

Effects of the addition of Nb₂O₅ to rhenium-based olefin metathesis catalysts

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Abstract

The effects of the addition of Nb₂O₅ to 6 wt.% Re₂O₇/Al₂O₃ metathesis catalysts were investigated. At least until 9 wt.% Nb₂O₅ loadings both tetrahedral and octahedral aluminum sites are evenly involved in the reaction between alumina and niobium oxide. Up to 12 wt.% Nb₂O₅ no significative influence was observed in the catalytic activity of the resulting systems. For higher niobia loadings, however, the catalytic activity decreased quickly. In such conditions a second rhenium species, probably [Nb]–OREO₃ was detected by TPR. ¹¹⁹Sn Mössbauer analyses showed that the reaction between the niobia-modified systems and SnBu₄ ([Sn]:[Re] = 0.55) led to the formation of only one kind of rhenium–tin site, with the tin atom attached to the surface by two Sn–O bonds. In contrast to what happens with the unmodified system, no physisorbed SnBu₄ was observed.

Keywords: Olefin metathesis; Rhenium oxide/alumina; Niobium oxide; Mössbauer; MAS NMR

1. Introduction

Rhenium oxide supported on alumina is a well known metathesis catalyst. Modification of the support by addition of another oxide (viz. V₂O₅, MoO₃, WO₃, B₂O₃, etc.) increases significantly the catalytic activity of the system [1]. Such an effect is usually correlated to an increase of the Brønsted acidity of the resulting system [2]. Addition of SnR₄ (R = alkyl) allows the metathesis of olefins bearing functional

groups [3]. Recently, other rhenium-based systems, i.e. MeReO₃/SiO₂–Al₂O₃ [4] or MeReO₃/Nb₂O₅ [5] have been described. Although such systems might be considered as models of active sites, MeReO₃/Nb₂O₅ is not active in metathesis of functionalized olefins [6]. Moreover, the catalytic activity of rhenium oxide supported on niobia is negligible [6]. On the other hand, it has been shown that the addition of niobia to several oxides such as SiO₂, Al₂O₃, ZrO₂ causes an increase on their acidity [7]. Therefore, the aim of this work was to determine the effects of the addition of niobium oxide both on the catalytic activity of Re₂O₇ supported on alumina and on the characteristics of the resulting systems.

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2. Experimental

2.1. Supports

Alumina-supported niobium oxide samples were prepared by pore-volume impregnation of the support (Al_2O_3 Aldrich, acidic, 150 mesh) using calculated amounts of niobium oxalate/oxalic acid aqueous solutions (niobium oxalate was supplied by C.B.M.M.). The samples were dried at 100°C overnight, followed by calcination at 550°C under an air stream for 6 h.

2.2. Catalysts

All Re_2O_7 catalysts were prepared by pore-volume impregnation of the supports with calculated amounts of ammonium perrhenate (Aldrich, > 99%), followed by overnight drying in air at 100°C . The catalysts were calcined at 550°C in a dry air stream (60 ml min^{-1}) for 2 h, followed by a nitrogen purge for 1 h, at the same temperature. After cooling to room temperature, the catalysts were transferred to the reaction vessel using Schlenk-tube techniques. Calculated volumes of SnBu_4 (Fluka, 98%) were then added via a syringe, keeping the molar ratio $[\text{Sn}]:[\text{Re}] = 0.55$.

MeReO_3 /support catalysts were prepared by addition of a hexane solution of MeReO_3 [8] to the support pretreated as described above for Re_2O_7 catalysts.

Metathesis of 1-hexene (Aldrich, 97%) was carried out in the liquid phase in a glass batch reactor, using toluene as a solvent and cyclohexane as an internal standard. The reaction was monitored by GC analysis (CG 37 D gas chromatograph) of the gas phase over a capillary column (OV 1, $20\text{ m} \times 0.10\text{ mm}$). Conversions were calculated as $2[\text{ethene}]/\{2[\text{ethene}] + [1\text{-hexene}]\}$.

All reactions were carried out at room temperature.

