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Determination of active centres in $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$ metathesis catalysts by titration method

Che Seman Mahmood^a, Mohd. Ambar Yarmo^a,
Sharifah Bee Derouane-Abd Hamid^{b,*}

^a Department of Chemistry, Faculty of Physical and Applied Sciences, Universiti Kebangsaan Malaysia, 43500 Bangi, Selangor, Malaysia

^b Leverhulme Centre for Innovative Catalysis, Department of Chemistry, The University of Liverpool, Liverpool L69 3BX, UK

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Abstract

A chemisorption technique has been developed for the quantitative determination of active centres in $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$ metathesis catalysts. Butene-2 and ethylene were used as chemical probes to generate metal–carbene species on the active centres of the catalyst and eventually propylene as product. Catalysts with metal loading from 2% to 8% Re were shown to contain active centres in an amount equivalent to 0.6–2.2% Re/g catalyst. Catalysts prepared in hydrochloric acid medium contain about 5% more active centres than those prepared in aqueous medium, as measured by metathesis of propylene. It was also demonstrated that the surface area of the support could further influence the activity of the catalysts. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Olefin metathesis proceeds through metal–carbene and metallocyclobutane intermediates. The existence of such species involving metal atoms of the catalyst has been demonstrated in various studies, mostly for homogeneous systems [1–3]. Based on the observation of the initial products resulting from the cross-metathesis of cyclic and acyclic olefins on $\text{WOCl}_4\text{-Et}_2\text{AlCl}$, Herisson and Chauvin [1] were the first to propose the carbene mechanism that was later supported by other researchers whose evidences in-

cluded the nature of the initial products, the stereoselectivity of the reaction, and the identification of the metal–carbenes present during metathesis in the presence of W, Mo, and Re-based catalysts [4–6]. In these systems, the formation of carbenes is usually facilitated by a co-catalyst that acts as an alkylating agent and supplies one or several alkyl groups. The resulting intermediate then undergoes α -hydrogen elimination en route to carbene.

For heterogeneous catalysts, such as $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$, with the absence of co-catalyst, the initial carbene species is generated on the catalyst surface when the reactant olefin, the only source of alkyl moiety, is adsorbed. The formation of this carbene involves hydrogen transfer between the metal atom of the support and the reactant olefin, leading to a metallocyclobutane, the precursor to metathesis [7,8].

* Corresponding author. Tel.: +44-151-7942937.

E-mail address: sharifhd@liverpool.ac.uk (S.B.D.-A. Hamid).

Even though the mode of production and the structure of the active carbene species are now well established, information on the number of active metal precursor sites and active centres are still very scarce. Some reports on the indirect titrations of active centres in such systems indicate that the number of active centres in $\text{Re}_2\text{O}_7\text{Al}_2\text{O}_3$ catalysts is very low [9–11]. In such quantifications, using NO poisoning, ethylene adsorption or hydrogen reduction, some uncertainty remains about the specificity and stoichiometry of the methods because poisoning or reduction of an active site does not take into account the contribution of adjacent sites. It has been demonstrated, indeed, that metathesis activity is easily suppressed by the presence of small amount of impurities, in particular, those carrying polar groups in the reactant olefin or on the alumina support [12,13]. Since the reactant olefin may also be involved in other side-reactions such as hydrogenation, double-bond isomerization, and polymerization [12–14], the selective isolation or probing (followed by titration) of sites or species exclusively responsible for metathesis has not yet been achieved with a high degree of confidence.

The $\text{Re}_2\text{O}_7\text{--Al}_2\text{O}_3$ system, which is known for its high activity and selectivity for metathesis even at room temperature and atmospheric pressure [15], offers an opportunity for the direct evaluation of metathetic carbene active centres since no other active species are present during the course of the reaction. This paper reports on the development of a chemical titration method for the direct quantification of active centres in the $\text{Re}_2\text{O}_7\text{--Al}_2\text{O}_3$ catalysts, using the classical 2-butene and ethylene metathesis reactions.

