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Olefin metathesis with mesoporous rhenium-silicium-aluminum mixed oxides obtained via a one-step non-hydrolytic sol-gel route

Karim Bouchmella^a, P. Hubert Mutin^{a,*}, Mariana Stoyanova^b, Claude Poleunis^c, Pierre Eloy^c, Uwe Rodemerck^b, Eric M. Gaigneaux^c, Damien P. Debecker^{c,*}

^a Institut Charles Gerhardt, UMR 5253, CNRS-UM2-ENSCM-UM1, Université Monpellier 2, cc 1701, Montpellier 34095, France ^b Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany ^c Institute of Condensed Matter and Nanoscience – MOlecules, Solids and reactiviTy (IMCN/MOST), Université catholique de Louvain, Croix du Sud 2 box L7.05.17, 1348 Louvain-La-Neuve, Belgium

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1. Introduction

ABSTRACT

Mesoporous Re–Si–Al, Re–Al, and Re–Si mixed oxides were obtained via a one-step non-hydrolytic sol–gel route followed by calcination. The texture and surface properties of the resulting catalysts were characterized by a combination of EDX, XRD, N₂-physisorption, XPS, ToF-SIMS, and NH₃-TPD. The loss of rhenium during calcination, the texture and the acidity of the catalysts depended on their composition. Migration of rhenium toward the surface occurred during the calcination treatment, as evidenced by XPS and ToF-SIMS. After calcination, ToF-SIMS showed the presence of well-dispersed ReO_x surface species. The influence of the composition of Re–Si–Al catalysts on their performances in the cross-metathesis of ethene and butene to propene was investigated. The specific activity of the Re–Si–Al catalysts was much higher than that of Re–Al catalysts, whereas the Re–Si sample was not active. The best Re–Si–Al catalysts displayed excellent specific activities (up to 45 mmol g⁻¹ h⁻¹) and apparent TOF values (98 × 10⁻³ s⁻¹).

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Olefin metathesis is one of the very few fundamentally novel reactions discovered in the last 50 years. Olefin metathesis over heterogeneous catalysts has various industrial applications in the fields of petrochemicals, oleochemicals, polymers, and specialty chemicals [1–3]. The first industrial process (the Phillips Triolefin Process) was used to produce ethene and 2-butene from propene with a heterogeneous catalyst. Nowadays, the reverse reaction is of interest because the demand for propene is high. Propene is mainly used in the production of polypropylene. The metathesis reaction is catalyzed by supported transition metal oxides [4], and the most successful metathesis catalysts are based on rhenium [5], molybdenum [6–8], or tungsten oxides [9]. Among them, the rhenium-based catalysts are highly interesting because they are very active and selective even at room temperature [10]. Another

advantage of rhenium catalysts is that they are more tolerant to functional groups such as esters than tungsten and molybdenum catalysts [2,3,11]. Rhenium catalysts are generally based on Re₂O₇ [12,13] supported on different oxide (TiO₂, Al₂O₃, SiO₂) or mixed oxide (SiO₂–Al₂O₃) supports. The activity of heterogeneous catalysts in olefin metathesis is influenced by the nature of the support [14]: for example, Re₂O₇/SiO₂–Al₂O₃ catalysts are known to be more active than Re₂O₇/Al₂O₃ [15], while Re₂O₇/SiO₂ catalysts are virtually inactive in olefin metathesis [16,17].

Impregnation is classically used to prepare supported rhenium oxide catalysts [13,18,19]. Well-dispersed surface ReO_x species can also be obtained by thermal spreading of bulk rhenium oxide physically mixed with a support [20,21]. Spreading of rhenium oxide species has also been observed during alcohol oxidation reactions [22]. Supported rhenium oxide catalysts can be prepared by grafting rhenium alkoxo complexes onto chlorinated alumina or silica–alumina [23] or by reaction of gaseous Re_2O_7 with the hydroxyl groups of a zeolite to form Si–OReO₃–Al species [24].

All of these methods are limited either by the number of commercially available supports or by the need to prepare tailored supports in separate steps. In addition, controlling the deposition of



^{*} Corresponding authors. Fax: +33 4 6714 3852 (P.H. Mutin), fax: +32 10 47 3649 (D.P. Debecker).

E-mail addresses: hubert.mutin@univ-montp2.fr (P. H. Mutin), damien.debecker@ uclouvain.be (D.P. Debecker).

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the active phase onto the surface of the support is not straightforward [25]. The active species must be dispersed in their most active form on the available surface avoiding the precipitation of rhenium oxide and the plugging of the pores. A specific problem encountered with rhenium-based catalysts is linked to the volatility of rhenium heptoxide [26]. Rhenium heptoxide sublimes at 535 K, which may lead to the loss of rhenium during the calcination step. Several authors point out this difficulty, independently of the support and the preparation method [21,27–31].

The sol-gel process appears attractive since it allows in principle the preparation of mixed oxide catalysts in one step. However, there are very few examples of rhenium-based catalysts obtained by a sol-gel method. Scheckler-Nahama et al. reported the preparation from HReO₄ and Al(OⁱPr)₃ precursors of a Re–Al metathesis catalyst, which proved to be far less active than a catalyst of similar composition obtained by impregnation [32]. This low activity was ascribed to the low Lewis acidity of the sol-gel derived catalyst and to the fact that a large proportion of Re atoms was occluded in the mass of the material and not accessible to propylene. Fabris et al. reported the synthesis of a Re-Si catalyst from (NH₄)ReO₄ and Si(OEt)₄, but this sample showed a low activity in octene selfmetathesis [33], ascribed again to a lower accessibility of Re species and to the general poorer activity of silica-supported rhenium oxide catalysts in the olefin metathesis. Yoboue et al. prepared a Re–Si catalyst from HReO₄ and Si(OEt)₄ which displayed high activity in the direct conversion of methanol to dimethoxymethane [34]. The authors used this one-pot sol-gel method to lessen the loss of rhenium and to tune the interactions between the metal and the support.

Although rhenium oxide catalysts supported on silica–alumina are more active in olefin metathesis than Re catalysts supported either on alumina or on silica, one-step sol–gel methods have not been used for the synthesis of Re–Si–Al ternary mixed oxides.

In recent years, the non-hydrolytic sol-gel (NHSG) method has attracted growing interest for the preparation of various oxide and mixed oxide materials [35]. The application of NHSG chemistry to the preparation of heterogeneous catalysts has been reviewed recently [36]. The NHSG route based on the reaction of chloride precursors with an ether ("ether route") is recognized as a powerful method for the single-step synthesis of mesoporous mixed oxides with controlled composition, homogeneity, and texture, avoiding the use of any reactivity modifier, templating agent, or further supercritical drying step [35,37]. As reviewed recently [38], this route has been successfully used to prepare various efficient binary and ternary mixed oxide catalysts, including Nb–V(–Si) [39], Si–Ti [40], Si–Zr [41], Ti–V [42,43], Ag(–Nb)–Al [44], or Si–Al–Mo [45].