2.3. BET measurements

The specific surface area of the supports were determined by the BET method on a Mi-

cromeritics Flow Sorb 2300 equipment. Measurements were performed with nitrogen as the adsorbate at -196°C , after pretreating the samples at 150°C under nitrogen for 1 h.

2.4. Temperature-programmed reduction

Temperature-programmed reduction of the Re_2O_7 catalysts was carried out with a hydrogen/nitrogen mixture (2:98) at atmospheric pressure in a conventional TPR setup. The gas mixture (20 ml min^{-1}) was passed over approximately 100 mg of the sample placed in a quartz tube. The temperature of the sample was increased linearly at a rate of $10^\circ\text{C min}^{-1}$.

2.5. MAS NMR measurements

All MAS NMR spectra were recorded on a Bruker AC 300 spectrometer operating at 75.47, 78.17 and 111.9 MHz for ^{13}C , ^{27}Al and ^{119}Sn , respectively. The probehead was a commercial double-tuned 7 mm double-bearing system from Bruker, allowing spinning frequencies up to 4 kHz. The samples were introduced in the zirconia rotors under a dry argon atmosphere in a glove box and tightly closed. For ^{13}C NMR, a typical cross-polarization scheme was used: 90° rotation of the ^1H magnetization (pulse length 9.7 μs), contact time of 5 ms and recording of the spectrum at high power decoupling. The delay between scans was fixed to 5 s to allow for the complete relaxation of the ^1H nuclei. Typically, 11 000 scans were accumulated. Chemical shifts are given with respect to TMS using adamantane as an external reference.

^{119}Sn NMR spectra were recorded by using a single pulse and high power decoupling, with a delay between each scan of 2.5 s. Typically, 30 000 scans were accumulated. The chemical shifts are given relative to SnMe_4 used as external reference and with the IUPAC convention for chemical shifts (higher values for higher frequencies).

^{27}Al NMR spectra were recorded by using a single impulsion sequence. The delay between scans was 1 s, and the number of scans was

typically 500. Chemical shifts are reported relative to $\text{Al}(\text{H}_2\text{O})_6(\text{NO}_3)_3$ used as an external reference.

2.6. Mössbauer measurements

The samples were transferred to the sample holder under an argon atmosphere. ^{119}Sn Mössbauer spectra were run in a standard equipment at liquid-nitrogen temperature, using a CaSnO_3 source maintained at room temperature. The isomer shifts are given with respect to this source.

3. Results

3.1. Physical characterization

3.1.1. Support

Modification of γ -alumina by addition of Nb_2O_5 caused an increase in its surface area which is a function of the niobia-loading (Fig. 1). ^{27}Al NMR spectra (peaks at 65, 53 and 3 ppm) were not affected, suggesting that both tetrahedral and octahedral Al sites are involved in the reaction. Crystallization of a Nb_2O_5 phase was not observed under our experimental conditions.

3.1.2. Re_2O_7 /support

The TPR profile for a 6 wt.% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ sample shows a reduction peak at 400°C (Fig. 2). Addition of Nb_2O_5 up to a 9 wt.% Nb_2O_5 loading has no effect in the reduction tempera-

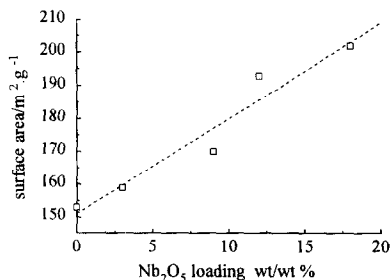


Fig. 1. Specific surface area (B.E.T.) of the modified supports as a function of Nb_2O_5 loading.