2. Experimental

2.1. Catalysts preparation

Catalysts containing 2, 4, and 8 wt.% of rhenium were prepared by wet impregnation of aqueous ammonium perrhenate (aqueous media) and 10% HCl in ammonium perrhenate solutions (acidic media) (Aldrich, 99.99%) onto γ -alumina, Al-X (BDH, 99 + %, BET surface area $192\text{ m}^2\text{ g}^{-1}$, pore volume

0.74 ml g^{-1} , 2 mm extrudate) and A-P (Procatalyse, 99%, BET surface area $257\text{ m}^2\text{ g}^{-1}$, pore volume 0.62 ml g^{-1} , 1 mm extrudate). After 12 h of soaking and occasional ultrasonic mixing, the excess water was evaporated at 90°C on a hotplate, and the sample was dried in an oven at 110°C for another 12 h. It was then calcined at 550°C for 6 h in a pure and dry air flow (20 ml min^{-1}). The catalyst was then further recalined for another 1 h prior to use. The rhenium content before and after calcination were determined by Neutron Activation Analysis (NAA).

2.2. Catalysts evaluation

The catalysts were tested for the metathesis of propylene to butene and ethylene. A freshly calcined catalyst sample (1 g) was transferred under dried argon into a 325-ml glass reactor maintained at 35°C and evacuated for 2 h before the introduction of propylene gas (Merck, > 99.7% purity) at a pressure of 1.05 kg m^{-2} . Gas sampling was done with a syringe through the silicone–rubber septum of the reactor at regular time intervals. Analysis was performed using a HP5890 Gas Chromatograph equipped with a PONA capillary column (50 m length), FID detector and isothermal elution with He at 50°C . A standard olefin $\text{C}_2\text{--C}_6$ gas mixture in helium (Scott Specialty Gases, Alltech, USA) was used for retention time determination and sensitivity correction.

2.3. Active centre determination

Freshly calcined catalyst samples were evacuated in the reactor, regulated at 35°C for 2 h. The activating olefin, 2-butene was then introduced (Merck, > 99.7% purity, *trans/cis* ratio of 2:1) at a pressure of 1.10 kg m^{-2} . The amount of the reactant introduced was calculated from the volume and pressure of the reactor at room temperature (30°C). After 2 h, in order to generate ethyl–carbene species on the rhenium atoms, the 2-butene in excess was evacuated for 2 h and the developer olefin, 15.01 mmol (325 ml) of ethylene (Merck, > 99.7% purity) was then introduced at 1.10 kg m^{-2} pressure. At all stages, the composition of the gas was determined by GC analysis.

3. Results and discussion

NAA results (Table 1) show that Re is retained quantitatively on the alumina after calcination, indicating Re_2O_7 is strongly bound to the alumina surface. In the absence of the chemical bonding, Re_2O_7 would certainly sublime during calcination. All the metal loadings used are below the theoretical monolayer coverage of the support which is about 18% Re_2O_7 [16]. Slightly higher values observed after calcination are attributed to the dehydration and partial dehydrogenation of the support.

The self-metathesis of propylene ($\text{C}_3^=$) to ethylene ($\text{C}_2^=$) and but-2-ene ($2-\text{C}_4^=$) on Re_2O_7 -alumina catalysts is represented by Eq. 1:



Fig. 1 shows propylene conversion as a function of time, reaching near-stationary conversion when about 45% of $\text{C}_3^=$ is consumed. At higher Re loading, faster rates are observed and near-stationary conversion is reached at shorter reaction time. The calculated thermodynamic equilibrium of the reaction at 27°C corresponds to 57.6% $\text{C}_3^=$ present in the mixture [17] (i.e. 43.4% conversion), which is in good agreement with the experimental observation. However, not all catalysts show 100% selectivity towards metathesis (Fig. 2). N2RX-F and N2RX-Cl catalysts yield not only $\text{C}_2^=$ and $2-\text{C}_4^=$, the main metathesis products, but also 1-butene ($1-\text{C}_4^=$) and pentenes ($\text{C}_5^=$) whose formations are attributed to

Table 1

Concentration of rhenium in catalysts as determined by NAA technique

Catalysts labeling is based on the theoretical percentage of rhenium loading and preparation medium, for example catalyst N8RX-F contains 8% Re and is prepared from an aqueous solution of NH_4ReO_4 on fresh support, and N2RX-Cl has a 2% Re loading and is prepared in HCl medium.

