub>2</sub> O <sub>3</sub> -Cl	–	1.90	–	–	–	198	0.46	–	–	–
8	Re-Al <sub>2</sub> O <sub>3</sub> -Cl	0.67	2.27	2.9	–	541 (178) <sup>a</sup>	199	0.46	–	–	–
9	Re-Al <sub>2</sub> O <sub>3</sub> (reforming)	6.98	<200 ppm	–	–	45	155	0.43	–	–	–
10	SiO <sub>2</sub> /meso	–	–	–	–	–	1285	1.18	46	37	9
11	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> /meso	–	–	–	3.40	–	949	0.79	47	33	14
12	Re-SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> /meso	1.50	1.52	5.3	3.40	44 (36) <sup>a</sup>	874	0.74	48	34	14
13	Al <sub>2</sub> O <sub>3</sub> /meso	–	–	–	–	–	686	0.50	72	29	43
14	Re-Al <sub>2</sub> O <sub>3</sub> /meso	2.87	3.23	5.9	–	124 (178) <sup>a</sup>	668	0.35	76	21	55

<sup>a</sup> Expected Al/Re molar ratio from rhenium grafting on the supports with [Re<sub>2</sub>Cl<sub>10</sub>]/EtOH solution.

<sup>b</sup> The mesopore volume  $V_p$  is determined at  $P/P_0 \approx 0.97$ .

<sup>c</sup> The mean pore diameter  $d_p = 4V_p/S_{\text{BET}}$ .

<sup>d</sup> The wall thickness  $w = a_0 - d_p$ .

<sup>e</sup> EDX analysis Si/Al = 2.56.

<sup>f</sup> EDX analysis Si/Al = 0.29.

flame ionization detector linked to a Delsi Enica 10 electronic integrator). GC-MS analyses were performed on a Trace GC 2000 series (ThermoQuest) coupled to a Trace MS.

### 3. Results and discussion

#### 3.1. Rhenium and chlorine contents of pre-catalysts

Two classes of materials can be distinguished in the grafting of Re(V) complexes (Table 1): silica-aluminas incorporate less Re than expected (see entries 2, 4, 12), whereas with pure alumina supports, there is apparently an increase in surface reactivity (see entries 6, 14). The corresponding Al/Re molar ratios (Table 1) are easily understood by the formation of soluble =Al-O-[Re] species commonly observed for other anchoring processes on silica or alumina [22–24,49]. This is related to the poor stability of the mesostructured alumina (entry 14). The analytical data suggest that some catalyst supports are chlorinated during the grafting process (entries 2, 4, 8, 12, 14). Thus, it was interesting to consider also chlorinated alumina. The pre-catalyst Re-Al<sub>2</sub>O<sub>3</sub>-Cl (entry 8), with 0.67 wt% Re has, with SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (75/25), the lowest number of Al sites to accommodate rhenium surface species. These results are interpreted by the stronger affinity of Re(V) species for residual Al(III)-OH than Si(IV)-OH groups (see Section 2.3.4); for Re-Al<sub>2</sub>O<sub>3</sub>-Cl, the low Re content can be explained by a deficiency of -OH groups, due to the presence of major =Al-Cl surface species (see Section 2.3.4 and Scheme 2). We observed that pure alumina supports (entries 6, 14) are better than silica-alumina (75/25) and, to some extent, silica-alumina (25/75) for rhenium grafting, since the entire Re(V) used in the synthesis is preferentially grafted onto the surface aluminum centers.

The Cl signals ( $K_{\alpha}$  line of EDX spectra) reveal that the chlorine distribution in the sample Al<sub>2</sub>O<sub>3</sub>-Cl is quasi-uniform over the alumina surface, with mean  $I_{\text{rel. Cl}}/I_{\text{rel. Al}}$  ca.  $49 \times 10^{-2}$ . Desorption of HCl and/or Cl<sub>2</sub> was controlled conductimetrically [17]; they desorb over the temperature range 70–600 °C ( $120 \text{ °C h}^{-1}$ , N<sub>2</sub>:  $0.85 \text{ cm}^3 \text{ s}^{-1}$ ). The detection limit of the method is 0.1% of the total chloride content of the samples. Analyzing the chlorine contents of the solids after the catalysis test showed that Cl was not released at room temperature.

EDX multiple-spot analysis revealed that rhenium distributions in the grafted solids were nearly homogeneous. However, samples prepared according to the conventional impregnation method us-

ing NH<sub>4</sub>ReO<sub>4</sub> (see Section 2.3.6) have very inhomogeneous distributions with ReO<sub>x</sub> or Re<sub>2</sub>O<sub>7</sub> clusters and uncovered zones (entry 9, Table 1).

#### 3.2. X-ray analysis

The X-ray diffraction pattern of calcined SiO<sub>2</sub>/meso before aluminum and rhenium grafting (Fig. 1a) displays three well resolved broad peaks at low angle, corresponding to the (100), (110) and (200) reflexions. Another peak, attributed to the (210) reflexion, is present at  $2\theta = 5.8^\circ$ , indicating that the hydrothermal treatment used in the synthesis (see Section 2.3.2) enhances the maturation of the solid, leading to organized mesoporous material. The three first reflexion peaks are also observed for SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>/meso (not shown) and Re-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>/meso (Fig. 1b) and their slight shift indicates that post-grafting of Al(III) and subsequently Re(V) onto mesoporous silica does not drastically modify its mesoporous structure in the bulk, the unit cell parameter  $a_0$  being approximately the same after these chemical modifications of the surface (see Table 1).

Low-angle powder X-ray diffraction patterns of calcined Al<sub>2</sub>O<sub>3</sub>/meso and Re-Al<sub>2</sub>O<sub>3</sub>/meso, exhibit only one very broad peak at  $2\theta$  around  $1.5^\circ$  (Fig. 2), indicating their relatively poor mesoporous organization. It is well known that mesoporous aluminas are more difficult to synthesize than siliceous analogues, and the diffraction patterns usually published, are very similar to those obtained in Fig. 2 [45]. Well-ordered mesoporous alumina materials have also been prepared [50] but the BET specific surface area is significantly lower.

