Use of $Re(C_5H_7O_2)_3$ in preparation of catalysts for olefin metathesis

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Received 2 March 1993; accepted 18 March 1993

New catalysts for olefin metathesis are obtained upon interaction between rhenium tris-acetylacetonate and γ-Al_2O_3 surface. After high temperature treatment in flows of O_2 and N_2 and addition of organometallic compound as a cocatalyst the activity of the resulting catalyst exceeds that of known Re/Al_2O_3 catalysts prepared by impregnation. The catalysts exhibit maximal activity at a cocatalyst surface concentration of 3×10^{-7} mol/m^2. Further increase of the cocatalyst concentration leads to deactivation.

Keywords: Metathesis; organometallic catalysts; cocatalysts; lead tetraethyl

1. Introduction

Re/Al_2O_3 catalysts are known to give the most active heterogeneous systems for olefin metathesis at low temperatures [1,2]. The conventional method of their preparation involves support impregnation with a solution of Re(VII) compounds followed by calcination in air or in O_2 flow [2–6]. In some cases, in order to increase the catalysts activity one may treat the support with organometallic compounds [2,4,6,7].

Upon calcining the initial rhenium compound decomposes and the precursor of the metathesis active center forms [2,3,5,6]. Organometallic compounds react with the catalyst producing organorhenium surface compounds, the latter being transformed subsequently into rhenium carbenes [2,4,6]. Physical methods used to examine the catalysts prepared by impregnation have shown that various Re compounds are formed on the surface of the support. Their concentration depends on many factors, including the conditions of impregnation and high temperature activation, support acidity, etc. [2–7].

The preparation of molybdenum-containing catalysts for metathesis has been recently described, where molybdenum–support interaction occurs when the impregnating solution contacts the Al_2O_3 surface [8,9]. Such catalysts have predominantly one type of surface compound [10,11].

This paper deals with a new method for preparing rhenium-containing catalysts for metathesis. It consists of anchoring the rhenium tris-acetylacetonate to the Al_2O_3 surface. The influence of some organometallic compounds on the activity of Re/Al_2O_3 catalysts prepared by different methods is also studied.

2. Experimental

Rhenium tris-acetylacetonate, $Re(C_5H_7O_2)_3$ (hereinafter $Re(acac)_3$), was prepared from ReO_3 and acetylacetonate via the procedure described in ref. [12].

To prepare the catalysts, γ-Al_2O_3 (200 m^2/g, with a particle size 0.5–0.25 mm) was treated with $Re(acac)_3$ solution in tetrahydrofuran for 8 h. Then it was washed with pure solvent and dried in a vacuum at 80°C. These materials are referred to as $Re(acac)_3/Al_2O_3$.

Reference catalysts were prepared via incipient wetness impregnation of the support with NH_4ReO_4 aqueous solutions [4]. Hereinafter the catalysts are referred to as Re_2O_7/Al_2O_3.

Before the reaction the catalyst (0.15 g) was exposed to O_2 at 550°C for 1 h, then for 1 h to N_2 and cooled down to 20°C. Then a cocatalyst ($Pb(C_2H_5)_4$, $Sn(C_4H_9)_4$, or $(C_6H_5)_2SiH_2$) solution in pentane ($C = 0.001$–0.04 mol/ℓ) was added under stirring. After 15 min the mixture temperature was increased to 50°C and the solvent was removed under N_2 flow.

The catalysts were tested for hexene-1 metathesis at 50°C, at a molar ratio olefin/Re = 5000. The activity was compared as a conversion of hexene-1 moles reacted per mole of Re by the process completion controlled on ethylene evolution. The total conversion of hexene-1 was defined from gas chromatography data (liquid phase) and from the volume of ethylene evolved. Hexene-1 conversion in all cases was never more than 25%.

IR-spectra were recorded with Specord 75IR (pellets with KBr).

3. Results

Contact of $Re(acac)_3$ solution in tetrahydrofuran with γ-Al_2O_3 surface results in solution bleaching and the support turns brown but the colour is preserved after repeated washing of the catalyst with pure solvent. By varying the concentration of the initial solution and the temperature of coating, one can obtain the catalysts with different Re contents (table 1). Acetylacetone addition to the initial solution hinders $Re(acac)_3$ adsorption by the support. If the acetylacetone concentration is 20 vol%, interaction of Re with γ-Al_2O_3 does not occur.

The IR-spectra of the catalyst and of the initial complex coincided practically completely, but the spectrum of acetylacetone adsorbed on the support is different (fig. 1).