Catalyst	Concentration of Re (wt.%)		
	Theoretical	Before calcination	After calcination
N8RX-F	8.00	7.80	7.95
N8RX-Cl	8.00	7.88	8.05
N4RX-F	4.00	3.95	3.97
N4RX-Cl	4.00	3.90	3.94
N2RX-F	2.00	1.85	1.94
N2RX-Cl	2.00	1.94	2.05

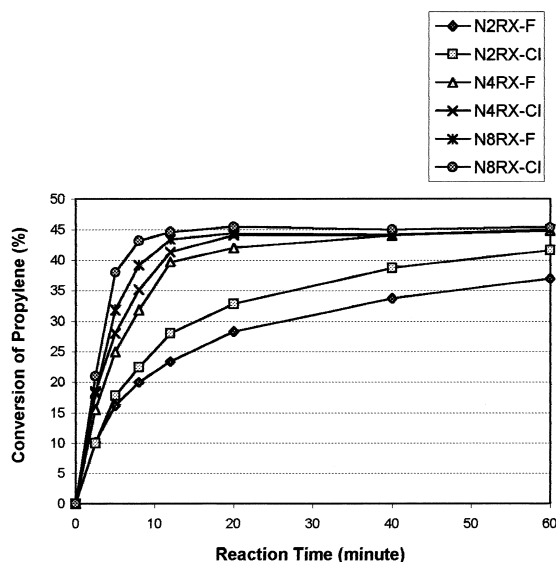
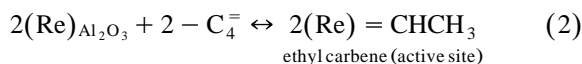


Fig. 1. Conversion of propylene on various catalysts systems against reaction time.

isomerization and subsequent metathesis. The later observations can be explained when considering that isomerization and dimerization of olefins can occur on the alumina surface at a much slower rate than metathesis in the presence of Bronsted acid sites or on Lewis sites at the surface of rhenium oxide [14,18,19]. It has also been reported that the presence of acidic hydroxyl groups on the support in the vicinity of metal cations enhances ethylene dimerization [20,21]. For the high loading catalysts, where the rhenium phase covers most of the available alumina surface, isomerization is suppressed, carbene formation and metathesis are predominant. Since olefins (at least in the case of $\text{C}_2^=$, $\text{C}_3^=$, and $2-\text{C}_4^=$) are selectively undergoing metathesis reaction over 4% and 8% Re-catalysts, a chemical titration method can be developed to determine the concentration of active centres assuming that only $\text{Re}=\text{C}_2$ species are formed and that all reaction parameters remain identical independent of the catalyst nature. As proposed by Commereuc and Chauvin [22,23], the active sites for metathesis consist of surface carbenes generated when the catalyst is contacted with the activating olefin. For $2-\text{C}_4^=$:



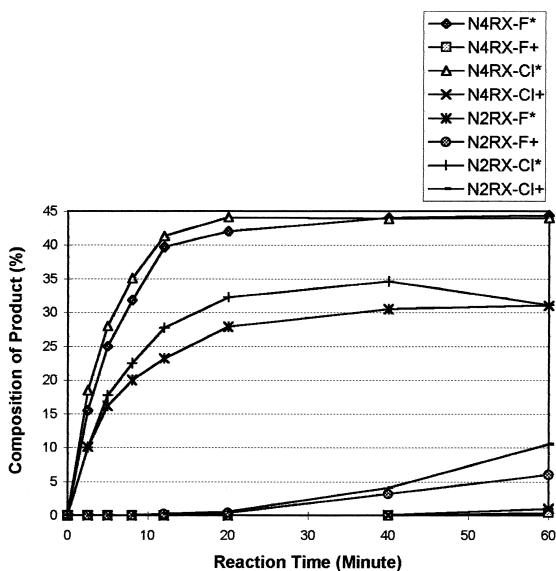
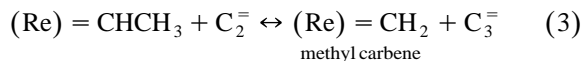


Fig. 2. Selectivity of reaction over various catalysts systems: compositions of reaction products of propylene over catalysts. (Note: * in the legend represents the $C_2^=$ and $2-C_4^=$ as metathesis products, and + represents $1-C_4^=$ and $C_5^=$ as products from other side-reactions).

When the active site is reacted with the developer olefin, in this case ethylene, propylene is produced, and its amount is a direct measure of the number of active sites created.