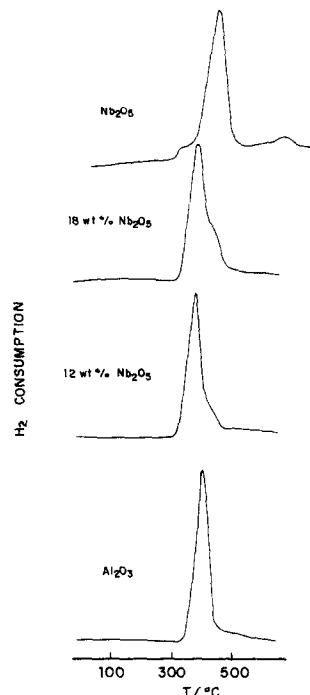


Fig. 2. TPR profiles of $\text{Re}_2\text{O}_7/\text{Nb}_2\text{O}_5-\text{Al}_2\text{O}_3$ catalysts.

ture. However, from 12 wt.% up to 18 wt.% Nb_2O_5 loading the reduction peak is shifted to 370°C and a shoulder at ca. 440°C appears. The TPR profile of rhenium oxide supported on niobia also presents a reduction peak at 440°C (Fig. 2). These results suggest that at low Nb_2O_5 loadings there is only one kind of rhenium site, i.e., $[\text{Al}]-\text{O}-\text{ReO}_3$; for higher Nb_2O_5 loadings, a second site, probably $[\text{Nb}]-\text{O}-\text{ReO}_3$, is also present.

3.2. Interaction between Re_2O_7 /support and SnBu_4

The reaction between Re_2O_7 /support and SnBu_4 was evidenced by a color change (from white to brownish) and evolution of butane. Although for the same support the extent to which the gas was released depended on the $[\text{Sn}]:[\text{Re}]$ ratio, it was never higher than 0.2 [butane]:[Sn]. Blank experiments with the support alone showed that the interaction between Al_2O_3 and SnBu_4 was not followed by a color change; 9 wt.% $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ and Nb_2O_5

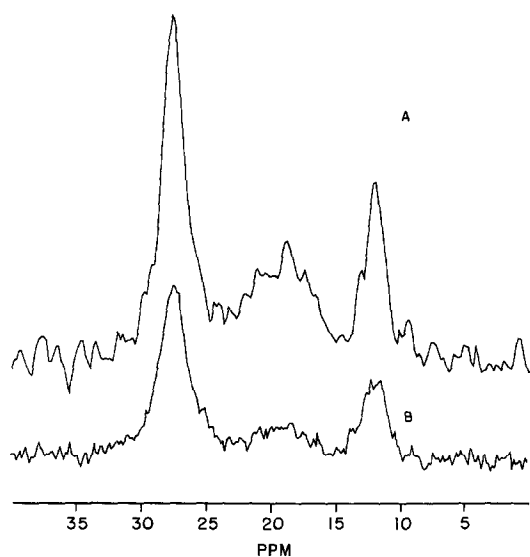


Fig. 3. ^{13}C CP-MAS NMR spectra of 6 wt.% $\text{Re}_2\text{O}_7/\text{Nb}_2\text{O}_5\text{-Al}_2\text{O}_3$ catalysts. (A) fresh sample; (B) after 20 regenerations (calcination followed by addition of SnBu_4).

alone, however, reacted slowly with SnBu_4 . Both oxides took at first a yellowish color, which turned to gray after ca. 24 h.

3.3. ^{13}C and ^{119}Sn NMR analyses

Fig. 3A shows the ^{13}C MAS NMR spectrum of 6 wt.% $\text{Re}_2\text{O}_7/9$ wt.% $\text{Nb}_2\text{O}_5\text{-Al}_2\text{O}_3/\text{SnBu}_4$ where three signals can be observed, at 12.0, 17–21 and 27.6 ppm. Although by comparison with literature data (Table 1)