#### 3.3. Dinitrogen sorption at 77 K

##### 3.3.1. Conventional supports: aluminas and silica-aluminas

Physisorption measurements of reference samples (bare supports) (Fig. 3) all exhibit type IV isotherms, according to IUPAC nomenclature [51], being characteristic of materials with wide pores and low specific surface areas ( $150\text{--}330 \text{ m}^2 \text{ g}^{-1}$ , see Table 1). It should be noted that the grafting of these supports with alkoxochloro complexes of Re(V) does not drastically change their surface properties, since  $V_p$ ,  $S_{\text{BET}}$  and the shape of the isotherms are approximately constant.

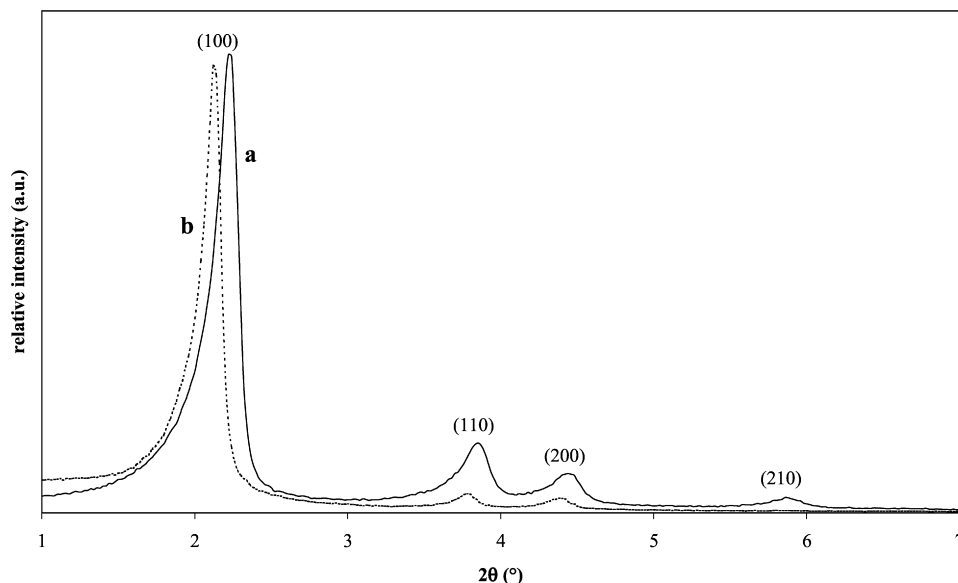


Fig. 1. X-ray powder diffraction patterns of calcined (a)  $\text{SiO}_2/\text{meso}$  and (b)  $\text{Re-SiO}_2\text{-Al}_2\text{O}_3/\text{meso}$ .

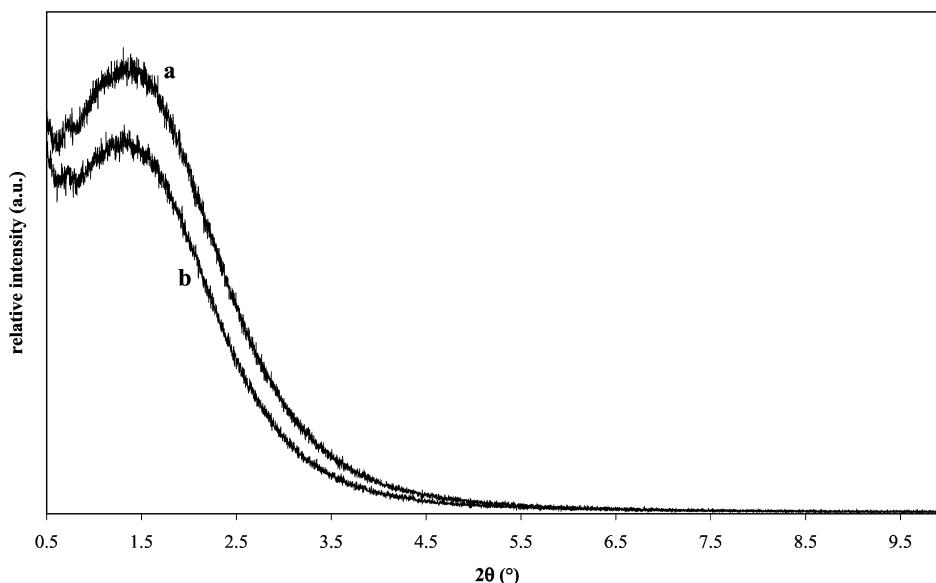


Fig. 2. X-ray powder diffraction patterns of calcined (a)  $\text{Al}_2\text{O}_3/\text{meso}$  and (b)  $\text{Re-Al}_2\text{O}_3/\text{meso}$ .

### 3.3.2. Mesoporous materials

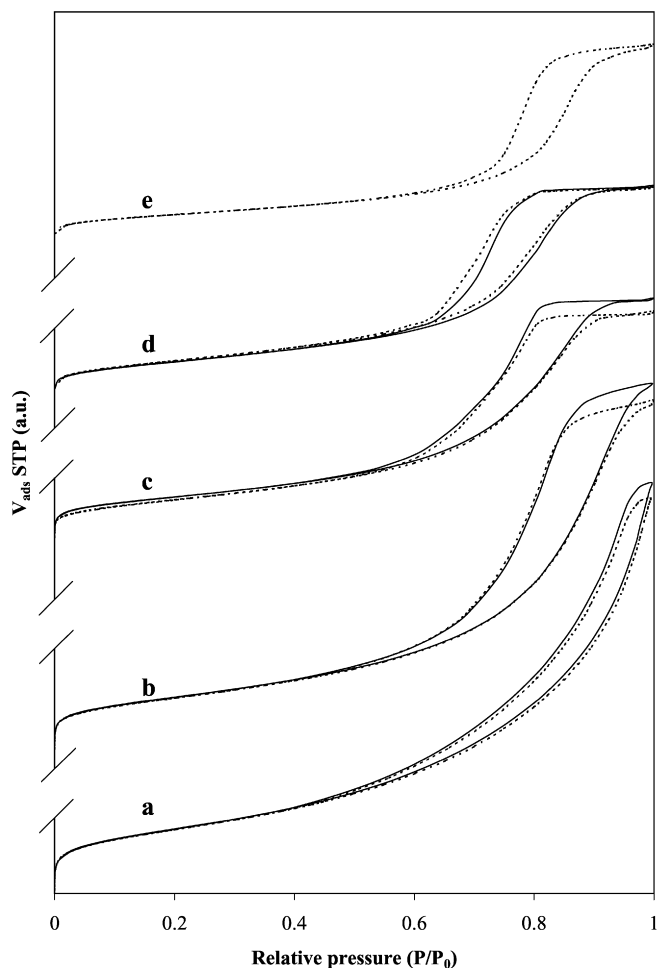
All the mesoporous supports (Fig. 4) display nearly hysteresis-free type IV isotherms, with a capillary condensation near  $P/P_0 = 0.3$ , except for  $\text{Al}_2\text{O}_3/\text{meso}$  and  $\text{Re-Al}_2\text{O}_3/\text{meso}$  for which the adsorbed  $\text{N}_2$  does not increase very much in the entire range of relative pressure.

