



Short Communication

Avoiding rhenium loss in non-hydrolytic synthesis of highly active Re–Si–Al olefin metathesis catalysts



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ABSTRACT

Rhenium oxide-based catalysts are highly active olefin metathesis catalysts. However, sublimation of rhenium heptoxide during the calcination step can lead to the loss of rhenium. We show that rhenium losses in Re–Si–Al mixed oxide catalysts synthesized by non-hydrolytic sol–gel can be avoided providing that strictly anhydrous conditions are kept in all the preparation steps and during storage. Re–Si–Al mixed oxides with various Re₂O₇ loadings and SiO₂/Al₂O₃ ratios were prepared, without any loss of rhenium. Catalysts were amorphous, exhibited good mesoporous textures and acidity and performed outstandingly in the metathesis of ethene and *trans*-2-butene to propene.

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1. Introduction

Olefin metathesis is an important reaction for several sectors of the chemical industry (organic synthesis, polymerization chemistry, petro-chemistry) [1]. For the metathesis of gaseous light alkenes, the most successful catalysts are those based on W, Re and Mo oxides [2–4]. Even though Re is expensive, rhenium-based catalysts are attractive because they are highly active and selective at low temperature [1, 5]. Re₂O₇/Al₂O₃ was even used industrially for the production of propene from ethene and 2-butene in the liquid phase at 35 °C and 60 bar (meta-4 process) [1].

Rhenium-based metathesis catalysts are generally prepared by incipient wetness impregnation of an oxide support, such as TiO₂, Al₂O₃, or SiO₂–Al₂O₃ [6–9]. Their activity depends on the nature of the support: thus, ReO_x/SiO₂–Al₂O₃ catalysts are known to be more active than Re₂O₇/Al₂O₃ [10], while ReO_x/SiO₂ catalysts are virtually inactive [11, 12]. A specific problem encountered with rhenium-based catalysts is linked to the volatility of rhenium [13], which, conjugated with the high price of rhenium has hindered industrial application of these catalysts [4]. Rhenium loss is often observed during the calcination and/or

regeneration steps, and has been ascribed to the volatility of rhenium heptoxide, which sublimates at 523 K [14,15]. Several authors have reported rhenium loss during the catalyst preparation, independent of the support and the preparation method (wet impregnation, incipient wetness and thermal spreading) [14,16–20]. According to the literature, the loss of rhenium is favored in the presence of water [16,21–23], at high Re loadings [17] and at high temperatures [19,22].

There are very few examples of rhenium-based metathesis catalysts obtained by a sol–gel method [24,25]. Non-hydrolytic sol–gel (NHSG) [26,27] is emerging as a powerful method to prepare tailored heterogeneous catalysts [28] and especially mesoporous mixed oxides [29]. Recently we have reported the NHSG synthesis of highly active Re–Si–Al metathesis catalysts [30], by reaction at 110 °C of ReCl₅, SiCl₄, AlCl₃ with a stoichiometric amount of ¹Pr₂O, followed by drying and calcination in ambient air. As anticipated from the particularly low Tammann temperature of rhenium oxide, migration of Re species during the calcination led to highly dispersed Re surface species. However, rhenium losses occurred during calcination of the samples with a low Al content, which nevertheless exhibited very interesting textures. No loss of rhenium during calcination was observed for the samples with a high Al content, but these materials showed only moderate specific surface areas.

Recently, we observed that the texture of Re–Si–Al oxide catalysts made by NHSG changed after exposure to moisture. This observation and the literature on the loss of rhenium, prompted us to re-investigate the NHSG synthesis of Re–Si–Al catalysts. In the present work, Re–Si–Al mixed oxides with Re₂O₇ loadings of 2, 10 or 20 wt.% and SiO₂/Al₂O₃ ratios of 17 or 0.3 (Table 1) were prepared by non-

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Table 1
Composition of the samples.

Sample	Experimental composition ^a (nominal)				
	Re/(Re + Si + Al) %	Re ₂ O ₇ (wt.%)	SiO ₂ (wt.%)	Al ₂ O ₃ (wt.%)	SiO ₂ /Al ₂ O ₃
Re2SA17	0.5 (0.5)	2.1 (2.0)	92.2 (92.1)	5.6 (5.9)	16.4 (15.6)
Re10SA17	2.9 (2.9)	10.8 (10.8)	84.7 (84.3)	4.5 (4.9)	18.8 (17.2)
Re20SA17	5.3 (5.6)	18.7 (19.6)	76.7 (75.6)	4.6 (4.8)	16.8 (15.7)
Re2SA0.3	0.5 (0.4)	2.1 (1.9)	20.0 (23.4)	78.0 (74.7)	0.26 (0.31)
Re10SA0.3	2.3 (2.4)	9.7 (10.0)	20.2 (21.1)	70.1 (68.9)	0.29 (0.31)
Re20SA0.3	5.4 (5.5)	20.8 (20.1)	18.3 (17.4)	60.9 (62.5)	0.30 (0.28)

^a Determined from ICP-AES results. Nominal compositions (under brackets) are calculated on the basis of the amount of each precursor introduced in each preparation.

hydrolytic sol-gel; anhydrous conditions were maintained in all the preparation steps (synthesis, washing, drying and calcination) and during the storage of the materials.