The ether route is based on the *in situ* formation of alkoxide groups by reaction of halide groups with the ether (Eq. (1)), followed by non-hydrolytic condensation between these alkoxide groups and the remaining chloride groups (Eq. (2)).

$$\mathbf{M}-\mathbf{Cl} + \mathbf{ROR} \to \mathbf{M}-\mathbf{OR} + \mathbf{RCl} \tag{1}$$

$$M-Cl + M-OR \rightarrow M-O-M + RCl$$
(2)

Recently, we have reported the NHSG synthesis of Mo–Si–Al mixed oxide catalysts [45] and on their excellent performances in propene self-metathesis [46].

In the present work, we describe the one-step NHSG synthesis of Re–Si–Al, Re–Al, and Re–Si catalysts by the ether route. The resulting materials were thoroughly characterized, and their catalytic performances in the metathesis of ethene and butene were investigated and compared to that of reference metathesis catalysts, including the molybdenum–silica–alumina catalysts proposed recently [46].

2. Experimental

2.1. Preparation of the catalysts

The non-hydrolytic sol-gel syntheses [47] were performed under an argon atmosphere using a glove box. SiCl₄ (Alfa Aesar, 99.9%), AlCl₃ (Alfa Aesar, 99.9%), and ReCl₅ (Alfa Aesar, 99.5%) were used as received. Diisopropyl ether (ⁱPr₂O) was purchased from Aldrich with 99% purity and was further dried by distillation over sodium wire. The catalysts were prepared in 2-g quantities in 80 ml autoclaves. The chloride precursors were introduced first in the autoclave, then a stoichiometric amount of ⁱPr₂O was added. More precisely, the number of moles of ⁱPr₂O is calculated, so that the number of ⁱPr groups in ⁱPr₂O is equal to the total number of Cl groups in the precursors. Finally, the solvent (10 ml of CH₂Cl₂) was introduced. The solution obtained was heated at 110 °C for 4 days under autogenous pressure (ca. 0.7 MPa). After cooling down to room temperature, the gel was washed with CH₂Cl₂ and dried at 20 °C under vacuum (10 Pa) for 1 h and then for 4 h at 120 °C. The xerogel was then crushed in a mortar and calcined in a muffle oven for 5 h at 500 °C (heating rate 10 K/min). The color of the resulting powders ranged from white to brown depending on their Al content. The Re-Al and Re-Si materials are labeled as ReX-Al and ReX-Si, respectively, where X represents the experimental Re/(Re + Si + Al) atomic ratio (in %). The Re–Si–Al materials are labeled ReX-SiAlY, where X is the Re/(Re + Si + Al) atomic ratio (in %) and Y the nominal Si/Al atomic ratio (see Table 1).

A rhenium catalyst supported on alumina with a Re/(Re + Si + Al) atomic ratio of 3% was prepared by the incipient wetness (IW) impregnation method and used as a reference catalyst; this sample is labeled IW-Re3/Al. Perrhenic acid, HReO₄ (Merck), was used as a precursor. γ -Al₂O₃ (Evonik) with a specific surface area of 240 m² g⁻¹ and a pore volume of 0.6 cm³ g⁻¹ was used as support material. After impregnation, the catalyst was dried at 150 °C for 3 h then calcined at 550 °C for 8 h.

2.2. Characterization of the catalysts

The atomic percentages of Re, Si, Al, and Cl were measured by energy dispersive X-ray spectroscopy (EDX). Measurements were carried out using an X-Max Silicon Drift Detector mounted on a FEI Quanta FEG 200 scanning electron microscope. To obtain reliable statistics in the analysis, the data for each sample were taken as the average of three separate measurements.

Powder X-ray diffraction (XRD) diffractograms of the fresh catalysts were obtained with a Philips X-Pert Pro II diffractometer using the K α radiation of Cu (λ = 1.5418 Å). The 2 θ range was recorded between 20° and 80° with rate of 0.02° s⁻¹.

 N_2 physisorption experiments were performed at 77 K on a Micromeritics Tristar sorptometer. The samples were outgassed at 150 °C under vacuum (2 Pa) overnight. The specific surface area was determined via the BET method in the 0.05–0.30 *P*/P₀ range. The pore size distribution was derived from the desorption branch using the BJH method. The average pore diameter was calculated as (4 × Pore Volume/BET specific surface area). The total micropore volume of the fresh samples was estimated using *t*-plot analysis.

X-ray photoelectron spectroscopy (XPS) was performed on a SSX 100/206 photoelectron spectrometer from Surface Science Instruments (USA) equipped with a monochromatized microfocus Al X-ray source (powered at 20 mA and 10 kV). The sample powders pressed in small stainless steel troughs of 4 mm diameter were placed on a ceramic carousel. The pressure in the analysis chamber was around 10^{-6} Pa. The angle between the surface normal and the axis of the analyzer lens was 55°. The analyzed area was approximately 1.4 mm², and the pass energy was set at

Nominal atomic ratios (N) of the (mixed) oxide samples compared to the experimental atomic ratios of the catalysts and supports before calcination (xerogels labeled X), after calcination (labeled C), and after the catalytic test (labeled P) derived from EDX. Because in some cases calcination resulted in the loss of Re, the catalysts have been named according to their actual composition after calcination and not after their initially targeted composition.

| Sample names | | Atomic ratios | | |
|--------------|---|-------------------|-------|-------------------|
| | | Re/(Re + Si + Al) | Si/Al | Cl/(Re + Si + Al) |
| Re3–Al | N | 0.024 | 0 | 0 |
| | X | 0.031 | 0 | 0.460 |
| | C | 0.029 | 0 | 0.012 |
| | P | 0.031 | 0 | 0.013 |
| Re0-Al | N | 0 | 0 | 0 |
| | X | na | na | na |
| | C | 0.00 | 0 | 0.026 |
| Re3–SiAl0.3 | N | 0.025 | 0.24 | 0 |
| | X | 0.024 | 0.30 | 0.410 |
| | C | 0.025 | 0.28 | 0.001 |
| | P | 0.028 | 0.26 | 0.003 |
| Re0-SiAl0.3 | N | 0 | 0.27 | 0 |
| | X | 0.000 | 0.23 | 0.350 |
| | C | 0.000 | 0.22 | 0.031 |
| Re1–SiAl14 | N | 0.028 | 14.3 | 0 |
| | X | na | na | na |
| | C | 0.007 | 14.2 | 0.000 |
| | P | 0.010 | 15.1 | 0.000 |
| Re0–SiAl14 | N | 0 | 13.4 | 0 |
| | X | 0.000 | 11.3 | 0.007 |
| | C | 0.000 | 13.3 | 0.000 |
| Re2–Si | N | 0.029 | NA | 0 |
| | X | 0.036 | NA | 0.025 |
| | C | 0.015 | NA | 0.001 |
| | P | 0.020 | NA | 0.002 |
| Re0-Si | N | 0 | NA | 0.0 |
| | X | na | na | na |
| | C | 0.000 | NA | 0.000 |
| IW-Re3/Al | N | 0.03 | 0 | 0 |
| | C | 0.03 | 0.000 | 0.000 |
| | P | 0.03 | 0.000 | 0.000 |

na = not analyzed, NA: not applicable.