The physisorption of dinitrogen onto mesoporous alumina can be related to a broad distribution of mesopores with an average diameter of 20–30 Å (Table 1, entries 13–14), resulting from a poor organization of the pore network and a high specific surface area ( $686 \text{ m}^2 \text{ g}^{-1}$ ) after calcination at moderate temperature (see Section 2.3.1). The modification of the surface properties of these mesoporous supports after Al and/or Re grafting depends on whether alumina or silica-alumina is involved. Pore volume and  $S_{\text{BET}}$  of mesoporous silica are clearly more affected by aluminum grafting than by subsequent rhenium grafting. The slight decrease in  $S_{\text{BET}}$  and the large change in  $V_p$  after rhenium grafting for  $\text{Al}_2\text{O}_3/\text{meso}$  may be due to some pore blocking and to the formation of soluble  $=\text{Al-O-}[\text{Re}]$  species (see Section 3.1).

### 3.4. Solid state $^{27}\text{Al}$ MAS-NMR

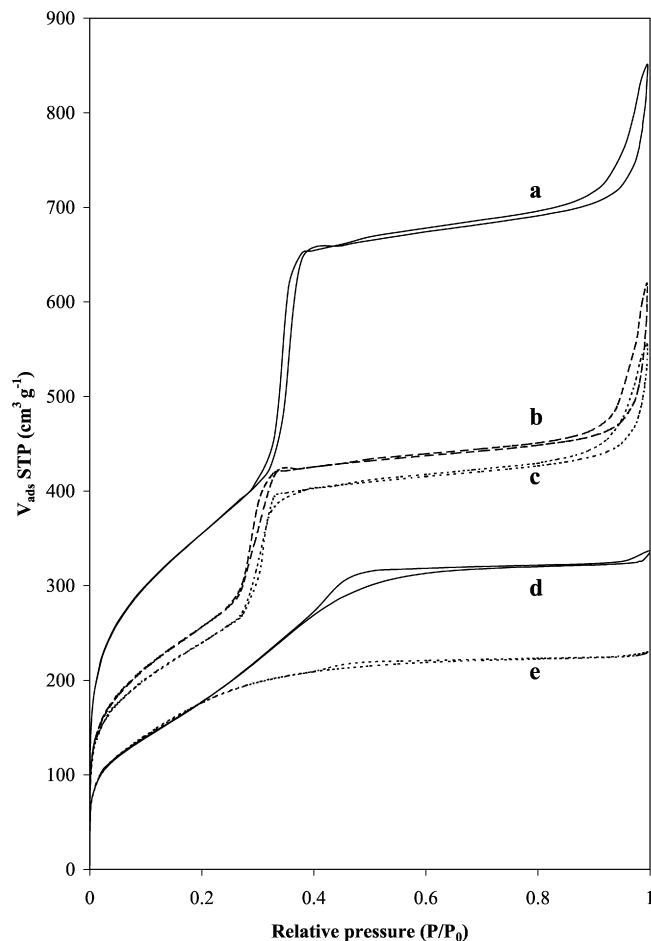
One-pulse  $^{27}\text{Al}$  MAS-NMR spectra of as-synthesized  $\text{Al}_2\text{O}_3/\text{meso}$  materials (Fig. 5a) give a broad peak centered at about 6 ppm and another centered at 67 ppm, attributed to hexa- and tetra-coordinated aluminum, respectively; for  $\text{SiO}_2\text{-Al}_2\text{O}_3/\text{meso}$  (not shown), there is an additional weak peak at 35 ppm.

The lack of crystallinity in typical silica-aluminas precludes the occurrence of relatively well separated  $^{29}\text{Si}$  MAS-NMR peaks found for zeolites with different  $n$  values in  $\text{Si}(\text{OAl})_n(\text{OSi})_{4-n}$  structural units. Thus, the deconvoluted  $^{29}\text{Si}$  MAS contributions near  $-90$ ,  $-100$  and  $-110$  ppm (with respect to TMS), attributed to  $\text{Si}(\text{OSi})_2(\text{OAl})_2$ ,  $\text{Si}(\text{OSi})_3(\text{OAl})$  and  $\text{Si}(\text{OSi})_4$ , respectively, also correspond to the  $\text{Q}_2$ ,  $\text{Q}_3$  and  $\text{Q}_4$  sites of pure silicas [21]. Similarly,  $^{27}\text{Al}$  spectra have not provided additional structural information, although further studies may differentiate  $\text{Al}_2\text{O}_3$  from  $\text{SiO}_2\text{-Al}_2\text{O}_3$ . After calcination (Fig. 5b), the distribution of the two coordinating sites of the aluminum center is modified and a new peak appears at 35 ppm. The 2D MQMAS spectra presented in Fig. 6 (see also  $\delta_{\text{iso}}$