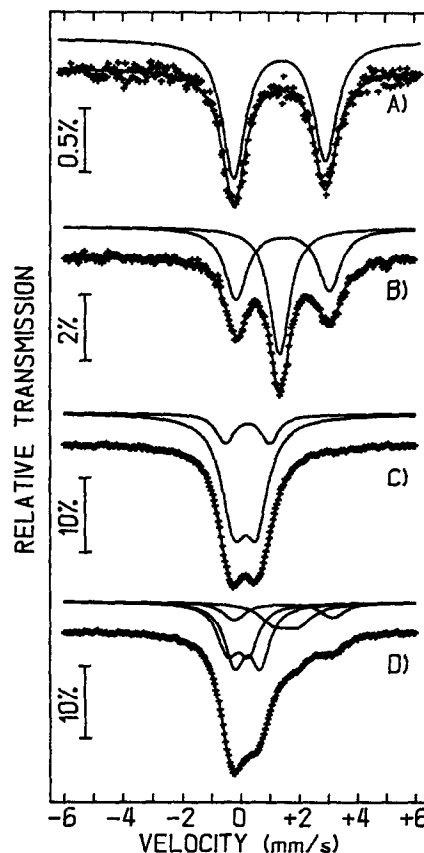


Fig. 4. ^{119}Sn Mössbauer spectra of: (A) 6 wt.% $\text{Re}_2\text{O}_7/\text{Nb}_2\text{O}_5\text{-Al}_2\text{O}_3/\text{SnBu}_4$; (B) 6 wt.% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3/\text{SnBu}_4$; (C) B after calcination; (D) C after addition of SnBu_4 .

these signals could be assigned to C_δ , C_α and $C_{\beta+\gamma}$ of $[\text{Re}]\text{-O-SnBu}_3$ species, the lack of a signal in the ^{119}Sn spectrum suggests that the tin

Table 1
 ^{13}C and ^{119}Sn chemical shifts for $\text{Re}_2\text{O}_7/\text{Nb}_2\text{O}_5\text{-Al}_2\text{O}_3/\text{SnBu}_4$ catalysts and related systems

System	$\delta(^{13}\text{C})$				$\delta(^{119}\text{Sn})$	Ref.
	C_α	C_β	C_γ	C_δ		
6 wt.% $\text{Re}_2\text{O}_7/\text{Nb}_2\text{O}_5\text{-Al}_2\text{O}_3/\text{SnBu}_4$	17–21	27.6	27.6	12.0	n.d. ^a	this work
After 20 regenerations + SnBu_4	16–21	27.5	27.5	11.4	n.d.	this work
$\text{Al}_2\text{O}_3/\text{SnBu}_4$ (physisorbed)	9.2	29.7	n.d.	13.5	–13	this work
	15–21	27.7	27.7	12.2	n.d.	this work
9 wt.% $\text{Nb}_2\text{O}_5\text{-Al}_2\text{O}_3/\text{SnBu}_4$ (physisorbed)	9.2	29.6	25.1	n.d.	–13	this work
6 wt.% $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$	16.4	27.5	27.5	12.3	103	[9]
$\equiv \text{AlOSnBu}_3$	15–19	26.9	26.9	13.0	80	[10]
$\equiv \text{SiOSnBu}_3$	15.1	26.8	26.8	12.8	106	[11]
$(\equiv \text{SiO})_2\text{SnBu}_2$	20.2	26.8	26.8	12.9	n.d.	[12]
SnBu_4	9.1	29.6	27.6	13.7	–13	[13]

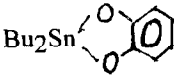
^a n.d. = not detected.

atom might be linked to the surface through two Sn–O bonds. In fact, as the ^{13}C signal assigned for C_α is so broadened, no clear conclusion could be drawn from NMR analyses. Blank experiments with the support alone, employing the same tin loadings, revealed the presence of physisorbed SnBu_4 species (Table 1). After 20 regenerations of the catalyst, followed by addition of another portion of SnBu_4 , the resulting ^{13}C NMR spectrum is essentially the same (Fig. 3B), the only difference being a broadening of the signals assigned to C_α and C_δ .

3.4. Mössbauer measurements

The Mössbauer spectrum for 6 wt.% $\text{Re}_2\text{O}_7/\text{Nb}_2\text{O}_5\text{-Al}_2\text{O}_3/\text{SnBu}_4$ (Fig. 4A) presents two slightly asymmetric absorption peaks, corresponding to one tin site characterized by IS (isomer shift) = 1.47 mm s^{-1} and QS (quadrupole splitting) = 3.34 mm s^{-1} . In the same experimental conditions (i.e., $[\text{Sn}]:[\text{Re}] = 0.55$), the spectrum of a 6 wt.% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3/\text{SnBu}_4$ sample shows three peaks (Fig. 4B). This spectrum is best fitted through one doublet (IS = 1.45