150 eV. Under these conditions, the resolution determined by the full width at half maximum (FWHM) of the Au $4f_{7/2}$ peak was around 1.6 eV. A flood gun set at 8 eV and a Ni grid placed 3 mm above the sample surface were used for charge stabilization. The following sequence of spectra was recorded: survey spectrum, C 1s, O 1s, Si 2p, Al 2p, Re 4f, and C 1s again to check the stability of charge compensation in function of time and the absence of degradation of the sample during the analysis. The binding energies were calculated with respect to the Al 2p peak fixed at 74.5 eV (or for the sample without alumina, the binding energies were calculated with respect to the Si 2p peak fixed at 103.0 eV). Data evaluation was performed with CasaXPS (Casa Software Ltd., UK), and some spectra were decomposed with the least squares fitting routine provided by the software with a Gaussian/Lorentzian (85/15) product function after subtraction of a non-linear baseline. Molar fractions were calculated using peak areas normalized on the basis of acquisition parameters and sensitivity factors provided by the manufacturer.

ToF-SIMS measurements were performed with an IONTOF V spectrometer (IONTOF GmbH, Münster, Germany). The samples were bombarded with a pulsed Bi_3^+ ion beam (30 keV). The analyzed area used in this work was a square of $500 \times 500 \mu$ m, and the data acquisition time was 60 s. Charge effects were compensated by means of an interlaced pulsed electron flood gun ($E_k = 20 \text{ eV}$). With these parameters, the primary ion dose

The acidity was evaluated by temperature-programmed desorption of NH₃ (NH₃-TPD) on a Micromeritics AutoChem 2910 apparatus with a thermal conductivity detector. A 100 mg sample was preheated in helium at 500 °C for 60 min (ramp 10 °C min⁻¹). Adsorption of NH₃ (5 vol.% in helium; flow rate 30 ml min⁻¹) was done at 100 °C for 45 min. Physisorbed NH₃ was removed by purging with helium at 100 °C for 1 h (flow rate 30 ml min⁻¹). The TPD measurement was conducted by heating the sample from 100 to 500 °C at a 10 °C min⁻¹ rate.

2.3. Metathesis reaction

Although industrial feeds comprise both cis- and trans-2-butene, the cross-metathesis of ethene and pure trans-2-butene to propene was selected as a model reaction to allow better comparison between catalysts with different *cis-trans* isomerization activity. Indeed, trans-2-butene usually reacts faster than cis-2-butene on Re catalysts. The activity of the catalysts was measured in a multi-channel apparatus, which allows fully automated control of gas flows and of three temperature zones (gas pre-heating, reactor, and post-reactor lines with 16-port valve) along with reactor switching and product sampling [48]. All catalysts were sieved and selected within the 200–315 µm granulometric fraction. The catalysts (200 mg) were introduced in quartz straight reactors (4 mm i.d.). Prior to reaction, the catalysts were activated for 2 h at 550 °C (temperature ramp of 5 K min⁻¹) in dry N₂ (8 ml min⁻¹) flow in each reactor). Afterward, the system was cooled down to the reaction temperature (40 $^{\circ}$ C) under the same N₂ flow. The reaction was carried out at 40 °C in a butene:ethene:N₂ (45:45:10 vol.%) total flow of 8 ml min⁻¹. *trans*-2-Butene (99.00%), ethene (99.95%), and N₂ (99.999%) were further purified over Molsieve 3A (Roth) filters. N₂ was also purified by an oxygen filter (Oxysorb-glass, Linde). The composition of the reaction gas was analyzed online by an Agilent 6890 GC. The separation of hydrocarbons was performed on a HP-AL/M column (30 m length, 0.53 mm i.d., 0.15 µm film thickness) applying a temperature ramp between 95 and 140 °C and FID detection. Product analysis took about 6.5 min for each injection. N2, used as internal standard, was analyzed on a HP Plot-Q column with TCD detection. The experiments were carried out at atmospheric pressure. The specific activity is defined as the number of moles of propene produced per gram of catalyst and per hour. The apparent turnover frequency (TOF) is defined as the number of moles of propene produced per mole of Re (considering the total Re content, even if only part of the Re is actually active) and per second.

3. Results

3.1. Synthesis, composition, and structure

A series of Re–Al, Re–Si, and Re–Si–Al mixed oxides with a nominal Re/(Re + Si + Al) atomic ratio of approximately 0.03 (corresponding to ~10 wt% Re₂O₇) were prepared for this study. The corresponding silica, alumina, and silica–alumina materials (without Re) were synthesized under the same conditions to investigate the influence of rhenium on texture and acidity. These Refree oxides are referred to as "supports" in this manuscript, by analogy with more classical preparation studies, even though they were not actually used as supports here. All the samples were obtained by a non-hydrolytic sol–gel route based on the reaction of the chlorides with ⁱPr₂O at 110 °C for 4 days [49], except for IW-Re3/Al which was prepared by incipient wetness impregnation of a commercial alumina. The nominal atomic ratios (labeled N) of

the samples (based on the amounts of reactants) are given in Table 1 and compared to the experimental atomic ratios determined by EDX analysis before calcination (labeled X, for "xerogel"), after calcination (C, for "calcined"), and after catalytic testing (P, for "post-test").

In all cases, the experimental Si/Al ratio calculated from EDX data was close to the nominal values, indicating that there was no loss of Si or Al during the synthesis steps. The chlorine content of the xerogels (uncalcined samples) was rather high, particularly for the Al-rich samples. This high chlorine content has to be related to the presence of uncondensed residual Cl groups (instead of hydroxyl groups in conventional sol–gel). In addition, adsorbed solvent (CH_2CI_2) or reaction by-product (ⁱPrCl) could also participate to the chlorine content. Nevertheless, most of this chlorine was removed upon calcination, and the final chlorine contamination was quite low in the silica-rich samples (0.1%) and higher in the Al-rich samples (1.2–3%).

No loss of rhenium was observed after calcination for the two samples with high Al content, Re3–SiAl0.3 and Re3–Al. Conversely, the experimental Re/(Re + Si + Al) ratio measured after calcination for the samples with low Al contents (Re2–Si and Re1–SiAl14) was significantly lower than the nominal one, indicating a loss of about 75% of the rhenium for Re1–SiAl14 and of about 50% for Re2–Si. Analysis of the Re2–Si xerogel (before calcination) showed that the loss of rhenium occurred during the calcination step (500 °C for 5 h) and not during the synthesis, washing, or drying steps.

The catalysts were analyzed using X-ray diffraction (diffractograms available as Supplementary material, Fig. S1). Regardless of the composition of the mixed oxides, all the samples appeared amorphous, indicating the absence of crystalline rhenium oxide domains larger than about 5 nm. For the IW-Re3/Al catalyst, broad peaks were observed at $2\theta = 32^{\circ}$, 37° , 46° , 61° , and 67° characteristic of the γ -alumina support (according to the PCPDFWIN database).