**Fig. 3.** Dinitrogen adsorption–desorption isotherms at 77 K. Solid lines, isotherms of the bare supports: (a)  $\text{SiO}_2\text{-Al}_2\text{O}_3$  (75/25), (b)  $\text{SiO}_2\text{-Al}_2\text{O}_3$  (25/75), (c)  $\text{Al}_2\text{O}_3$  and (d)  $\text{Al}_2\text{O}_3\text{-Cl}$ . Dashed lines, isotherms of the grafted supports after thermal treatments: (a)  $\text{Re-SiO}_2\text{-Al}_2\text{O}_3$  (75/25), (b)  $\text{Re-SiO}_2\text{-Al}_2\text{O}_3$  (25/75), (c)  $\text{Re-Al}_2\text{O}_3$ , (d)  $\text{Re-Al}_2\text{O}_3\text{-Cl}$  and (e)  $\text{Re-Al}_2\text{O}_3$  (reforming).

and  $\overline{C_{Q\eta}}$  values) allow us to attribute this intermediate peak unambiguously to penta-coordinated Al. Calcined  $\text{SiO}_2\text{-Al}_2\text{O}_3$  displays approximately the same spectrum (not shown) as mesoporous materials but the distribution of aluminum surface species is slightly different (very little penta-coordinated Al, denoted Al(5)), although the peaks at 67, 35 and 6 ppm are poorly resolved. For  $\gamma\text{-Al}_2\text{O}_3$ , the spectrum (not shown) of the calcined sample is also poorly resolved but there is no peak corresponding to penta-coordinated Al. Under our conditions, with the lack of an internal standard and the very real possibility that a significant fraction of the Al is not detected once the materials are calcined, the  $^{27}\text{Al}$  NMR of amorphous oxides at intermediate field strengths is notoriously non-quantitative. The grafting of materials by  $\text{Re(V)}$  species (Figs. 5b, 5c, 6a, and 6b) does not modify the  $^{27}\text{Al}$  NMR spectra, meaning that the overall structure is unchanged by grafting and thermal treatment. We must keep in mind that  $^{27}\text{Al}$  MQ-MAS NMR spectrometry is not sensitive enough to differentiate surface modifications from bulk properties. The signals are asymmetric with a tailing high-field edge and a steep low-field edge (Fig. 5), characteristic of a distorted environment. The MQ-MAS signals obtained for the Al species (Fig. 6) are very spread out along the QIS axis (Quadrupolar induced shift) indicating a large distribution of quadrupolar constants. This confirms the disorder [52].

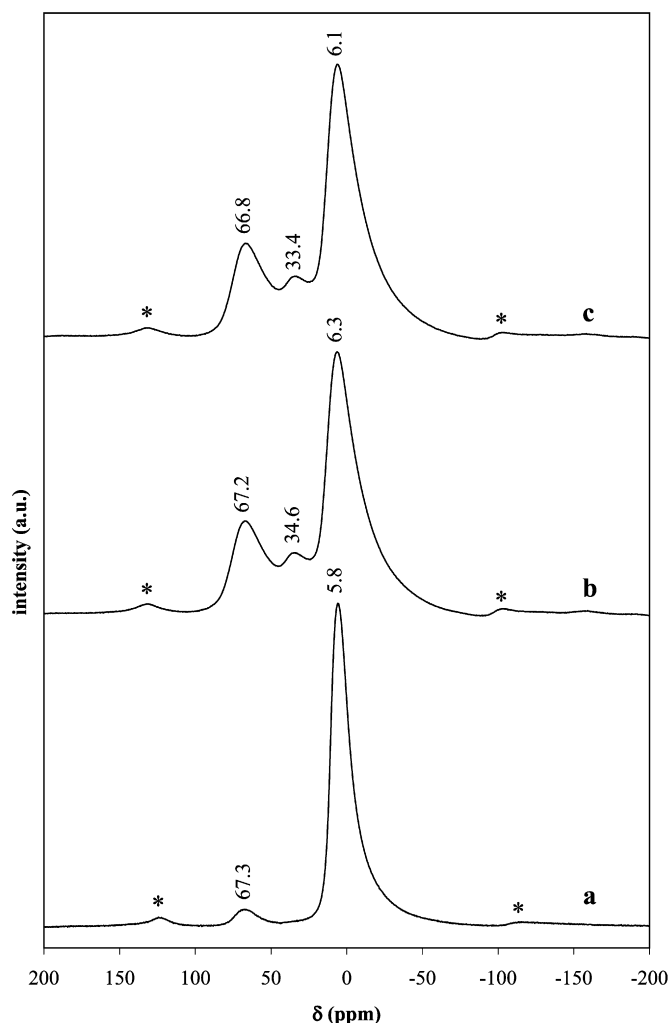


**Fig. 4.** Dinitrogen adsorption–desorption isotherms at 77 K of calcined: (a)  $\text{SiO}_2/\text{meso}$ , (b)  $\text{SiO}_2\text{-Al}_2\text{O}_3/\text{meso}$ , (c)  $\text{Re-SiO}_2\text{-Al}_2\text{O}_3/\text{meso}$ , (d)  $\text{Al}_2\text{O}_3/\text{meso}$  and (e)  $\text{Re-Al}_2\text{O}_3/\text{meso}$ .

### 3.5. Solid state $^1\text{H}$ MAS-NMR

It appears that calcined alumina and silica–alumina mesoporous materials cannot be easily distinguished by  $^{27}\text{Al}$  MAS-NMR (vide supra), whereas  $^1\text{H}$  NMR spectra (Fig. 7) clearly indicate that both mesoporous silica–alumina and alumina possess Brønsted acid sites, in different amounts and strengths. The peaks at 1.0–1.7 ppm (Fig. 7a) and at 0.9–2.0 ppm (Fig. 7b) are attributed to isolated (non-interacting) terminal Al–OH and silanol groups [53–55]. As shown previously [54], microdomains with Y zeolite structure can exist in “non-equilibrated” partially dehydrated samples. They give weak signals and chemical shift values near 4 ppm (3.7 and 3.6 ppm, Fig. 7, a and b). Adventitious water is difficult to exclude from mesoporous materials and even from conventional supports that are “practically dry” [54]. The peak at 5.4 ppm (Fig. 7b) is attributed to hydroxyl and residual water [56–58]. With “in equilibrium amorphous materials,” all protons in silica-rich silica–aluminas are associated with isolated silanol sites and OH groups bonded to aluminum atoms with a low symmetry environment [36,54,58,59]. However, we are not able to estimate the relative strength of these Brønsted acid sites in silica–alumina (3.7 ppm) and in alumina (3.6 and 5.4 ppm), although there are more protons in alumina than in silica–alumina. The lack of a signal near 7 ppm, characteristic of strong Brønsted acid sites [56], indicates that they are absent from  $\text{SiO}_2\text{-Al}_2\text{O}_3/\text{meso}$  sample [57].