Table 2
 ^{119}Sn Mössbauer data for $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3/\text{SnBu}_4$ catalysts and some related compounds

		IS (mm s^{-1}) ^a	QS (mm s^{-1}) ^b	Ref.
6 wt.% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3/\text{SnBu}_4$				
Fresh sample	(site I)	1.45	3.20 (56%)	^c
	(site II)	1.35	0.00 (44%)	^c
After calcination	(site III)	0.14	0.76 (83%)	^c
	(site IV)	0.22	1.53 (17%)	^c
After calcination and exposure to air	(site III)	0.01	0.51 (71%)	^c
	(site IV)	0.08	1.05 (29%)	^c
After calcination + SnBu_4	(site I)	1.44	3.37 (10%)	^c
	(site IIa)	1.55	0.79 (18%)	^c
	(site III)	0.11	0.73 (31%)	^c
	(site IV)	0.22	0.87 (38%)	^c
6 wt.% $\text{Re}_2\text{O}_7/\text{Nb}_2\text{O}_5\text{-Al}_2\text{O}_3/\text{SnBu}_4$				
Fresh sample	(site I)	1.47	3.34	^c
After 20 regenerations ^d	(site I)	1.49	2.94 (14%)	^c
	(site III)	0.07	0.56 (53%)	^c
	(site IV)	0.14	1.33 (33%)	^c
$\text{Al}_2\text{O}_3/\text{SnBu}_4$	(site II)	1.36	0.00 (34%)	^c
		1.39	3.01 (66%)	^c
$\text{Nb}_2\text{O}_5\text{-Al}_2\text{O}_3/\text{SnBu}_4$	(site II)	1.42	0.00 (11%)	^c
		1.43	3.11 (89%)	^c
$\text{Nb}_2\text{O}_5/\text{SnBu}_4$	(site II)	1.33	0.00 (20%)	^c
		1.43	2.93 (80%)	^c
6 wt.% $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$	(site X)	1.41	2.90 (59%)	[9]
	(site Y)	1.58	4.04 (41%)	[9]
Deactivated	(site X)	1.35	2.65 (65%)	[9]
	(site Y)	1.43	3.39 (35%)	[9]
Bu_3SnOPh		1.42	2.85	[14]
		1.52	3.62	[14]
SnO_2		0	0.53	[15]
$\text{SiO}_2/\text{SnBu}_4$ (physisorbed)		1.38	0	[16]
SnBu_4		1.35	0	[17]

^a Accuracy: 0.02 mm s^{-1} ; ^b Accuracy: 0.04 mm s^{-1} and 5% for relative concentrations in parentheses; ^c this work; ^d regeneration = calcination followed by addition of SnBu_4 .

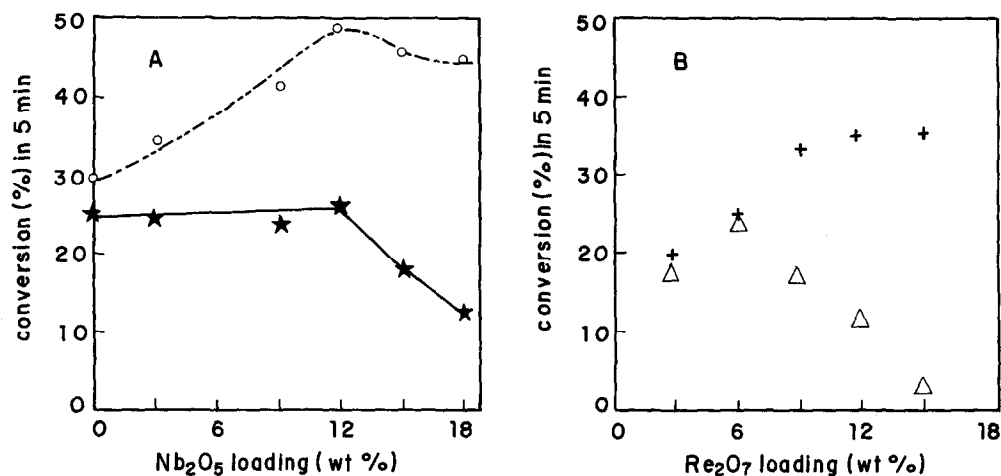


Fig. 5. Catalytic activity in metathesis of 1-hexene. (A) as a function of Nb₂O₅ loading for: ○ MeReO₃; ★ 6 wt.% Re₂O₇/Nb₂O₅-Al₂O₃; (B) as a function of Re₂O₇ loading for: + support = Al₂O₃; Δ support = 9 wt.% Nb₂O₅-Al₂O₃. Room temperature, [Re]:[1-hexene] = 1:200.