2. Experimental section

2.1. Preparation of the catalysts

In order to avoid water, all the manipulations were done under a dry argon atmosphere using classical glovebox and Schlenk techniques, the reaction was performed in glass tubes sealed under vacuum, the calcination was performed under a dry air atmosphere, and the catalysts were stored in a glovebox under dry argon prior to use. The catalysts were prepared by reaction of the chloride precursors with a stoichiometric amount of diisopropyl ether (¹Pr₂O): the number of moles of ¹Pr₂O was calculated so that the number of ¹Pr groups in ¹Pr₂O was equal to the total number of Cl groups in the precursors. SiCl₄ (99.9%), AlCl₃ (99.9%), and ReCl₅ (99.5%) were purchased from Alfa Aesar and used as received. ¹Pr₂O (Aldrich, 99%) was dried by distillation over sodium wire. CH₂Cl₂ was dried by distillation over CaCl₂. The catalysts were prepared in 1.5 g quantities in 80 mL sealed glass tubes. The chloride precursors were introduced first, then ¹Pr₂O and finally CH₂Cl₂ (10 mL). The tube was sealed and heated at 110 °C for 4 days under autogenous pressure (ca. 0.7 MPa). After cooling down to room temperature, the tube was opened in a glovebox, washed under a dry argon atmosphere with CH₂Cl₂, dried at 20 °C under vacuum (10 Pa) for 1 h and then for 4 h at 120 °C. The resulting xerogel was crushed in a mortar in a glovebox and calcined in a tube furnace under dry air (50 mL min⁻¹) for 5 h at 500 °C (heating rate 10 °C min⁻¹), leading to a white powder.

The samples are labeled RexSAy, where x represents the Re₂O₇ loading in wt.% (x = 2, 10 and 20) and y is the Si/Al molar ratio (y = 17 and 0.3) (Table 1).

2.2. Characterization of the catalysts

The elemental analysis (Re, Si and Al) of the samples was carried out at the Service Central de Microanalyse of the Centre National de la Recherche Scientifique (CNRS) in Vernaison (France), using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The atomic percentages of Re, Si, Al and Cl were obtained by energy dispersive X-ray spectroscopy (EDX), using an X-Max Silicon Drift Detector mounted on a FEI Quanta FEG 200 scanning electron microscope. The values given for each sample correspond to the average of three measurements. Powder X-ray diffraction (XRD) diffractograms were obtained with a Philips X-Pert Pro II diffractometer using the K α radiation of Cu ($\lambda = 1.5418 \text{ \AA}$). The 2 θ range was recorded between 10° and 80° with rate of 0.02° s⁻¹. N₂ 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 is calculated as (4 × Pore Volume / BET specific surface area). The

total micropore volume of the fresh samples was estimated using t-plot analysis. The acidity was evaluated by temperature programmed desorption of ammonia (NH₃-TPD) on a Micromeritics AutoChem 2910 apparatus with a thermal conductivity detector. Samples (100 mg) were loaded in the glove box and then pretreated 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. Catalytic test

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 activities. 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 equipped with 16-port valve) along with reactor switching and product sampling [31]. All catalysts were sieved in the 200–315 μm granulometric fraction. The catalysts (100 mg) were introduced in straight quartz 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). Afterwards the system was cooled down to the reaction temperature (40 °C) under the same N₂ flow. The reaction was carried out at 40 °C in a *trans*-2-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%) (Linde) were further purified over Molsieve 3A (Roth) filled columns. N₂ was additionally purified by an oxygen filter (Oxysorb-glass, Linde). The composition of the reaction gas was analyzed online by an Agilent 6890 gas chromatograph. 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), using a temperature ramp between 95 and 140 °C and FID detection. Each analysis took about 6.5 min. N₂, used as an internal standard, was analyzed on a HP Plot-Q column with TCD detection. The experiments were carried out using a slight overpressure to prevent contamination. The specific activity was 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 in the reaction) and per second.

3. Results and discussion

3.1. Synthesis and characterization of the materials

Elemental analysis by ICP-AES showed that the experimental composition of the catalysts was very close to the nominal one (Table 1), independent of the SiO₂/Al₂O₃ ratio or the Re₂O₇ loading.

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