The  $^1\text{H}$  NMR spectrum (Fig. 7c) of  $\text{Ph}_2\text{SiH}_2$  adsorbed on  $\text{Al}_2\text{O}_3/\text{meso}$  shows well resolved maxima. EDX data support a

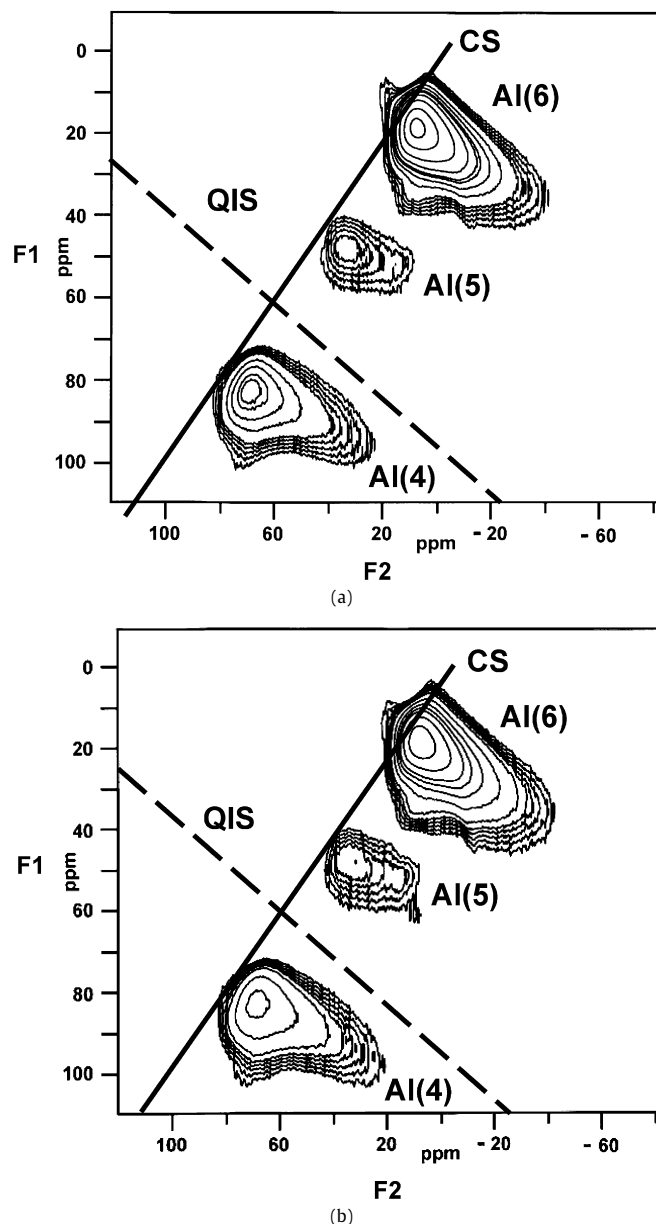


**Fig. 5.** One-pulse  $^{27}\text{Al}$  MAS-NMR spectra at 9.4 T of: (a)  $\text{Al}_2\text{O}_3/\text{meso}$  (as-synthesized), (b) calcined  $\text{Al}_2\text{O}_3/\text{meso}$  and (c) calcined  $\text{Re-Al}_2\text{O}_3/\text{meso}$ . \*: spinning sidebands.

homogeneous distribution of the Si of the promoter in these experiments. The peaks near 7 ppm and 4.5 ppm belong to aromatic and Si–H protons, respectively. They are at 7.58, 7.36, 7.33 and 4.93 ppm in the liquid. The rest of the spectrum, being identical to that of  $\text{Al}_2\text{O}_3/\text{meso}$ , indicates that  $\text{Ph}_2\text{SiH}_2$  does not interact strongly with the alumina surface, even if the change of chemical shift from liquid to surface species may suggest a certain proximity. However, the increase in the peak widths (Fig. 7d) indicates that rhenium grafting onto  $\text{Al}_2\text{O}_3/\text{meso}$  may induce: (i) a stronger  $\text{Ph}_2\text{SiH}_2/\text{Re}$  surface species interaction, (ii) a paramagnetic system due to the proximity of rhenium and protons. We propose that Fig. 7d is the fingerprint of a strong promoter ( $\text{Ph}_2\text{SiH}_2$ )/Re surface complex interacting with an agostic Si–H...Re bonding as found for  $[\text{Ph}_2\text{SiH}_2\text{Re}_2(\text{CO})_8]$  [39].

### 3.6. Catalysis tests

Conversion in 1-octene metathesis increases with the catalyst activation temperature, but for better performance and comparative study, the systems were activated with  $\text{Bu}_4\text{Sn}$  or  $\text{Ph}_2\text{SiH}_2$ . In this paper, a preliminary comparative study is based on 1-octene metathesis (Table 2). 1-Octene is a moderately demanding olefin, much less reactive than 2-pentene; it is one of the most appropriate substrates for semi-quantitative studies, other bulky olefins, such as 2-methyl-2-pentene being unable to coordinate with the



