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Catalysis Communications



journal homepage: www.elsevier.com/locate/catcom

Short Communication

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



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ARTICLE INFO

Article history: Received 4 August 2014 Received in revised form 10 September 2014 Accepted 12 September 2014 Available online 22 September 2014

Keywords: Alkene metathesis Rhenium Mesoporous mixed oxides Non-aqueous sol-gel Silica-alumina

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

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regeneration steps, and has been ascribed to the volatility of rhenium heptoxide, which sublimes 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 ⁱPr₂O, 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 reinvestigate the NHSG synthesis of Re–Si–Al catalysts. In the present work, Re–Si–Al mixed oxides with Re_2O_7 loadings of 2, 10 or 20 wt.% and SiO_2/Al_2O_3 ratios of 17 or 0.3 (Table 1) were prepared by non-

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Com	position	of the	samples.

Sample	Experimental composition ^a	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 (ⁱPr₂O): the number of moles of ⁱPr₂O was calculated so that the number of ⁱPr groups in ⁱPr₂O 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 ⁱPr₂O 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 Re_2O_7 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 ($\lambda = 1.5418$ Å). The 2 θ range was recorded between 10° and 80° with rate of $0.02^{\circ} \text{ s}^{-1}$. 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 BIH method. The average pore diameter is calculated as $(4 \times \text{Pore Volume} / \text{BET specific surface area})$. 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 16port 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 (Oxysorbglass, 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 SiO_2/Al_2O_3 ratio or the Re_2O_7 loading.



Fig. 1. N₂-physisorption isotherms of the catalysts with (a) Si/Al \approx 17 and (b) Si/Al \approx 0.3.

In particular the Re_2O_7 content was identical (within the uncertainty of elemental analysis) to the targeted one, which means that no Re was lost during the calcination step, even for the alumina-poor formulations $(SiO_2/Al_2O_3 \sim 17)$ or at high Re loadings. This finding confirms the importance of avoiding the hydration of Re surface species in order to avoid Re volatilization. The extreme volatility of hydrated Re surface species has previously been noted for Re/SiO₂ catalysts [16,21].

As shown in Fig. 1, the nitrogen physisorption isotherms of the samples were typical of mesoporous solids. All of the samples exhibited high specific surface areas (from 420 to 730 m² g⁻¹) and pore volumes (from 0.5 to 1.8 cm³ g⁻¹), along with negligible microporosity (Table 2).

Table 2 shows that both V_p and D_p decreased when the Re loading increased. The highest specific surface areas were obtained for the Re10SA17 and Re20SA17 samples with low alumina content. The Re10SA0.3 and Re20SA0.3 samples with a high alumina content showed somewhat lower specific surface areas. Remarkably, the V_p and D_p values found for Re10SA0.3 are two to three times higher than those reported previously for a catalyst with a similar composition which was washed and calcined under ambient conditions (the catalyst was labeled "Re3SiAl0.3" in our previous paper but it corresponds to Re10SA0.3 in the present labeling system) [30].

Regardless of their composition, all the materials appeared amorphous to X-ray diffraction (diffractograms available as supplementary material, Figure S1), indicating the absence of crystalline rhenium oxide domains larger than about 5 nm.

The metathesis activity of rhenium oxide supported on silica–alumina catalysts is known to be strongly influenced by the acidity of the catalysts. Temperature programmed desorption of ammonia (NH₃-TPD) (thermograms available as supplementary material, Figure S2) showed a broad desorption peak centered at about 200 °C, indicating the

Table 2 Textural properties of the samples: specific surface area (S_{BET}), total pore volume (V_P) and average pore diameter (D_P).

Sample	$S_{BET} (m^2 g^{-1})$	$V_{p} (m^{3}g^{-1})$	$D_{p}(nm)$
Re2SA17	480	1.8	15
Re10SA17	730	1.0	5
Re20SA17	630	0.9	6
Re2SA0.3	540	1.6	12
Re10SA0.3	530	1.0	8
Re20SA0.3	420	0.5	4

presence of weak acidic sites. The thermograms of the materials containing 10 and 20 wt.% of Re_2O_7 showed a NH₃ desorption peak above 450 °C, indicating the presence of stronger acidic sites for these samples, particularly for the alumina-poor materials.