Since both reactions 2 and 3 are in equilibrium, excess of $2-C_4^=$ and $C_2^=$ are required to ensure that both steps are quantitative in order to form and develop all carbene species from the active sites, respectively. Obviously, evacuation of the $2-C_4^=$ in excess is required after the first step. An olefin/Re mole ratio greater than 50 was always used throughout the experiments. We also observed that, upon contact with the catalysts, $2-C_4^=$ rearranged via metathesis to reach an equilibrium mixture of the *trans* and *cis* isomers with a ratio of 2.7:1. No other products were observed for the reaction on fresh catalysts with rhenium loadings of 4 and 8 wt.%, but with 2 wt.% loading some other gaseous products

were also present as mentioned earlier, an indication that metathesis, was accompanied by isomerization and dimerization side-reactions. This observation was more obvious for the low-loading catalyst prepared in HCl medium (catalyst N2RX-Cl). The same trend was also observed when examining the gas composition following the ethylene development stage for the experiments shown in Fig. 3. Production of $C_3^=$ on the high loading catalysts was selective and completed within the first hour, but small amounts of $1-C_4^=$, $2-C_4^=$, and $C_5^=$ formed after 1 h. It appears that reaction 3 on 2% Re-catalysts is not the only reaction to occur (low $C_3^=$ production), and that although it dominates in the initial stage, it is accompanied by other side-reactions involving dimerization propylene produced from conventional carbene species (reaction 3) can still, however, be estimated by subtraction of those from other reactions, and can be done by extrapolation of the straight line of the respective lines in Fig. 3 to reaction time zero from which the propylene is known. Another simple propylene quantification approach is by considering the amount produced within the first hour of development by ethylene.

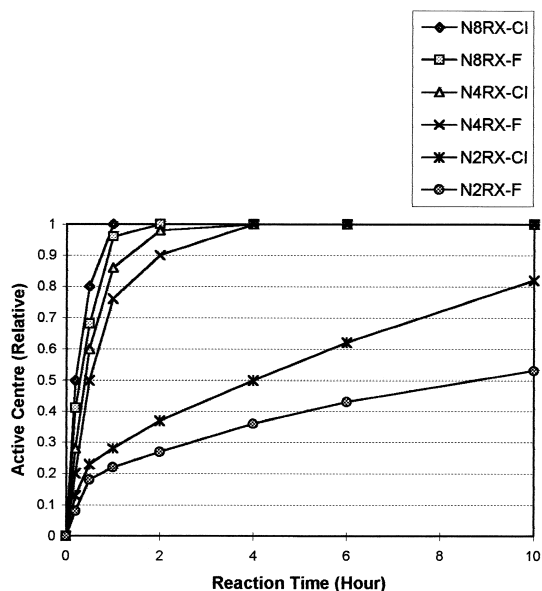


Fig. 3. Development of propylene vs. the time catalysts exposed to ethylene, the developer olefin.

Table 2

Catalyst	Active centre	
	Percentage of Re atom active	Active Re/g catalyst
<i>(a) Active centre of catalysts as determined by the chemisorption technique</i>		
N8RX-F	18.0	1.44
N8RX-Cl	19.8	1.58
N4RX-F	26.2	1.05
N4RX-Cl	27.4	1.10
N2RX-F	30.3	0.61
N2RX-Cl	34.3	0.69
<i>(b) Active centre of catalysts prepared on Al-P support as determined by the chemisorption technique^a</i>		
N8RP-F	24.7	1.97
N8RP-Cl	27.8	2.22
N4RP-F	28.5	1.14
N4RP-Cl	30.2	1.28
N2RP-F	36.0	0.72
N2RP-Cl	35.4	0.71

^aSame labeling system as for the previous catalyst series is applied.

The number of active centres determined by our chemical titration method is presented in Table 2a. They are generally higher than those reported previously by others [9–11] using indirect poisoning and reduction methods. Catalysts prepared in the presence of HCl solution, especially at low loading, show activity when compared to those prepared in aqueous solutions. Low metal loading yields more dispersed Re species and thus a higher percentage of active Re in the catalysts. The adsorption of perrhenate ions in the presence of acid was shown to lead to the formation of more Bronsted acid sites on the alumina surface, which enhances metathesis activity [24,25].

To ascertain these results and to confirm the validity of our methods, a comparable series of catalysts was prepared using another source of γ -alumina, Al-P (Procatalyse, 99 + %, BET surface area $257 \text{ m}^2 \text{ g}^{-1}$, pore volume 0.62 ml g^{-1} , 1 mm extrudate). Evaluation of these catalysts for the metathesis of propylene showed that they had higher activity although same trends of selectivity were observed. Applying the titration method reported here, the active centre concentrations in this series of catalysts were determined. The results are shown in Table 2b. The active centre concentrations for this series of catalysts (supported on Al-P) are higher than those for corresponding catalysts supported on

Al-X alumina, the percent increment in active Re being about constant through the series. A possible reason for the higher number of active centres in the Al-P supported catalyst, and, therefore, the increased metathesis activity is the difference in the surface areas of the supports, since this is a factor determining the dispersion of Re species. Table 2b also confirms that impregnation in HCl medium leads to better catalysts.