**Fig. 6.** Sheared  $^{27}\text{Al}$  ( $I = 5/2$ ) 3QMAS-NMR spectra at 9.4 T of calcined: (a)  $\text{Al}_2\text{O}_3/\text{meso}$ , hexa-coordinated Al, denoted Al(6) ( $\delta_{\text{CS}}^{\text{iso}} = 10.91$  ppm,  $\overline{C_{Q\eta}} = 4.66$  MHz), penta-coordinated Al, denoted Al(5) ( $\delta_{\text{CS}}^{\text{iso}} = 38.19$  ppm,  $\overline{C_{Q\eta}} = 5.32$  MHz), tetra-coordinated Al, denoted Al(4) ( $\delta_{\text{CS}}^{\text{iso}} = 73.82$  ppm,  $\overline{C_{Q\eta}} = 5.26$  MHz) and (b)  $\text{Re-Al}_2\text{O}_3/\text{meso}$ , hexa-coordinated Al ( $\delta_{\text{CS}}^{\text{iso}} = 11.73$  ppm,  $\overline{C_{Q\eta}} = 4.60$  MHz), penta-coordinated Al ( $\delta_{\text{CS}}^{\text{iso}} = 38.36$  ppm,  $\overline{C_{Q\eta}} = 5.40$  MHz), tetra-coordinated Al ( $\delta_{\text{CS}}^{\text{iso}} = 73.04$  ppm,  $\overline{C_{Q\eta}} = 5.17$  MHz).

metal center. Because ethylene was released from the reaction mixture, the equilibrium was shifted towards the products and conversions as high as 99–100% were achieved.

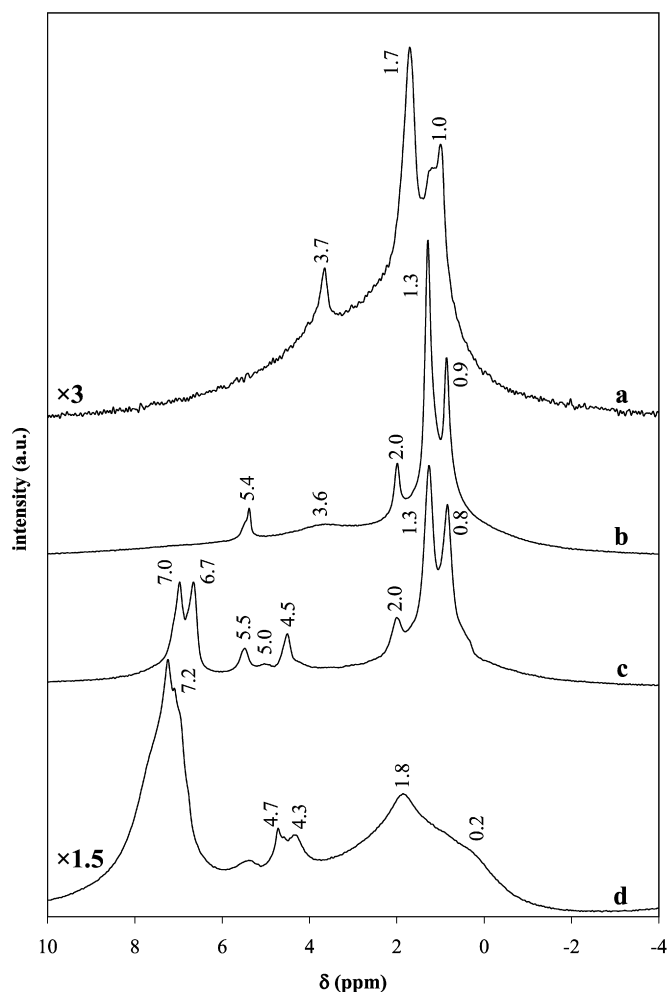
#### 3.6.1. $\text{Bu}_4\text{Sn}$ as promoter

With  $\text{Bu}_4\text{Sn}$  as promoter, silica–aluminas do not behave like alumina supports: the first group shows high conversions and low selectivities for 7-tetradecene (cis and trans), denoted  $\text{C}_{14}$  (runs 1, 2 and 6) and the second class of supports displays fair conversions (56–90%) and high selectivities for  $\text{C}_{14}$  (runs 3, 4, 5 and 7). Two competitive reactions are involved for the first group (runs 1, 2, 6): metathesis and isomerization. This observation is often described as the result of the existence of Brønsted acid sites on

**Table 2**  
1-Octene metathesis over Re-containing catalysts, after 24 h reaction at 20 °C in PhCl or without solvent

Run	Pre-catalyst	Promoter	Conv. (%)	Sel. C <sub>14</sub> (%)	Other major products selectivity (%)	TOF (h <sup>-1</sup> )
1	Re–SiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub> (75/25)	Bu <sub>4</sub> Sn	93	34	28 (C <sub>13</sub> ), 18 (C <sub>12</sub> )	17
2	Re–SiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub> (25/75)	Bu <sub>4</sub> Sn	89	63	25 (C <sub>13</sub> ), 8 (C <sub>12</sub> )	6
3	Re–Al <sub>2</sub> O <sub>3</sub>	Bu <sub>4</sub> Sn	56	100	–	2
4	Re–Al <sub>2</sub> O <sub>3</sub> –Cl	Bu <sub>4</sub> Sn	90	96	<4 (C <sub>13</sub> )	10
5	Re–Al <sub>2</sub> O <sub>3</sub> (reforming)	Bu <sub>4</sub> Sn	78	100	–	0.8
6	Re–SiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub> /meso	Bu <sub>4</sub> Sn	99	30	31 (C <sub>13</sub> ), 23 (C <sub>12</sub> ), 13 (C <sub>11</sub> )	5
7	Re–Al <sub>2</sub> O <sub>3</sub> /meso	Bu <sub>4</sub> Sn	80	99	–	2
8	Re–Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>	Ph <sub>2</sub> SiH <sub>2</sub>	84	42	35 (C <sub>13</sub> ), 6 (C <sub>12</sub> )	3
9	Re–Al <sub>2</sub> O <sub>3</sub> (reforming) <sup>a</sup>	Ph <sub>2</sub> SiH <sub>2</sub>	78	89	4 (C <sub>15</sub> ), 4 (C <sub>13</sub> )	0.8
10	Re–Al <sub>2</sub> O <sub>3</sub> –Cl <sup>a</sup>	Ph <sub>2</sub> SiH <sub>2</sub>	61	20	31 (C <sub>13</sub> ), 10 (C <sub>12</sub> ), 24 (C <sub>9</sub> ), 10 (C <sub>7</sub> )	7
11	Re–Al <sub>2</sub> O <sub>3</sub> /meso <sup>a</sup>	Ph <sub>2</sub> SiH <sub>2</sub>	80	74	20 (C <sub>13</sub> )	2

<sup>a</sup> No solvent.