Table 1
Hexene-1 metathesis over Re/Al_2O_3 catalysts

Catalyst	Content Re (% mass)	Specific surface (m/g^2)	SC Re[a]	Cocatalyst	SC coc[b]	C[c]
$Re(acac)_3/Al_2O_3$	1.13	199	3.05	–	–	240
	2.8	199	7.6	–	–	290
	2.8	199	7.6	$Pb(C_2H_5)_4$	3.5	1460
	2.8	199	7.6	$Sn(C_4H_9)_4$	3.5	1000
	2.8	199	7.6	$(C_6H_5)_2SiH_2$	3.0	800
	3.9	198	10.6	–	–	310
Re_2O_7/Al_2O_3	1.5	198	4.1	–	–	170
	5.0	196	13.7	–	–	180
	5.0	196	13.7	$Pb(C_2H_5)_4$	2.5	720
	5.0	196	13.7	$Sn(C_4H_9)_4$	3.0	600
	5.0	196	13.7	$(C_6H_5)_2SiH_2$	3.0	510
	14.0	179	42.0	–	–	190

[a] Re surface concentration, 10^{-7} mol Re/m^2.
[b] Cocatalyst surface concentration, 10^{-7} mol cocatalyst/m^2.
[c] Conversion, mol hexene-1/mol Re.

The initially prepared catalysts are not active in metathesis of hexene-1 at 20–50°C or of propylene at 20–250°C (propylene metathesis was performed as in ref. [8]). Due to activation in O_2 and N_2 at 550°C the activity in hexene-1 metathesis of $Re(acac)_3/Al_2O_3$ catalysts is much higher than that of Re_2O_7/Al_2O_3 independently of Re concentration (table 1). The difference in activity is more pronounced

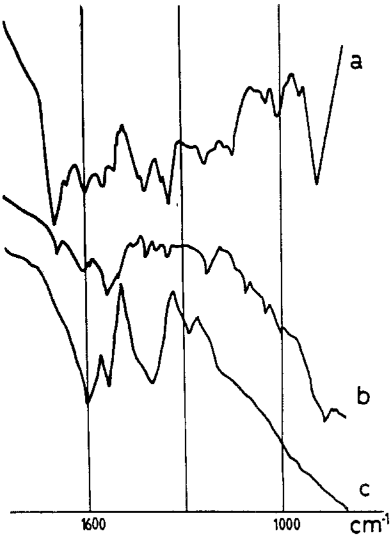

Fig. 1. IR-spectra: (a) $Re(acac)_3$, (b) $Re(acac)_3/Al_2O_3$ (2.8% Re), (c) $C_5H_8O_2/Al_2O_3$.

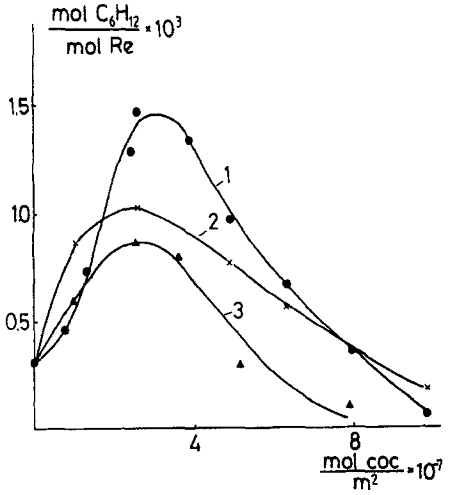

Fig. 2. The effect of cocatalysts on the Re(acac)$_3$/Al$_2$O$_3$ (2.8% Re) activity: (1) Pb(C$_2$H$_5$)$_4$, (2) Sn(C$_4$H$_9$)$_4$, (3) (C$_6$H$_5$)$_2$SiH$_2$.

after the catalysts are treated with pentane solution of Pb, Sn and Si organometallic compounds. The promoting effect increases in the sequence: $(C_6H_5)_2SiH_2 < Sn(C_4H_9)_4 < Pb(C_2H_5)_4$ (table 1, fig. 2). Considerable increase of activity is observed even when the molar ratio cocatalyst/Re (hereinafter coc/Re) is 0.05. As the cocatalyst amount is increased further the activity passes through the maximum and then falls monotonously (fig. 2). The optimal values of coc/Re are different for the catalysts with different Re content, independently of preparation method (fig. 3). Upon increase of rhenium concentration the interval of opti-