3.2. Texture

The texture of the samples strongly depended on their composition: the specific surface area varied between 150 and 800 m² g⁻¹ and the pore volume between 0.3 and 1.5 cm³ g⁻¹ (Table 2). The N₂ adsorption–desorption isotherms were all of type IV (according to the BDDT classification), typical of mesoporous materials (Fig. 1) [50]. *t*-Plot analysis indicated that most of the specific surface area (>88%) was located in mesopores.

The texture of the supports strongly depended on the Si/Al ratio, with a minimum (in terms of specific surface area and pore volume) for Si/Al = 0.3. In all cases, the addition of Re led to a significant decrease in the pore volume. For the samples with high Al content (Re3–Al, Re3–SiAl0.3), the specific surface area did not depend on the Re content. On the other hand for the samples with low Al content (Re1–SiAl14 and Re2–Si), the presence of Re increased markedly the specific area as compared to the Re-free

Table 2 Textural properties of the calcined samples obtained by N_2 -physisorption at 77 K.

| Sample | $S_{\rm BET} (m^2 { m g}^{-1})$ | $V_p ({ m cm}^3{ m g}^{-1})$ | D_p (nm) | $S_{\mu} ({ m m}^2{ m g}^{-1})$ |
|-------------|----------------------------------|------------------------------|------------|---------------------------------|
| Re3–Al | 360 | 0.6 | 6 | 13 |
| Re0-Al | 360 | 1.1 | 12 | 37 |
| Re3-SiAl0.3 | 190 | 0.3 | 5 | 20 |
| Re0-SiAl0.3 | 160 | 0.7 | 17 | 18 |
| Re1-SiAl14 | 630 | 0.9 | 6 | 24 |
| Re0-SiAl14 | 290 | 1.5 | 21 | 4 |
| Re2–Si | 810 | 0.8 | 4 | 73 |
| Re0–Si | 550 | 1.5 | 11 | 63 |
| IW-Re3/Al | 230 | 0.5 | 9 | 17 |

samples. This behavior might be related to a catalytic effect of Lewis acidic Re species on the condensation reactions during the synthesis, leading to a higher degree of condensation for the Re-containing samples.

3.3. Surface analysis

The surface composition of selected xerogels and catalysts was studied by XPS in order to evidence a possible migration of rhenium toward the surface during the calcination. As calcination resulted in important Re losses in the silica-rich samples, only the alumina-rich samples for which no loss of Re occurred were analyzed (Table 3).

The high amount of carbon and chlorine found for the xerogels has to be related to the presence of OⁱPr and Cl residual groups inherent to the non-hydrolytic route used. After calcination, the surface carbon content decreased to about 12 at.%, corresponding to the usual contamination by atmospheric carbon. The surface chlorine content decreased to 1.1 at.% for the alumina–rhenium catalyst and to 0.1 at.% for the silica–alumina–rhenium catalysts.

The surface Re/(Re + Si + Al) atomic ratios found for the xerogels by XPS were lower than the bulk Re/(Re + Si + Al) atomic ratio found by EDX, suggesting that Re species are located more in the bulk of the materials. This might be caused by a higher condensation rate around the Re precursors. On the other hand, after calcination, the surface Re/(Re+Si+Al) atomic ratio increased significantly. Since the bulk composition did not change for these materials, this implies that Re species do migrate toward the surface upon thermal treatment. A similar phenomenon was previously observed for vanadium, molybdenum, and tungsten in Ti-V, Ti-V-Mo, Ti-V-W, and Si-Al-Mo mixed oxide catalysts prepared by NHSG [43,45,51]. However, the surface Re/(Re + Si + Al) atomic ratio found for the IW-Re3/Al sample prepared by impregnation remains higher than the ratio found for the calcined xerogels, suggesting that part of the Re species remains in the bulk after calcination. It has to be recalled that XPS explores a depth of up to 10 nm, with the very large proportion of the signal arising from the first few nanometers. As we are considering high surface area solids, the analysis depth is not negligible compared to the thickness of the pore walls; thus, the effect seen in Fig. 2 is presumably underestimated. ToF-SIMS, probing the outermost surface of the samples, confirms the effect (vide infra).

XPS also indicated that at the surface of the xerogels, rhenium was mainly present at the +4 oxidation state. Calcination resulted in the oxidation of these surface species to mainly the +7 and +6 oxidation states (see Fig. S2 in Supplementary material).

ToF-SIMS measurements were performed to probe the composition of the outermost surface of the catalysts (before and after calcination) and the nature of the ReO_x surface species. The total count can vary from one analysis to another, and the sensibility factor is different and unknown for each ion. Therefore, the relative intensities do not reflect the actual surface concentration of each species (for example, the Cl⁻ detected from the Re3-Al xerogel accounts for \sim 43% of the total intensity, whereas XPS indicated a much lower surface concentration). However, different catalysts can be compared on the basis of the relative intensities of ions of interest. We focused on the ions containing rhenium, on chloride, and on the organic ions (Table 4). ToF-SIMS results confirmed XPS experiments by showing that both Cl and C contamination decreased significantly after calcination and that chlorine contamination remained more important in alumina-rich samples than in silica-rich samples. The carbon contamination on NHSG-made catalysts was slightly higher than on the impregnated catalyst. The proportion of Re-containing ions in silica-rich xerogels was significantly lower than in alumina-rich xerogels.



Fig. 1. N2 adsorption-desorption isotherms at 77 K obtained for Re0-Al, Re0-SiAl0.3, Re0-SiAl14, Re0-Si, Re3-Al, Re3-SiAl0.3, Re1-SiAl14, and Re2-Si.

 Table 3

 Surface characterization by XPS on the xerogels (X) and calcined (C) alumina-rich catalysts.

| Sample | C (at.%) | O (at.%) | Cl (at.%) | Al (at.%) | Si (at.%) | Re (at.%) |
|---------------|----------|----------|-----------|-----------|-----------|-----------|
| Re3–Al X | 23.8 | 46.8 | 7.3 | 21.7 | 0 | 0.3 |
| Re3-Al C | 12.1 | 56.7 | 1.1 | 29.1 | 0 | 1.0 |
| Re3-SiAl0.3 X | 29.7 | 43.7 | 4.8 | 15.9 | 5.5 | 0.3 |
| Re3-SiAl0.3 C | 12.3 | 56.9 | 0.1 | 22.7 | 7.1 | 0.8 |
| IW-Re3/Al C | 8.4 | 59.1 | 0 | 31.1 | 0 | 1.4 |



Fig. 2. Surface Re/(Si + Al + Re) atomic ratios (XPS, gray bars) and bulk Re/ (Si + Al + Re) atomic ratios (EDX, black squares) for xerogels and calcined catalysts.