**Fig. 7.** <sup>1</sup>H MAS NMR spectra at 9.4 T of calcined: (a) SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>/meso, (b) Al<sub>2</sub>O<sub>3</sub>/meso, (c) Ph<sub>2</sub>SiH<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/meso and (d) Ph<sub>2</sub>SiH<sub>2</sub>/Re–Al<sub>2</sub>O<sub>3</sub>/meso.

silica–alumina, which are believed to enhance the rate of isomerization. However, since most of the samples display approximately the same acidity (Lewis and Brønsted acid sites in both samples, of comparable strengths), acidity cannot be the only parameter responsible for the observed differences at room temperature.

Among silica–alumina supports (runs 1, 2 and 6), silica-rich materials (runs 1 and 6) behave in the same manner, indicating that mesoporous supports do not improve the catalytic activity, even at higher Cl and Re contents (run 6, with Table 1, entry 12). Moreover, the turnover frequency (TOF) is three times less with the mesoporous supports (runs 1 and 6). Aluminum-rich materials (run 2)

display results intermediate between alumina (run 3) and silica-rich materials (run 1).

With alumina supports, conversion and selectivity are related to the physical and/or chemical treatments performed before the catalysis tests. The yield with mesoporous alumina (run 7) is slightly better than with alumina (run 3) and Re–Al<sub>2</sub>O<sub>3</sub> (reforming) (run 5) corresponding to the pre-catalyst obtained by capillary impregnation with NH<sub>4</sub>ReO<sub>4</sub> (see Section 2.3.6). Chlorinated alumina (run 4), although it contains one of the lowest Re wt%, displays the highest activity of all the catalysts (high conversion, selectivity and best TOF of selective catalysts). As for silica–alumina, the use of mesoporous supports does not markedly improve the catalytic activity of Re–alumina, whatever the physical and/or chemical treatments before the catalysis test. Oikawa et al. [25] have also observed approximately the same conversion for 1-octene metathesis with 6 wt% Re (prepared with NH<sub>4</sub>ReO<sub>4</sub>) on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or mesoporous Al<sub>2</sub>O<sub>3</sub> (TOF = 2 h<sup>-1</sup>). However, Hamtil et al. [30], with catalysts prepared by thermal spreading of ammonium perrhenate on alumina, have claimed that mesoporous supports are better than  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with the same loading (83% conversion after 10 h at 40 °C, TOF = 34 h<sup>-1</sup>, 7 wt% Re).

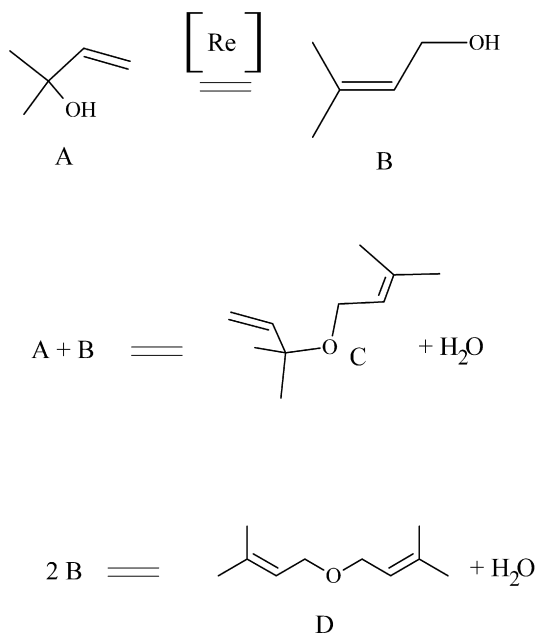
### 3.6.2. Ph<sub>2</sub>SiH<sub>2</sub> as promoter

Several experiments with alumina supports have been performed using Ph<sub>2</sub>SiH<sub>2</sub> as promoter without solvent, in order to create in situ “Re–O–Al–O–Si” species with hydrido entities such as Si–H···Re keeping in mind the crystal structure [39] of [Ph<sub>2</sub>SiH<sub>2</sub>Re<sub>2</sub>(CO)<sub>8</sub>] (runs 8 to 11). For Re–Al<sub>2</sub>O<sub>3</sub>, the conversion is improved (run 8), but with others, it remains of the same order (runs 9 and 11) or is below the previous values (run 10) with Bu<sub>4</sub>Sn as promoter. In all cases, the selectivities obtained with Ph<sub>2</sub>SiH<sub>2</sub> as co-catalyst are below the values obtained with Bu<sub>4</sub>Sn. It should be emphasized that there is no synergy between Ph<sub>2</sub>SiH<sub>2</sub> and the alumina pre-catalysts, but there is an interaction of Ph<sub>2</sub>SiH<sub>2</sub> with the Re centers, as evidenced by the <sup>1</sup>H NMR spectra (vide supra, Fig. 7d), and it leads to isomerization and metathesis.

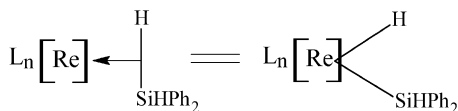
### 3.6.3. Isomerization properties of rhenium complexes at room temperature

According to previous investigations, allylic alcohols undergo apparent double-bond isomerization at room temperature when catalyzed by [ReCl<sub>x</sub>(OR)<sub>y</sub>] complexes or species grafted on alumina [17]. This was illustrated by the isomerization of 2-methyl-3-buten-2-ol (A) to 3-methyl-2-buten-1-ol (B), in the absence of air and water (equilibrium is obtained in 3 min at 20 °C), with subsequent formation of ethers C and D (Scheme 3). The product B is indicative of the formation of alkoxo complex intermediates and of a cyclic rhenium-centered transition state [17,60,61]. Dialkyl ethers C and D are acid and/or rhenium-catalyzed (see Supplementary material, 1).





**Scheme 3.** Isomerization of allylic alcohols and subsequent formation of allylic ethers.

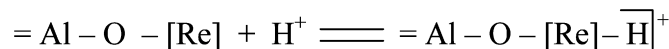


**Scheme 4.** Proposed formation of [Re]-H species for the isomerization of alkenes via a hydride addition-elimination mechanism [4].