mm s⁻¹; QS = 3.20 mm s⁻¹) and one singlet (IS = 1.35 mm s⁻¹). Blank experiments revealed that reaction of alumina alone with SnBu₄ also leads to two tin sites, a singlet characterized by IS = 1.36 mm s⁻¹, and a doublet with IS = 1.39 mm s⁻¹ and QS = 3.01 mm s⁻¹. By comparison with literature data (Table 2) [16,17], the singlet can be assigned to SnBu₄ only physisorbed on the support. The presence of such physisorbed species was also detected on Nb₂O₅ and 9 wt.% Nb₂O₅-Al₂O₃ when these supports were allowed to interact with SnBu₄ (Table 2).

After calcination of the Re₂O₇/Al₂O₃/SnBu₄ catalysts two tin sites were observed (Fig. 4C): sites III (IS = 0.14 mm s⁻¹; QS = 0.76 mm s⁻¹) and IV (IS = 0.22 mm s⁻¹; QS = 1.53 mm s⁻¹). Exposure to air caused a shift to lower values for IS and QS for both sites (Table 2). When SnBu₄ was added to a fresh calcined catalyst (Fig. 4D) only site I was restored. Physisorbed SnBu₄ was no longer detected. Instead, another site appeared (IIa), with IS = 1.55 mm s⁻¹ and QS = 0.79 mm s⁻¹, which might be due to a reaction involving SnBu₄ and sites III or IV. For the niobia-modified system the presence of a physisorbed SnBu₄ was never observed. Moreover, even

after 20 regenerations species like IIa could not be detected.

3.5. Catalytic activity¹

Fig. 5A shows that for 6 wt.% Re₂O₇ samples the catalytic activity in the metathesis of 1-hexene was not affected for niobia loadings up to 12 wt.%. For higher Nb₂O₅ loadings, however, it decreased rapidly. In the same conditions, a parallel set of experiments carried out with 1 wt.% MeReO₃ showed that the catalytic activity of the resulting systems increased with the niobia loading, reaching a maximum for the catalyst containing 12 wt.% Nb₂O₅. In Fig. 5B it can be seen that, for a 9 wt.% Nb₂O₅-Al₂O₃ support, the catalytic activity of Re₂O₇ reaches a maximum for a 6 wt.% Re₂O₇ loading. This behavior is quite different from that observed in the case of Re₂O₇/Al₂O₃ catalysts whose catalytic activity *per* rhenium atom increases at least up to 12 wt.% Re₂O₇. This result agrees well with literature data: reports vary in the

¹The rhenium loadings were chosen based on literature data [5,18,19].

range 12–18 wt.% Re_2O_7 , depending on the alumina employed [18–20]. For the Re_2O_7 /support systems, the selectivity for the primary metathesis products (> 95% on alumina alone) was slightly reduced by the modified support (> 92% for 9 wt.% Nb_2O_5).