It is proposed that the chemical titration method described in this paper offers a direct means to quantify the active centres of other metathesis catalyst systems provided they are selective towards metathesis via one type of carbene species ($\text{Re} = \text{C}2$) and that both reactions 2 and 3 are made quantitative.

4. Conclusions

Heterogeneous metathesis catalysts were prepared by wet impregnation of an ammonium perrhenate solution onto high-surface-area alumina supports. A simple chemical titration method based on the sequential chemisorption of butene-2 and ethylene as chemical probes has been developed to determine the concentration of active centres. It was found that in

addition to metal loading, the preparation medium and the surface area of the support also determine the number of active centres responsible for the metathesis activity.

References

- [1] J.L. Herisson, Y. Chauvin, *Makromol. Chem.* 141 (1970) 161.
- [2] J. Kress, M. Wesolek, J.A. Osborn, *J. Chem. Soc., Chem. Commun.* (1977) 514.
- [3] K.J. Ivin, *Olefin Metathesis*, Academic Press, London, 1983.
- [4] R.H. Grubbs, C. Hoppin, *J. Am. Chem. Soc.* 101 (1979) 1499.
- [5] K. Tanaka, K. Miyahara, K. Tanaka, *Chem. Lett. (Japan)* (1980) 632.
- [6] R. Schrock, S. Rocklage, J. Wengrovius, G. Rupprecht, J. Fullman, *J. Mol. Catal.* 8 (1980) 73.
- [7] M. Ephritikhine, M.L.H. Green, R.E. McKenzie, *J. Chem. Soc., Chem. Commun.* (1976) 619.
- [8] K. Tanaka, in: Y. Imamoglu, B. Zumreoglu-Karan, A.J. Amass (Eds.), *Olefin Metathesis and Polymerization Catalysis*, NATO ASI Ser. Kluwer Academic Publishers, Dordrecht, The Netherlands, 1989.
- [9] A.A. Olsthoorn, C. Boelhouwer, *J. Catal.* 44 (1976) 207.
- [10] A.W. Aldag, C.J. Lin, A. Clark, *J. Catal.* 51 (1978) 278.
- [11] A.F. Danilyuk, V.L. Kuznetsov, V.A. Schmachkov, D.I. Kochubey, A.L. Chuvilin, Y.I. Yermakov, *J. Mol. Catal.* 46 (1988) 209.
- [12] P. Amigues, Y. Chauvin, D. Commereuc, C.T. Hong, C.C. Lai, Y.H. Liu, *J. Mol. Catal.* 65 (1991) 39.
- [13] J.A. Moulijn, J.C. Mol, *J. Mol. Catal.* 46 (1988) 1.
- [14] R.M. Edreva-Kardjieva, A.A. Andreev, *J. Mol. Catal.* 46 (1988) 201.
- [15] J.C. Mol, in: Y. Imamoglu, B. Zumreoglu-Karan, A.J. Amass (Eds.), *Olefin Metathesis and Polymerization Catalysis*, NATO ASI Ser. Kluwer Academic Publishers, Dordrecht, The Netherlands, 1989.
- [16] F.D. Hardcastle, I.E. Wacks, J.A. Horsley, G.H. Via, *J. Mol. Catal.* 46 (1988) 15.
- [17] J.C. Mol, J.A. Moulijn, *Adv. Catal.* 24 (1975) 131.
- [18] A. Ozaki, K. Kimura, *J. Catal.* 3 (1964) 395.
- [19] D.T. Laverty, J.J. Rodney, A. Steward, *J. Catal.* 45 (1976) 110.
- [20] K. Kimura, A.-I. Hideo, A. Ozaki, *J. Catal.* 18 (1970) 271.
- [21] N. Takahishi, A. Ozaki, T. Keii, *J. Am. Chem. Soc.* 97 (1975) 7489.
- [22] D. Commereuc, Y. Chauvin, *Proc. 9th. International Symp. On Olefin Metathesis*, 21–26 July, 1991, Collegeville, PA, USA, Abstracts, p. 1.
- [23] Y. Chauvin, D. Commereuc, *J. Chem. Soc., Chem. Commun.* (1992) 46.
- [24] M. Sibeijn, J.A.R. van Veen, A. Bliet, J.A. Moulijn, *J. Catal.* 145 (1994) 416.
- [25] X. Xiaoding, J.C. Mol, C. Boelhouwer, *J. Chem. Soc., Faraday Trans. 1* 82 (1986) 2707.