These results were extended to three rhenium complexes:  $[ReO_3(OSiR_3)]$  ( $R = Me, Ph$ ) [62] and MTO [63,64]. The mechanism, with a 1–3 oxygen shift, does not correspond to classical isomerization of alkene, which is a more demanding process, without a transition metal complex. Thus, at room temperature, 1-octene is completely isomerized in the presence of a catalyst with an acidity function  $-H_0 = 12$  ( $H_2SO_4$ , 100%) with the formation of tertiary carbocations [65]. To the best of our knowledge, the highly acidic solids ( $\gamma$ -alumina/ $H_2O(g)$ , sulfated zirconia, chlorinated alumina, etc.) are only active for the isomerization of butenes at higher temperature (250 °C for  $\gamma$ - $Al_2O_3$ ). Control experiments with the bare thermally treated supports, including chlorinated alumina (without grafted rhenium species), confirm the absence of isomerization at room temperature with 1-octene. As an example, sulfated  $\gamma$ -alumina showed 50% selectivity towards isobutene at approximately 50% conversion of butenes only at 450 °C and mass hour space velocity, GHSV of  $0.6 \text{ g cm}^{-3} \text{ h}^{-1}$  [66]. Interestingly, even at room temperature, isomerization of 1-octene or product olefins is very high (runs 1, 2, 6, 8, 10 and 11). This can only be explained by a mechanism involving hydrido rhenium [Re]-H species (see Supplementary material, 2), which are more easily generated with silanes such as  $Ph_2SiH_2$  (Scheme 4), a hydride reagent [39] or by protonation of the rhenium centers by surface Brønsted species (silica-alumina). Many inorganic complexes behave as Lewis bases due to electron-rich metal centers and protonation is a common reaction (see Scheme 5 for Re-H formation by  $H^+$  addition and [4]).

### 3.6.4. Chlorinated alumina systems

It appears that the activity of  $Re-Al_2O_3$  can be increased by treating the oxide first with an acid ( $HCl/H_2$  mixture) capable of



**Scheme 5.** Proposed formation of [Re]-H complex by protonation [4].

reacting with the Al centers of the alumina. This forces the alkoxochlororhenium complexes to interact subsequently with residual surface hydroxyl groups, leading to a better distribution of the  $=Al-O-Re$  active sites. Rigorous proof of heterogeneity was obtained by: (i) filtering the catalyst at the reaction temperature before completion of the reaction and testing the filtrate and (ii) analyzing the rhenium content of the filtrate (leaching of active species does not occur in the presence of weak nucleophilic reagents such as 1-octene and chlorobenzene). A correlation between metathesis activity and  $ZnCl_2$ -modified aluminas has been noted, but no structures for the grafted sites were proposed [26]. Zinc halides and halocomplexes with  $Cl^-$  ions may also serve as chlorinating agents of the support, leading also to a better dispersion of MTO.

## 4. Conclusion

Estimation of the number of active sites in conventional  $ReO_x/\gamma-Al_2O_3$  catalysts (7 wt%) prepared with  $NH_4ReO_4$  (or  $HReO_4$ ), suggests that less than 1% of the rhenium deposit is really active for 1-octene metathesis. In contrast, the intimate grafting of rhenium alkoxochloro species appears to be a reliable alternative for preparing room-temperature active catalysts with low rhenium contents (e.g. 0.4–0.7 wt%).

Mesoporous solids ( $Al_2O_3/meso$ ,  $SiO_2-Al_2O_3/meso$ ) were prepared and compared to standard amorphous supports ( $\gamma$ -alumina, silica-aluminas with 25 and 75 wt%  $SiO_2$ ). The synthesis of these mesoporous materials with high specific surface areas was not, at present, the trump card for metathesis under very mild conditions. Variable amounts of penta-coordinated aluminum ( $Al(5)$ ) are evidenced by NMR studies, and they probably do not create preferred sites for anchoring rhenium centers. Conventional supports such as alumina, reacted with rhenium alkoxochloro complexes, with subsequent thermal treatments, show a clear increase in surface reactivity. From the molar ratio  $Cl/Re$ , it appears that there is a partial spreading and a promoting effect of chlorine, which is confirmed with chlorinated alumina and grafted chloro rhenium species. The precursors thus obtained display interesting catalytic activity towards terminal olefin metathesis. The ease and low cost of their synthesis without sophisticated ligands, as compared to mesoporous materials, make them good candidates for alkene reactions at room temperature. The use of low-nuclearity rhenium complexes should be considered for the preparation of fully recyclable catalysts with site isolation of surface species, low metal content and high dispersion.

We think that  $=Al-Cl$  groups have a protecting role in preventing deactivation and dimerization of rhenium surface species and thus a stabilizing effect. Systems with pure alumina and chlorinated alumina supports, rhenium species and  $Bu_4Sn$  lead to the formation of 7-tetradecene and ethylene at 90–100% 1-octene conversion. Coupling silica-alumina based catalysts with  $Bu_4Sn$  or alumina with a silane (here  $Ph_2SiH_2$ ) leads to isomerization and self- and cross-metathesis by dual catalysis due to hydrido and/or carbene rhenium species.  $^1H$  NMR studies show a strong interaction between rhenium center and  $Ph_2SiH_2$ . Work is continuing on the search for highly efficient low rhenium-content catalysts.

Mesoporous materials have no decisive advantage over industrial extruded oxides. The challenge is to better control the assembly, hydrolysis and condensation mechanisms in order to obtain narrow pore size distributions and excellent thermal stability. Some of the catalysts prepared now may have applications for

the conversion of alkenes and even of alkanes by the combination of dehydrogenation/hydrogenation reactions under study in our group. We think that promising synthetic perspectives may also arise if it is possible to switch selectively from metathesis to isomerization and back again at room temperature. There are many examples of the development of useful synthetic methods where the “occasional occurrence” of olefin isomerization reactions combined with another reaction opens up useful synthetic methods [4,67]. Tailor-made catalysts can be pure metathesis or “assisted Tandem” catalysts.

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### Supplementary material

The online version of this article contains additional supplementary material.

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