4. Discussion

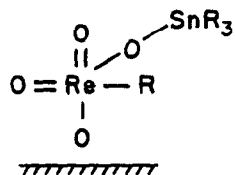
It has been demonstrated that at low-loaded $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ catalysts ReO_4^- ions unevenly replace the five different types of hydroxyl groups on the γ -alumina surface; most of the rhenium preferentially replaces basic hydroxyls [21,22] or is adsorbed on coordinatively unsaturated Al^{3+} sites, leading to a low number of active sites [22]. Increasing the rhenium loading leads to a higher replacement of acidic hydroxyl groups and thus to a higher concentration of active sites [22]. On the other hand, addition of Nb_2O_5 to $\gamma\text{-Al}_2\text{O}_3$ causes an increase in both Lewis and Brønsted acid sites whose numbers reach a maximum for 5 and 19 wt.% Nb_2O_5 , respectively [7]. If the catalytic activity of the rhenium systems were to be accounted for only by the surface acidity, one would expect the addition of Nb_2O_5 to such systems to increase their activity, which was not observed: within experimental error, the catalytic activity of 6 wt.% Re_2O_7 systems remains constant for up to 12 wt.% Nb_2O_5 loadings (Fig. 5A). Also, an increase in the surface area did not correspond to an increase in the catalytic activity (Fig. 1 and Fig. 5A). However, TPR results showed that from 12 up to 18 wt.% Nb_2O_5 the main reduction peak was shifted to lower temperatures; there also appeared a second peak, at 440°C, which could be assigned to $[\text{Nb}]\text{-O-ReO}_3$ sites as it has been shown that only this kind of rhenium species can be formed on the surface of inorganic oxides [23–25]. These results suggest that $[\text{Nb}]\text{-O-ReO}_3$ sites are not active in olefin metathesis. Thus, at lower niobia loadings, the surface hydroxyl groups involved in the reaction with rhenium might be

either the $\equiv\text{Al-OH}$ or the bridging OH groups (attached to both a niobium atom and an aluminum atom), resulting, after calcination, in one kind of rhenium site, $[\text{Al}]\text{-O-ReO}_3$ (one reduction peak). For higher niobia loadings, $[\text{Nb}]\text{-O-ReO}_3$ sites would be unavoidable, and the catalytic activity should decrease. Such an explanation is consistent with the fact that for 9 wt.% Nb_2O_5 loadings the catalytic activity decreases for rhenium loadings higher than 6 wt.% Re_2O_7 ; for higher rhenium loadings, there would be also more rhenium atoms bonded to niobium sites.

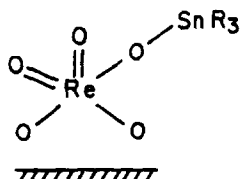
It has been demonstrated that there is no direct correlation between the reductibility of the rhenium atoms and the catalytic activity [26]. Now, our results have shown that an increase in the Brønsted (or Lewis) acidity of the support does not necessarily imply a higher activity of the resulting $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ systems. Thus, it seems more probable that the catalytic activity of such systems is related to the strength of Re-O -support bonds which should allow mild reduction of the rhenium centers (to create active sites) [23].

In the case of MeReO_3 , although a correlation between catalytic activity and Lewis acidity has been observed, it appeared that both Lewis and Brønsted acid sites should be present in order to allow metathesis reactions [5]. The different behavior observed for these two systems ($\text{MeReO}_3/\text{support}$ and $\text{Re}_2\text{O}_7/\text{support}/\text{SnBu}_4$) in metathesis of 1-hexene only reinforce the assumption that there is a difference in the nature of the active centers for each system.

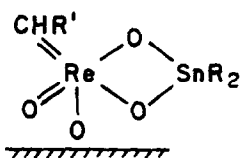
Reaction of $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ or $\text{Re}_2\text{O}_7/\text{Nb}_2\text{O}_5\text{-Al}_2\text{O}_3$ catalysts with SnBu_4 results in only one kind of rhenium-tin site. By comparison with data previously reported for $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$, for which two sites have been detected [9], it can be seen that the IS and QS values obtained in this work (Table 2) are intermediate between those assigned to species like **A**, **A'** (site X) and **B**, **C** (site Y).



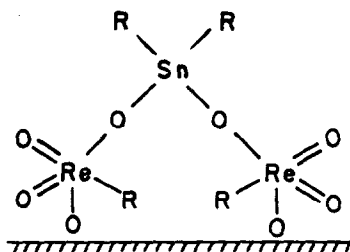
A



A'



B



C

Moreover, the IS and QS values for $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3/\text{SnBu}_4$ or $\text{Re}_2\text{O}_7/\text{Nb}_2\text{O}_5-\text{Al}_2\text{O}_3/\text{SnBu}_4$ are closer to those detected for site Y in $\text{Re}_2\text{O}_7/\text{SiO}_2-\text{Al}_2\text{O}_3/\text{SnBu}_4$ after deactivation by air exposure. In that case, it was suggested that the solvation of the rhenium species might cause a weakening of the Re–O–