After calcination, the proportion of Re-containing ions decreased in silica-rich samples, in agreement with the loss of rhenium observed by EDX. In the case of alumina-rich samples (no loss of Re observed by EDX), the proportion of Re-containing ions in the calcined samples was significantly higher than in the xerogels. This is consistent with the migration of Re species toward the surface already evidenced by XPS. Remarkably, the proportion of Re-containing ions in the calcined Re3–Al sample (0.78) is

 Table 4

 Relative contribution of peaks of interest in the ToF-SIMS spectra. Each data point is an average on three measurements.

| | Re/(Re + Si + Al) ^a | Cl/(Re + Si + Al) ^b | Organic/(Re + Si + Al) ^c |
|---------------|--------------------------------|--------------------------------|-------------------------------------|
| Re2–Si X | 0.11 | 0.17 | 0.33 |
| Re2-Si C | 0.10 | 0.01 | 0.15 |
| Re1-SiAl14 X | 0.16 | 0.10 | 0.29 |
| Re1-SiAl14 C | 0.08 | 0.03 | 0.28 |
| Re3-SiAl0.3 X | 0.39 | 1.78 | 0.31 |
| Re3-SiAl0.3 C | 0.52 | 0.46 | 0.15 |
| Re3–Al X | 0.55 | 3.15 | 0.45 |
| Re3-Al C | 0.78 | 0.68 | 0.13 |
| IW-Re3/Al C | 0.82 | 0.02 | 0.08 |
| | | | |

^a Intensity of all Re-containing ions ($Re_xO_y^-$, $ReAIO_x^-$, $Re_xCI_y^-$) summed and divided by the sum of the intensity of all inorganic peaks ($AI_xO_y^-$, $AI_xO_yH_z^-$, $Si_xO_y^-$, Si_xO_y , H_z^- , $AISIO_4^-$, $Re_xO_7^-$, $ReAIO_7^-$, $Re_xCI_7^-$).

^b Intensity of the Cl⁻ peak divided by the sum of the intensity of all inorganic peaks.

^c Intensity of all organic ions (C⁻, $C_x H_y^-$, $C_x H_y O_z^-$) divided by the sum of the intensity of all inorganic peaks.

similar to the proportion found in the IW-Re3/Al sample (0.82), where the Re is deposited onto the surface.

It must be noted that in the alumina-rich xerogels (Re3–SiAl0.3, Re3–Al), about 40–60% of the Re-containing anions were chlorinated anions Re_xCl_y^- (Table 5). Surprisingly, no oxychloride $\text{Re}_x\text{Cl}_y\text{O}_z^-$ anions were detected. The proportion of chlorinated Re anions drops to $\approx 2-3\%$ for the silica-rich xerogels (Re1–SiAl14 and Re2–Si). In the catalysts (after calcination), the percentage of chlorinated Re anions is very low (<2%).

ToF-SIMS brings further information on the nuclearity of the Re species present at the outermost surface of the catalysts. Before calcination, di- and trinuclear Re anions are detected, particularly for the xerogels with high alumina content. After calcination, practically all of the Re anions detected in the mixed oxide catalysts contained only one Re atom, as in the sample prepared by impregnation (also calcined), suggesting a similar degree of dispersion for all the catalysts (Table 5).

3.4. Acidity

The metathesis activity of rhenium oxide supported on silicaalumina catalysts is known to be strongly influenced by the acidity

Composition of the rhenium-containing negative ions detected by ToF-SIMS on fresh xerogels (X) and calcined samples (C). All Re-containing ions detected in the negative ToF-SIMS spectra have been split in four categories whose contributions are expressed in% of the total intensities of Re-containing ions: "Mono-ReO" refers to mononuclear oxygenated Re anions (ReO_y^- , ReAI_y^-); "Poly-ReO" refers to polynuclear oxygenated Re anions ($\text{Re}_x \text{O}_y^-$, x > 1); "Mono-ReCI" refers to mononuclear chlorinated Re anions (ReC_y^-), "Poly-ReCI" refers to mononuclear chlorinated Re anions (ReC_y^-), "Poly-ReCI" refers to mononuclear chlorinated Re anions (ReC_y^-), "Poly-ReCI" refers to polynuclear chlorinated Re anions (ReC_y^-), "Poly-ReCI" refers to polynuclear chlorinated Re anions ($\text{Re}_x \text{Cl}_y^-$, x > 1).

| | | | | • |
|---------------|------------|------------|-------------|-------------|
| | "Mono-ReO" | "Poly-ReO" | "Mono-ReCl" | "Poly-ReCl" |
| Re2-Si X | 95.0 | 2.3 | 1.0 | 1.7 |
| Re1-SiAl14 X | 95.9 | 2.3 | 0.4 | 1.4 |
| Re3-SiAl0.3 X | 51.3 | 0.8 | 33.2 | 14.7 |
| Re3–Al X | 37.4 | 0.6 | 47.4 | 14.6 |
| Re2-Si C | 97.9 | 0.7 | 0.5 | 0.9 |
| Re1-SiAl14 C | 97.2 | 0.6 | 1.2 | 1.0 |
| Re3-SiAl0.3 C | 97.9 | 0.2 | 1.8 | 0.1 |
| Re3–Al C | 98.4 | 0.2 | 1.3 | 0.1 |
| IW-Re3/Al | 99.7 | 0.2 | 0.1 | 0.0 |
| | | | | |

of the support. We used temperature-programmed desorption of ammonia (NH₃-TPD) to probe the acidity of the different catalysts and of the corresponding supports. The thermograms (Fig. 3) of the different samples showed a broad desorption peak centered at about 200 °C, indicating the presence of weak acidic sites, and ammonia desorbed up to 450 °C, indicating the presence of stronger acidic sites. The desorption profiles of Re0–Si and Re2–Si samples were nearly flat, indicating very low acidity.

The amount of NH_3 molecules desorbed per gram of sample at the end of the TPD experiment (mmol $NH_3 g^{-1}$) is given in Table 6. To take into account the difference in specific surface area, the results are also expressed as the number of molecules of NH_3 desorbed per nm² of sample surface ("acid site density," $NH_3 nm^{-2}$).

When alumina is not present in the formulation (ReO–Si and Re2–Si), the samples are virtually not acidic. The acid site density was similar (~0.8 NH₃ nm⁻²) for silica–alumina and alumina supports (ReO–Al, ReO–SiAlO.3, and ReO–SiA14). According to the data in Table 6, the acid site density decreased in the following order: Re3–SiAlO.3 > Re3–Al > Re1–SiAl14 > Re2–Si. The acidity of the alumina-rich catalysts (Re3–Al and Re3–SiAl0.3) was much higher than that of the corresponding supports.

3.5. Catalytic activity

The calcined samples were tested in the cross-metathesis of butene and ethene to propene at 40 °C. The activity was dependent on the composition of the catalyst and was markedly improved when a silica–alumina was used as a "support" instead of pure alumina or silica (Fig. 4). As expected, the Re–Si catalyst was virtually inactive. The Re3–SiAl0.3 sample produced propene at a specific activity of 45 mmol g⁻¹ h⁻¹, which corresponds to a yield in propene of \approx 51%, thus lower than the maximum yield predicted by the thermodynamic equilibrium (63%). Fig. 4 also shows that deactivation was relatively slow compared to Mo-based catalysts tested under the same experimental conditions [46]. After 2 h on stream, the activity of the Re-based samples was about 90% of their initial activity. Importantly, EDX analysis of the catalysts after the catalytic test showed that no loss of rhenium occurred during the test (Table 1).

