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

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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, N_2-physisorption, XPS, ToF-SIMS, and NH_3-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}).

1. Introduction

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 Re_2O_7 [12,13] supported on different oxide (TiO_2, Al_2O_3, SiO_2) or mixed oxide (SiO_2–Al_2O_3) supports. The activity of heterogeneous catalysts in olefin metathesis is influenced by the nature of the support [14]: for example, Re_2O_7/SiO_2–Al_2O_3 catalysts are known to be more active than Re_2O_7/Al_2O_3 [15], while Re_2O_7/SiO_2 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–$OReO_3$–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

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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 $HReO_4$ and $Al(O^iPr)_3$ 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 $(NH_4)ReO_4$ and $Si(OEt)_4$, but this sample showed a low activity in octene self-metathesis [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 $HReO_4$ 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)).

$$\text{M-Cl} + \text{ROR} \rightarrow \text{M-OR} + \text{RCl} \tag{1}$$

$$\text{M-Cl} + \text{M-OR} \rightarrow \text{M—O—M} + \text{RCl} \tag{2}$$

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. $SiCl_4$ (Alfa Aesar, 99.9%), $AlCl_3$ (Alfa Aesar, 99.9%), and $ReCl_5$ (Alfa Aesar, 99.5%) were used as received. Diisopropyl ether ($^iPr_2O$) 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 $^iPr_2O$ was added. More precisely, the number of moles of $^iPr_2O$ is calculated, so that the number of ^iPr groups in $^iPr_2O$ is equal to the total number of Cl groups in the precursors. Finally, the solvent (10 ml of CH_2Cl_2) 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 CH_2Cl_2 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, $HReO_4$ (Merck), was used as a precursor. γ-Al_2O_3 (Evonik) with a specific surface area of 240 $m^2\,g^{-1}$ and a pore volume of 0.6 $cm^3\,g^{-1}$ 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 Kα radiation of Cu (λ = 1.5418 Å). The 2θ 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/P_0 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 mm^2, and the pass energy was set at