Sn bonds. Thus, if the species formed in $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3/\text{SnBu}_4$ systems are of the same type as those present in $\text{Re}_2\text{O}_7/\text{SiO}_2-\text{Al}_2\text{O}_3/\text{SnBu}_4$ (site Y), weaker Sn–O–Re bonds might be caused by stronger Re–O–Al bonds. Indeed, TPR studies for several rhenium-based metathesis catalysts indicated that the strength of the Re–O–Al bonds is higher for $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ than for $\text{Re}_2\text{O}_7/\text{SiO}_2-\text{Al}_2\text{O}_3$ [26]. Thus, formation of only species like A or A', with Sn–O–Re bonds stronger than in the case of $\text{Re}_2\text{O}_7/\text{SiO}_2-\text{Al}_2\text{O}_3/\text{SnBu}_4$ is not likely. Moreover, ^{119}Sn NMR results do not support species A, A'. A third possibility would be the attachment of the tin atom to the surface through both Sn–O–Re and Sn–O–Al or Sn–O–Nb bonds. However, the latter hypothesis would imply a more asymmetric tin site and thus higher values for QS when compared to those obtained for $\text{Re}_2\text{O}_7/\text{SiO}_2-\text{Al}_2\text{O}_3/\text{SnBu}_4$ [9]. Therefore, site Y (species B or C) seems the most likely to be present on the surface of $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3/\text{SnBu}_4$ or $\text{Re}_2\text{O}_7/\text{Nb}_2\text{O}_5-\text{Al}_2\text{O}_3/\text{SnBu}_4$ catalysts. As the presence of site Y is favored for the niobia-modified system (no physisorbed tin species), it is also likely that C should be the major species. This means that there are pairs of Re sites on the surface so that SnBu_4 reacts with two Re atoms at the same time. Note, however, that for a 6 wt.% $\text{Re}_2\text{O}_7/(\text{Al}_2\text{O}_3$ or 9 wt.% $\text{Nb}_2\text{O}_5-\text{Al}_2\text{O}_3)$ the surface concentration of rhenium atoms would be ca. 0.5 atoms per nm^2 .

When the 6 wt.% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3/\text{SnBu}_4$ catalyst was calcined under air the resulting ^{119}Sn Mössbauer spectrum reveals the presence of two tin sites: none of them seems to correspond to an SnO_2 phase (Table 2). However, after exposure to air a tin oxide phase was indeed detected. Thus, the non-observation of such a phase in a fresh calcined catalyst (during its first regeneration) might be due to a low tin coverage which makes it difficult for tin atoms to be closer to each other. Indeed, after 20 regenerations an SnO_2 phase could be detected in the case of $\text{Re}_2\text{O}_7/\text{Nb}_2\text{O}_5-\text{Al}_2\text{O}_3/\text{SnBu}_4$. This re-

sult is in agreement with data reported for $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnR}_4$, for which two tin sites have been observed after calcination: an SnO_2 phase and a polymeric ionic Sn(IV) species [9].

5. Conclusions

Modification of 6 wt.% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts has no significant effect on the catalytic activity of the resulting systems (in metathesis of 1-hexene) up to 12 wt.% Nb_2O_5 . At higher niobia loadings the presence of $[\text{Nb}]\text{-OReO}_3$ species, not active, causes a decrease in the catalytic activity. Upon reaction with SnBu_4 only one kind of rhenium–tin site is formed, with the tin atom attached to the surface through two SnO bonds. The presence of physisorbed SnBu_4 is not detected on the niobia-modified system as opposed to what happens for 6 wt.% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3/\text{SnBu}_4$. Nevertheless, this higher reactivity towards SnBu_4 seems not to result in a higher number of active sites as the catalytic activity is not increased. It also may be concluded that for the rhenium-based niobia-modified catalysts the acidity of the support has no influence on the catalytic activity of such systems, the strength of the Re-O -support bonds being the main factor.

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