Under our experimental conditions, ethene and *trans*-2-butenes were mainly converted to propene and cis-2-butene (Fig. 5). The formation of other by-products by secondary processes (1-butene, 1-pentene, *trans*-2-pentene, *cis*-2-pentene, and hexenes) remained very low in all cases. Propene selectivity increased with conversion. It must be recalled that *cis*-2-butene, which is formed by isomerization of trans-2-butene over acid sites, can still undergo the metathesis reaction with ethene, to produce the desired propene (see Scheme in Supplementary information). As the *cis/trans* isomerization is an equilibrated reaction, cis-2-butene can also convert back to trans-2-butene. Thus, cis-2-butene is not "lost" for the reaction of interest and can to some extent be considered as a reactant, in which case the selectivity for propene is always very high (above 90%) for all the catalysts displaying significant activity. It is noteworthy that the cis/trans ratio (taken after 14 min on stream) was similar (\approx 0.44) in all cases (excepted over Re2Si which exhibited negligible conversion), suggesting that the cis/trans isomerization reaction was fast compared to the metathesis reaction.

4. Discussion

4.1. Effect of the composition on the properties of the catalysts prepared by NHSG

The non-hydrolytic sol-gel method offers a very simple route to mesoporous Re(-Si)-Al catalysts. The composition of the silicaalumina matrix can be easily adjusted, and this parameter plays an important role on the loss of Re during calcination, as well as on the texture, the acidity and the activity of the catalysts. Most Re-based metathesis catalysts reported in the literature are supported catalysts prepared by impregnation of alumina or silica-alumina supports [13,18,19]. In this work, we prepared by



Fig. 3. NH₃-TPD thermograms of the "supports" (left) and the catalysts (right), normalized to sample weight.

Amount of NH_3 desorbed, determined by TPD in the 100–500 °C temperature range for the rhenium catalysts and the "supports."

| Sample | $\rm NH_3$ desorbed (mmol $\rm NH_3~g^{-1}$) | Acid site density ($NH_3 nm^{-2}$) |
|-------------|---|--------------------------------------|
| Re3–Al | 1.1 | 1.8 |
| Re0-Al | 0.4 | 0.7 |
| Re3-SiAl0.3 | 1.5 | 4.8 |
| Re0-SiAl0.3 | 0.2 | 0.8 |
| Re1-SiAl14 | 0.3 | 0.3 |
| Re0-SiAl14 | 0.4 | 0.8 |
| Re2–Si | 0.02 | 0.01 |
| Re0-Si | 0.02 | 0.02 |
| IW-Re3/Al | 0.2 | 0.5 |



Fig. 4. Specific metathesis activity versus time on stream. The effect of the support and the Re contents can be visualized within the series: Re3–Al, Re3–SiAl0.3, Re1– SiAl14, Re2–Si compared to the best molybdenum catalyst reported Mo13–SiAl14 [45] and to IW-Re3/Al.

incipient wetness impregnation of a γ -alumina support a Re/Al catalyst (IW-Re3/Al) that was used as a "reference" for comparing to the samples prepared by NHSG.

The acidity of the mixed oxide samples strongly depends on their composition. While the silica and the Re–Si mixed oxide samples are virtually not acidic, silica–alumina and alumina-based samples exhibited a significant acidity. As classically observed with Re-based catalysts, we were confronted to the loss of rhenium during the calcination of the catalysts. Rhenium volatilization is, however, suppressed in the alumina-rich samples. This is consistent with previous observations made for impregnated catalysts [18]. Losses of Re have been ascribed to the sublimation of rhenium heptoxide, which can be significant when the interactions between ReO_x species and the support are poor, as in the case of silica which is not acidic. Conversely, when rhenium species interact strongly with more acidic supports such as alumina or silica–alumina, the loss of rhenium during calcination is much lower.

According to XRD, all the samples are amorphous, suggesting a good dispersion of Re species. One important drawback of catalysts prepared by one-step sol-gel synthesis is that a large part of the active phase is located in the pore walls and thus not accessible to the reactants. This is also true in the case of the xerogels in which the Re species are most probably dispersed in the bulk of the material. However, as anticipated from the particularly low Tammann temperature of rhenium oxide, migration of Re species toward the surface occurs during the calcination step. Both XPS and ToF-SIMS data show that the Re surface concentration increases after calcination for the samples that do not lose rhenium



Fig. 5. Selectivity for propene (\blacklozenge), *cis*-2-butene (\blacktriangle), and by-products (\blacksquare) which includes traces of 1-butene, isobutene, butadiene, pentenes, and hexenes. The full symbols correspond to NHSG samples, empty symbols correspond to the IW-Re3Al sample (the empty red triangle is almost superposed with the full red triangle). Data taken at 14 min time on stream.

during calcination. Furthermore, ToF-SIMS results suggest that this migration can be very effective since the relative contribution of Re ions from Re3–Al and IW-Re3/Al is similar. After calcination, practically, only monomeric rhenium oxide ions are detected from the surface of the NHSG catalysts, as in the case of the catalyst prepared by incipient wetness impregnation. Calcination also results in the "cleaning" of the catalyst surface, as Cl and carbon contaminations are drastically reduced.

The highest specific surface areas are obtained for the Re–Si sample and the Re–Si–Al sample with high silica content. Addition of alumina in the composition of the mixed oxides significantly decreases the specific surface area (see Table 2). The specific activity (Table 7), however, does not follow the same trend, as the Re–Si sample with the highest specific surface area is practically inactive, while Re3–SiAl0.3, the sample with the lowest specific surface area, clearly outperforms all other Re-based catalysts, including the catalyst IW-Re3/Al prepared by impregnation.

To take into account the active phase loading, Table 7 gives the apparent turnover frequency (TOF). One should keep in mind that (i) only a very small fraction (typically around 1% [52]) of the active element in metathesis catalysts actually leads to active sites, and (ii) this fraction probably varies from one formulation to another. Additionally, part of the Re may remain in the bulk of the mixed oxide. To also take into account the effect of the texture, the apparent TOF values were divided by the specific surface area ("areal TOF" in Table 7).

In terms of apparent TOF, the most active catalysts are again the Re–Si–Al samples. The very high TOF value observed for Re1–SiAl14 is difficult to interpret in comparison with Re3–SiAl0.3 because several parameters vary at the same time. The Si/Al ratio is higher, the loss of rhenium during calcination leads to a low Re loading, and the Re surface concentration determined by XPS (0.24 at.%) is also significantly lower than the values found for the other calcined catalysts (Table 3). At the same time, ToF-SIMS experiments indicate the presence of similar Re surface species in Re1–SiAl14 and Re3–SiAl0.3. Thus, the high TOF value found for the Re3–SiAl0.3 is likely related to its particularly high specific surface area, as suggested by the "areal TOF" values reported in Table 7.