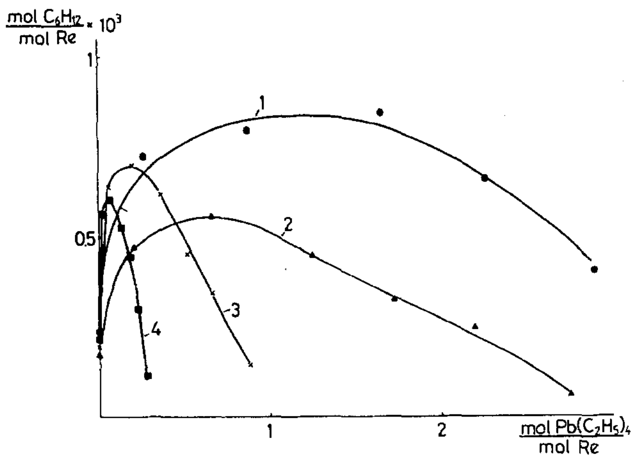

Fig. 3. The dependence of Re/Al$_2$O$_3$ catalyst activity on the molar ratio Pb(C$_2$H$_5$)$_4$/Re. (1) Re(acac)$_3$/Al$_2$O$_3$ (1.13% Re), (2) Re$_2$O$_7$/Al$_2$O$_3$ (1.5% Re), (3) Re$_2$O$_7$/Al$_2$O$_3$ (5.0% Re), (4) Re$_2$O$_7$/Al$_2$O$_3$ (14.0% Re).

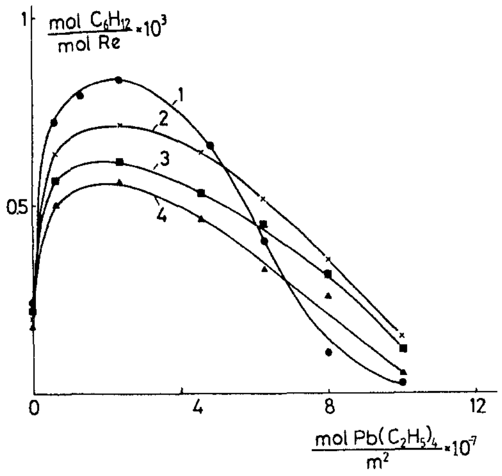

Fig. 4. The dependence of Re/Al_2O_3 catalyst activity on the $Pb(C_2H_5)_4$ surface concentration (see comments to fig. 3).

mal coc/Re ratio narrows. Thus, Re(acac)$_3$/Al_2O_3 (1.13% Re) is highly active within the wide interval of coc/Re = 0.25–2.5, while the interval for Re_2O_7/Al_2O_3 (14% Re) is 0.1.

Fig. 4 shows the dependence of catalyst activity on $Pb(C_2H_5)_4$ surface concentration. Whatever the Re content and the method of preparation, all the catalysts exhibit maximal activity, when the surface concentration is (2–3) × 10^{-7} mol of $Pb(C_2H_5)_4/m^2$. The promoting effect of other cocatalysts – $(C_6H_5)_2SiH_2$ and $Sn(C_4H_9)_4$ – is also maximal at the same concentration (fig. 2).

4. Discussion

Acetylacetonates of metals interact with OH groups on Al_2O_3 surface with ligands splitting off and evolution of free acetylacetone into the solution [13]. When MoO_2(acac)$_2$ reacts with a support the acetylacetonate ligands split off and the surface compound $(Al{-}O)_2MoO_2$ forms. In this case the catalyst IR-spectrum contains the bands typical for acetylacetonate adsorbed on Al_2O_3 surface [11]. The IR-spectra of Re(acac)$_3$/Al_2O_3 exhibit the absorption bands of the initial Re(acac)$_3$ but different from those of $C_5H_8O_2/Al_2O_3$ (fig. 1). Thus, acetylacetonate ligands coordinated to rhenium are retained in the surface compound.

Excess of acetylacetonate has been reported to hinder the interaction between Re(acac)$_3$ and support. Hence, the reaction between Re(acac)$_3$ and Al_2O_3 accompanied by the acetylacetonate ligands splitting off is reversible. Thus, anchoring of Re(acac)$_3$ to the Al_2O_3 surface can be described by the scheme

$$[Al{-}OH]_{3-x} + Re(C_5H_7O_2)_3 \longrightarrow [Al{-}O]_{3-x}Re(C_5H_7O_2)_x + (3-x)C_5H_8O_2\,,$$

where $x = 1, 2$. In the surface species at least one acetylacetonate ligand coordinated to Re is retained. In all probability, the initial form of $Re(acac)_3/Al_2O_3$ is not active in metathesis due to the Re coordination saturation. High-temperature activation results in the removal of ligands remained after coating and in the formation of metathesis active centers. $Re(acac)_3/Al_2O_3$ catalysts exceed Re_2O_7/Al_2O_3 in activity (table 1). Obviously, this is due to the higher uniformity of surface compounds and, hence, to the higher concentration of active centers.