The amount of NH₃ molecules desorbed per gram of sample at the end of the TPD experiment is given in Table 3, together with the acid site density, which takes into account the specific surface area of the materials. The amount of desorbed NH₃ roughly increased with the Re loading, as reported previously by Räty and Pakkanen for Re catalysts supported on γ -Al₂O₃ [32]. The Re20SA0.3 sample, with a high Re loading and a high alumina content was the most acidic sample, in terms of the amount of NH₃ desorbed and the density of acid sites.

3.2. Catalytic activity

The calcined samples were tested in the cross-metathesis of ethene and *trans*-2-butene to propene at 40 $^{\circ}$ C (Fig. 2). The by-products detected were 1-butene, 1-pentene, *trans*-2-pentene, *cis*-2-pentene and hexenes. Fig. 2 shows that the deactivation was relatively slow. EDX analysis of the spent catalysts showed that whatever the composition no loss of rhenium occurred during activation and reaction (compositions available as supplementary material, Table S1).

As shown in Fig. 2, the specific activity was highly dependent on the composition of the materials. The activity of the alumina-rich samples increased with the Re_2O_7 loading, whereas the activity of alumina-poor samples reached a maximum for the sample with 10 wt.% Re_2O_7 loading. For a given Re_2O_7 loading, the specific activity of the Al-rich samples is significantly higher than that of the Al-poor samples, the most active samples being Re20SA0.3 and Re10SA0.3 (Table 4).

Table 3	
Acidity measured by NH_3 -TPD (100–500 °C).

Sample	Acidity		
	$\rm NH_3$ desorbed (mmol g ⁻¹)	Density of acid sites (nm^{-2})	
Re2SA17	0.5	0.6	
Re10SA17	2.2	1.8	
Re20SA17	2.5	2.4	
Re2SA0.3	2.5	2.8	
Re10SA0.3	2.3	2.6	
Re20SA0.3	2.8	4.0	

Table 4

Specific activity and apparent turnover frequency (taken at 10–14 min on stream) for the different RexSAy samples.

Sample	Specific activity (mmol $g^{-1} h^{-1}$)	"TOF" (10 ⁻³ s ⁻¹)
Re2SA17	3	10
Re10SA17	56	35
Re20SA17	47	17
Re2SA0.3	12	38
Re10SA0.3	87	60
Re20SA0.3	101	33



Fig. 2. Specific metathesis activity versus time on stream of the Re-Si-Al catalysts.

The Re20SA0.3 sample shows the highest specific activity and produced propene at a 101 mmol $g^{-1} h^{-1}$ rate (data taken at 10–14 min time on stream), which corresponds to a yield in propene of $\sim 57\%$, slightly below the equilibrium yield (63%). To our knowledge, this is the highest specific activity reported in the propene metathesis or its reverse reaction using a mixed oxide catalyst. The Re10SA0.3 catalyst, with a more reasonable Re₂O₇ loading, appears even more interesting, with an excellent specific activity of 87 mmol $g^{-1} h^{-1}$ and a high "TOF" value of $60 \cdot 10^{-3} \text{ s}^{-1}$, nearly twice higher than the values reported for a catalyst with a similar composition ("Re3SiAl0.3"), which was the most active catalyst in our previous report [30]. It is remarkable that by a one-step sol-gel route Re-Si-Al metathesis catalysts can be obtained with such high metathesis activity, which nevertheless remains lower than that of well-defined Re(VII)-carbene complexes grafted onto silica (TOF = $250 \cdot 10^{-3} \text{ s}^{-1}$ at 20 °C) by a surface organometallic chemistry approach [33].

4. Conclusions

The non-hydrolytic sol-gel method offers a very simple route to highly active mesoporous Re–Si–Al metathesis catalysts, starting from commercially available chloride precursors. We demonstrate here that when the whole preparation procedure as well as the storage was carried out under strictly anhydrous conditions, Re sublimation during calcination of alumina-poor formulations was suppressed, even at very high rhenium loading. In addition, under these conditions Re–Si–Al materials with very high specific surface areas could be obtained whatever the Si/Al ratio or Re loading. This allowed us to obtain highly active mixed oxide metathesis catalysts, showing unprecedented specific activities.

Acknowledgments

The authors from ICGM acknowledge the Ministère de l'Enseignement Supérieur et de la Recherche and the Centre National de la Recherche Scientifique (CNRS) in France for financial support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2014.09.024.

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