Both the specific activities and the areal TOF values vary in the following order: Re3–SiAl0.3 > Re1–SiAl14 > Re3–Al \gg Re2–Si. This

Comparison of the activity of the rhenium- and the molybdenum-based metathesis catalysts. Activity expressed as specific activity (in mmol of metathesis products per gram of catalyst and per hour), apparent turnover frequency TOF (in mol of reactants converted per mole of active metal and per second), and as areal TOF (mol of reactants converted per mole of active metal and per second), and as areal TOF (mol of reactants converted per mole of active metal and per second).

| Sample | M/(M + Si + Al) (%) | $SSA~(m^2~g^{-1})$ | Specific activity (mmol $g^{-1} h^{-1}$) | TOF (10^{-3} s^{-1}) | Areal TOF $(10^{-6} s^{-1} m^{-2})$ |
|-----------------------------|---------------------|--------------------|---|--------------------------------|---------------------------------------|
| Re2–Si | 2 | 810 | 0.2 | 0.5 | 0.6 |
| Re3–Al | 3 | 360 | 11.3 | 14.6 | 40.6 |
| Re3-SiAl0.3 | 3 | 190 | 45.2 | 57.4 | 302 |
| Re1-SiAl14 | 0.7 | 630 | 20.7 | 98.5 | 156 |
| IW-Re3/Al | 3 | 230 | 24 | 32.3 | 140 |
| Mo13-SiAl14 ^a | 13 | 490 | 44.5 | 9.1 | 1.9 |
| AER-Mo7/SiAl13 ^b | 7 | 480 | 32 | 12.8 ^d | 26.7 ^d |
| FSP-Mo1/SiAl1 ^c | 1 | 167 | 17.8 | 71.3 | 430 ^d |

^a Reported in [45]. The catalyst (10 wt% MoO₃, 5.7 wt% Al₂O₃, 84 wt% SiO₂) was re-tested here in the metathesis of ethene and 2-butene, under the same conditions as the Re-based catalysts.

^b Reported in [52]. The catalyst (10 wt% MoO₃, 5.7 wt% Al₂O₃, 84 wt% SiO₂, 0.4 wt%) was prepared by a one-pot aerosol synthesis and tested under identical conditions.

^c Reported in [8]. The catalyst (1 wt% MoO₃, 69 wt% Al₂O₃, 30 wt% SiO₂) was prepared by a one-pot flame spray pyrolysis and tested in the propene metathesis at 40 °C.

^d Calculated from the published data.

points out to a clear effect of the composition of the matrix on the metathesis activity. A similar support effect was already reported for supported rhenium- or molybdenum-based metathesis catalysts [14-17]. This support effect is most likely related to the presence of acidic sites, which are considered to play a major role in the generation of active species for the metathesis reaction [13]. Based on studies on impregnated catalysts, it was put forward that the activity of the Re active centers was determined by their interactions with the support. ReO_x species deposited on an acidic support such as silica-alumina are themselves more acidic (or electron deficient), which is beneficial for their activation upon contact with the olefin. It is noteworthy that the sample with the highest specific activity (Re3-SiAl0.3) is also the sample with the highest amount of acidic sites according to NH₃-TPD. The nature (Lewis or Brönsted) and the strength of the acidic sites are most likely important parameters which deserve further study.

The specific activity and apparent TOF values of the Re3–SiAl0.3 catalyst are significantly higher than that of the catalyst IW-Re3/Al prepared by impregnation, showing the importance of the composition of the matrix. On the other hand, the activity of the Re3–Al sample is lower than that of IW-Re3/Al. This could be due in part to a lower surface concentration of ReO_x species as suggested by XPS and also to the fact that Re–3Al is amorphous, whereas the support used for the impregnation is a crystalline γ -alumina support.

4.2. Comparison of Si–Al–Re and Si–Al–Mo metathesis catalysts prepared by different methods

In Table 7, we compare the metathesis activity of the rheniumbased catalysts prepared by NHSG and incipient wetness impregnation to that of molybdenum-based catalysts synthesized by different methods. All of these catalysts were tested under exactly the same conditions in the cross-metathesis of butene and ethene or in the self-metathesis of propene. The Mo–Si–Al catalyst prepared by NHSG (Mo13–SiAl14) [46] was initially tested in the self-metathesis of propene but was re-tested here in the cross-metathesis of ethene and 2-butene, leading to a similar activity. The Mo–Si–Al catalyst prepared via a one-pot aerosol route (AER-Mo7/SiAl13) was tested under the same conditions [53], while the catalyst obtained by flame spray pyrolysis (FSP-Mo1/SiAl1) was tested under the same conditions but in the metathesis of propene [8].

The molar content of the active phase used in rhenium catalysts is much lower than in molybdenum catalysts. This is important, given the price of rhenium starting materials. Nevertheless, the specific activity of our most active catalyst, Re3–SiAl0.3, is as high as that of the Mo-based catalyst prepared by NHSG, Mo13–SiAl114 [46,53], which itself outclassed in terms of specific activity other Mo-based metathesis catalysts, including the ones prepared by the aerosol route [53] and flame spray pyrolysis [8]. The latter method was shown to yield highly active catalysts, but only at very low loadings, resulting in relatively low specific activities.

5. Conclusions

This study presents a simple, one-step NHSG method to prepare highly active Re–Si–Al metathesis catalysts with well-controlled Si/Al ratios and good textures, starting from commercially available chloride precursors.

The loss of rhenium during calcination could be avoided by playing on the Al content: no loss of rhenium occurred in alumina-rich formulations. Moreover, no loss of rhenium occurred during catalytic tests. During the calcination, Re species migrate toward the surface, leading to highly dispersed Re surface species, comparable to the species found at the surface of a calcined Re/Al catalyst prepared by impregnation.

The activity of these NHSG catalysts in the cross-metathesis of ethene and *trans*-2-butene directly depends on their composition. The Re–Si–Al catalysts are significantly more active than the Re–Al catalyst, while the Re–Si catalyst was inactive. The most active NHSG catalyst (Re3–SiAl0.3) showed a very high specific activity, as high as that of the best Mo–Si–Al catalyst reported and significantly higher than a reference Re/Al catalyst with a similar Re content prepared by impregnation. A large number of acidic sites, a high surface area, and well-dispersed ReO_x species appear to be the key parameters to reach a high activity.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2013.02.016.