Upon addition of organometallic compounds to the catalyst, rhenium organic surface compounds form. The latter contact with an olefin and form the metathesis active centers, metallocarbenes, easier than the initial rhenium surface oxides do [2,4,6]. The cocatalysts can also reduce the Re surface compounds which makes possible the formation of rhenium surface compounds with oxidation state of 5^+ or 6^+, active in metathesis [3,6,14,15]. $Pb(C_2H_5)_4$ provides the maximal promoting effect (fig. 2). One may explain the above phenomenon in terms of a higher reactivity of the ethyl free radical as compared to those of butyl and phenyl (fig. 2) [4]. At the optimal coc/Re ratio the activity of $Pb(C_2H_5)_4$ promoted catalyst is more than five times as high as that of the initial one (table 1).

The change in coc/Re and rhenium concentration in the catalyst showed the catalysts with different rhenium content to exhibit the maximal activity at various coc/Re ratios (fig. 3). A rise of Re concentration results in the decrease of coc/Re ratio at which the catalyst activity is a maximum, and the absence of an optimal coc/Re value for all the catalysts probably indicates the lack of selective interaction between Re surface compound and cocatalyst.

However, the relationship between the catalyst activity and cocatalyst surface concentration (fig. 4) has one maximum for all the catalysts. Regardless of preparation method and Re content all the catalysts show maximal activity, when $Pb(C_2H_5)_4$ surface concentration is 3×10^{-7} mol/m^2 (fig. 4). The same surface concentration is also optimal for other cocatalysts: $(C_6H_5)_2SiH_2$ and $Sn(C_4H_9)_4$ (fig. 2). An increase of cocatalyst surface concentration causes the activity to fall monotonously. When cocatalyst content is 10×10^{-7} mol/m^2, the catalyst activity is lower than that of the unpromoted samples (fig. 4).

Our results indicate that at a surface concentration of less than 3×10^{-7} mol/m^2, the cocatalyst interacts mostly with the support surface and the radicals evolved interact with rhenium. Thus obtained rhenium organic compounds contact with olefin and transform into the active centers of metathesis – rhenium carbenes [2,4,6]. When the cocatalyst concentration is more than 3×10^{-7} mol/m^2, the specific activity decreases due to the following factors:

(a) The blocking of the active centers becomes more and more marked due to the direct interaction of Re with a cocatalyst producing compounds with Re–O–Pb (Sn, Si) bond [16].

(b) Rhenium is reduced to the lowest oxidation state by the products of reaction between cocatalyst and support. As a result the surface compounds are not active in metathesis [2,3,14,15].

The optimal surface concentration of a cocatalyst for the $Re(acac)_3/Al_2O_3$ catalysts is close to that of rhenium (figs. 2,3). Re_2O_7/Al_2O_3 catalysts show the maximal activity within the wide range of coc/Re ratios. When rhenium content increases, the coc/Re ratio optimal for the surface decreases (fig. 3). Hence, organometallic compounds activate $Re(acac)_3/Al_2O_3$ more selectively than Re_2O_7/Al_2O_3. Accounting for the higher activity of $Re(acac)_3/Al_2O_3$ catalysts in metathesis (table 1), one may conclude that $Re(acac)_3/Al_2O_3$ contains more active centers (or their oxide precursors) as compared to Re_2O_7/Al_2O_3.

5. Conclusion

A new method of Re/Al_2O_3 catalyst preparation is proposed which consists of anchoring the rhenium tris-acetylacetonate $Re(C_5H_7O_2)_3$ to the support surface. IR-spectroscopy shows the acetylacetonate ligands coordinated to rhenium are retained intact in the surface compounds. Catalysts obtained upon activation in O_2 and N_2 suppress those obtained via impregnation procedure in activity, due to the higher concentration of the active centers. The effect of some organometallic compounds on the catalyst activity is studied. The modified catalysts are found to have the maximal activity when the cocatalyst surface concentration is 3×10^{-7} mol/m^2. Further increase of the cocatalyst concentration results in a monotonous fall of activity, since rhenium surface compounds which are non-active in metathesis start to form. The latter either contains the Re–O–Pb (Sn, Si) bond or is the over reduced rhenium organic surface compound.

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