References

- [1] J.C. Mol, J. Mol. Catal. A: Chem. 213 (2004) 39-45.
- [2] J.C. Mol, Green Chem. 4 (2002) 5-13.
- [3] B.B. Marvey, Int. J. Mol. Sci. 10 (2009) 213-220.
- [4] K.J. Ivin, I.C. Mol (Eds.), Olefin Metathesis and Metathesis Polymerization, second ed., 1996.
- [5] J. Aguado, J.M. Escola, M.C. Castro, B. Paredes, Appl. Catal., A 284 (2005) 47-57. [6] D.P. Debecker, M. Stoyanova, U. Rodemerck, A. Leonard, B.-L. Su, E.M.
- Gaigneaux, Catal. Today 169 (2011) 60–68. [7] D.P. Debecker, M. Stoyanova, U. Rodemerck, E.M. Gaigneaux, J. Mol. Catal. A: Chem. 340 (2011) 65-76.
- [8] D.P. Debecker, B. Schimmoeller, M. Stoyanova, C. Poleunis, P. Bertrand, U. Rodemerck, E.M. Gaigneaux, I. Catal. 277 (2011) 154–163.
- [9] H. Liu, S. Huang, L. Zhang, S. Liu, W. Xin, L. Xu, Catal. Commun. 10 (2009) 544-548
- [10] J.C. Mol, J.A. Moulijn, Adv. Catal. 24 (1975) 131-171.
- C. Coperet, New J. Chem. 28 (2004) 1–10.
- [12] H. Balcar, R. Hamtil, N. Zilkova, Z. Zhang, T.J. Pinnavaia, J. Cejka, Appl. Catal., A 320 (2007) 56-63.
- [13] J.C. Mol, Catal. Today 51 (1999) 289-299.
- [14] D.P. Debecker, D. Hauwaert, M. Stoyanova, A. Barkschat, U. Rodemerck, E.M. Gaigneaux, Appl. Catal., A 391 (2011) 78-85.
- [15] A. Andreini, X. Xu, J.C. Mol, Appl. Catal. 27 (1986) 31-40.
- [16] C.J. Lin, A.W. Aldag, A. Clark, J. Catal. 45 (1976) 287-296.
- [17] J.C. Mol, A. Andreini, J. Mol. Catal. 46 (1988) 151–156.
- [18] B. Mitra, X. Gao, I.E. Wachs, A.M. Hirt, G. Deo, Phys. Chem. Chem. Phys. 3 (2001) 1144-1152.
- [19] M. Stoyanova, U. Rodemerck, U. Bentrup, U. Dingerdissen, D. Linke, R.W. Mayer, H.G.J. Lansink Rotgerink, T. Tacke, Appl. Catal., A 340 (2008) 242-249.
- [20] H. Balcar, R. Hamtil, N. Zilkova, J. Cejka, Catal. Lett. 97 (2004) 25-29. [21] X. Secordel, A. Yoboue, S. Cristol, C. Lancelot, M. Capron, J.-F. Paul, E. Berrier, J.
- Solid State Chem. 184 (2011) 2806-2811. C.-B. Wang, Y. Cai, I.E. Wachs, Langmuir 15 (1999) 1223-1235.
- [23] P.C. Bakala, E. Briot, Y. Millot, J.-Y. Piquemal, J.-M. Bregeault, J. Catal. 258 (2008) 61 - 70
- [24] H.S. Lacheen, P.J. Cordeiro, E. Iglesia, Chem. Eur. J. 13 (2007) 3048-3057.
- [25] R. Spronk, I.C. Mol. Stud. Surf. Sci. Catal. 75 (1993) 2071-2074.
- [26] R.H. Blom, C.H. Kline, Hydrocarbon Process. Pet. Refin. 42 (1963) 132-134.
- [27] M.A. Banares, L.J. Alemany, M. Lopez Granados, M. Faraldos, J.L.G. Fierro, Catal. Today 33 (1997) 73-83.
- [28] M.A. Vuurman, D.J. Stufkens, A. Oskam, J. Mol. Catal. 76 (1992) 263-285.

- [29] R. Spronk, J.A.R. van Veen, J.C. Mol, J. Catal. 144 (1993) 472-483.
- [30] F.D. Hardcastle, I.E. Wachs, J.A. Horsley, G.H. Via, J. Mol. Catal. 46 (1988) 15-36. [31] M. Valigi, D. Cordischi, D. Gazzoli, C.P. Keijzers, A.A.K. Klaassen, J. Chem. Soc.,
- Faraday Trans. 1 (77) (1981) 1871-1882.
- [32] F. Schekler-Nahama, O. Clause, D. Commereuc, J. Saussey, Appl. Catal., A 167 (1998) 237-245.
- [33] M. Fabris, C. Aquino, A.J. Ward, A. Perosa, T. Maschmeyer, M. Selva, Top. Catal. 52 (2009) 315-321.
- [34] A. Yoboue, A. Susset, A. Tougerti, D. Gallego, S.V. Ramani, M. Kalyanikar, D.S. Gauvin, J.-F. Paul, E. Berrier, Chem. Commun. 47 (2011) 4285–4287.
- P.H. Mutin, A. Vioux, Chem. Mater. 21 (2009) 582-596. [35]
- [36] D.P. Debecker, P.H. Mutin, Chem. Soc. Rev. 41 (2012) 3624-3650.
- V. Lafond, P.H. Mutin, A. Vioux, Chem. Mater. 16 (2004) 5380-5386.
- [38] D.P. Debecker, V. Hulea, P.H. Mutin, Appl. Catal., A 451 (2013) 192–206.
- [39] F. Barbieri, D. Cauzzi, F. De Smet, M. Devillers, P. Moggi, G. Predieri, P. Ruiz, Catal. Today 61 (2000) 353-360.
- [40] A.M. Cojocariu, P.H. Mutin, E. Dumitriu, F. Fajula, A. Vioux, V. Hulea, Chem. Commun. (2008) 5357-5359.
- [41] H. Kaper, K. Bouchmella, P.H. Mutin, F. Goettmann, ChemCatChem 4 (2012) 1813-1818
- [42] A.F. Popa, P.H. Mutin, A. Vioux, G. Delahay, B. Cog, Chem. Commun. (2004) 2214-2215
- [43] D.P. Debecker, K. Bouchmella, R. Delaigle, P. Eloy, C. Poleunis, P. Bertrand, E.M. Gaigneaux, P.H. Mutin, Appl. Catal., B 94 (2010) 38-45.
- C. Petitto, H.P. Mutin, G. Delahay, Chem. Commun. 47 (2011) 10728-10730. [44]
- [45] D.P. Debecker, K. Bouchmella, C. Poleunis, P. Eloy, P. Bertrand, E.M. Gaigneaux, P.H. Mutin, Chem. Mater. 21 (2009) 2817–2824.
- D.P. Debecker, K. Bouchmella, M. Stoyanova, U. Rodemerck, E.M. Gaigneaux, [46] P.H. Mutin, Catal. Sci. Technol. 2 (2012) 1157–1164.
- [47] A. Vioux, Chem. Mater. 9 (1997) 2292-2299.
- [48] M. Sibeijn, J.C. Mol, Appl. Catal. 67 (1991) 279-295.
- [49] W. Gerrard, A.H. Woodhead, J. Chem. Soc. (1951) 519–522.
 [50] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, Pure Appl. Chem. 57 (1985) 603–619.
- [51] D.P. Debecker, R. Delaigle, K. Bouchmella, P. Eloy, E.M. Gaigneaux, P.H. Mutin, Catal. Today 157 (2010) 125-130.
- [52] K. Amakawa, S. Wrabetz, J. Kroehnert, G. Tzolova-Mueller, R. Schloegl, A. Trunschke, J. Am. Chem. Soc. 134 (2012) 11462-11473.
- [53] D.P. Debecker, M. Stoyanova, F. Colbeau-Justin, U. Rodemerck, C. Boissiere, E.M. Gaigneaux, C. Sanchez, Angew. Chem., Int. Ed. 51 (2012) 2129–2131.