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Olefin metathesis catalyst. Part II. Activation and characteristics of a 'molecular' tungsten unit on silica

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Abstract

A heterogeneous precursor with respect to the metathesis of olefins has been prepared by a controlled thermal reaction between π -C₅H₅W(CO)₃Cl and a silica support. Activated by iBuAlCl₂ the catalyst is reusable without any loss of tungsten. Compared to the WO₃/SiO₂ system, the new catalyst is superior with respect to conversion and initial rate. Characteristics of the precursor and activated system have been determined by different techniques, such as GC-MS, XPS, XRD and TGA-DTA.

Keywords: GC-MS; Metathesis; Olefins; Silica; Supported catalysts; Surface chemistry; Tungsten; XPS; XRD

1. Introduction

In previous reports we studied R_nCl_{3-n}SnW(CO)₃Cp (R = alkyl, phenyl n = 0–3) [1–3] and XW(CO)₃Cp (X = Cl, I) [4] derivatives as catalytic precursors for the metathesis of olefins. In combination with iBuAlCl₂/O₂, homogeneous catalytic systems with high activity and selectivity are generated.

A recent paper [5] describes the synthesis and catalytic activity of a system based on a polymer-bonded HW(CO)₃Cp precursor. After reactivation by iBuAlCl₂ the catalyst can be reused several times, however with a marked loss of tungsten.

In this paper we report on the synthesis, catalytic activity and characteristics of a heterogeneous precursor prepared by a surface reaction of ClW(CO)₃Cp with a silica support.

2. Experimental section

2.1. Materials and products

Support. Silica Polypor SPG (surface area BET: 322 m²/g, pore volume: 2.77 cm³/g) was used as support.

Products. ClW(CO)₃Cp was prepared using well known procedures [6]. (NH₄)₂WO₄ (Aldrich) is used as received. Chlorobenzene (Merck) was distilled twice from P₂O₅ in an argon atmosphere and stored on molecular sieves in an argon atmosphere. iBAC = Isobutylaluminium dichloride (Ethyl Corporation) was diluted in chlorobenzene and stored in an argon atmosphere. 2-Pentene (Janssen Ch.) 71% *trans*, 29% *cis* was distilled and stored on molecular sieves in an argon atmosphere.

Preparation of the WO_x/SiO₂ precursor. A 6.5 wt-% precursor (one free silanol/nm² [7]) is pre-

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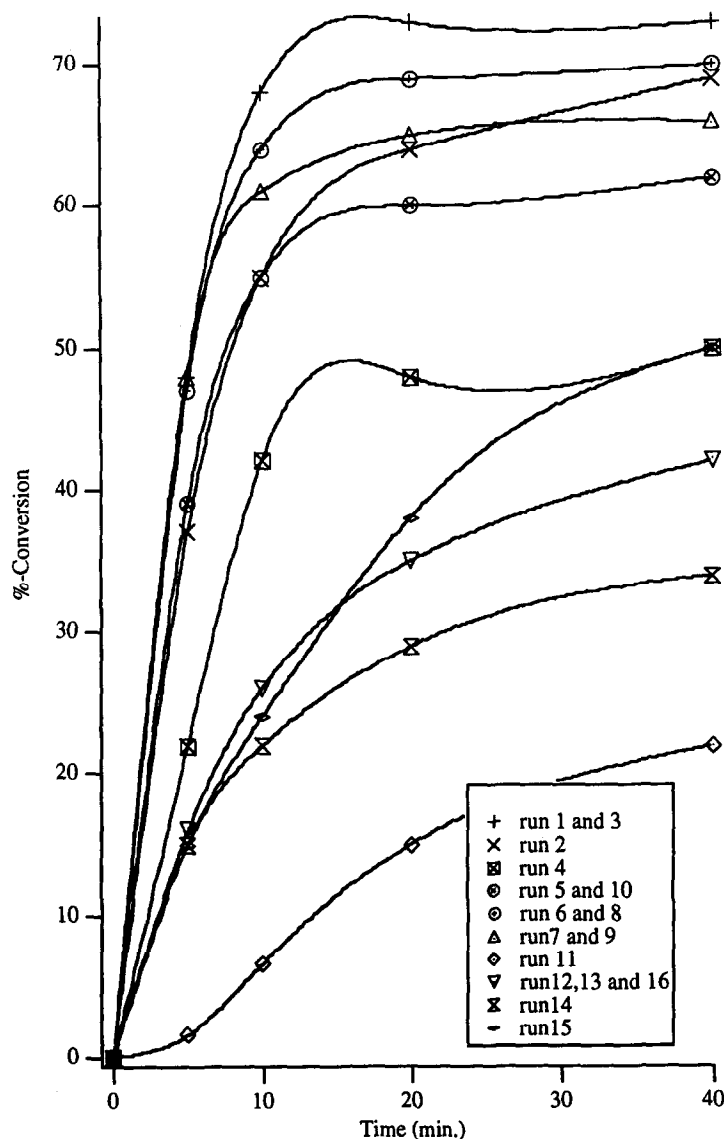


Fig. 1. % Conversion of 2-pentene vs. time for runs 1 to 16.

pared by a controlled thermal reaction between $\text{ClW}(\text{CO})_3\text{Cp}$ and the silanol groups on the silica surface. A 50 ml amount of chlorobenzene is added to 1 g of silica (Polypor SPG) in a Schlenk type reactor. Then a solution of 0.221 g $\text{ClW}(\text{CO})_3\text{Cp}$ in 5 ml of chlorobenzene is injected. The mixture is stirred vigorously and heated for 3 h at 130°C in a dry argon atmosphere. The solvent is evaporated and the reaction is completed by further heating at 130°C for 3 h. The modified silica is cooled down to room tempera-

ture in open air and then washed several times with chlorobenzene to dissolve any unreacted product.

Preparation of the WO_3/SiO_2 precursor. A WO_3/SiO_2 precursor [8] with a loading of 9 wt-% is prepared by wet impregnation of the silica support (Polypor SPG) with an aqueous solution of ammonium paratungstate of appropriate concentration. The mixture is stirred vigorously and the excess water is removed by evaporation at 80°C under reduced pressure. The sample is dried

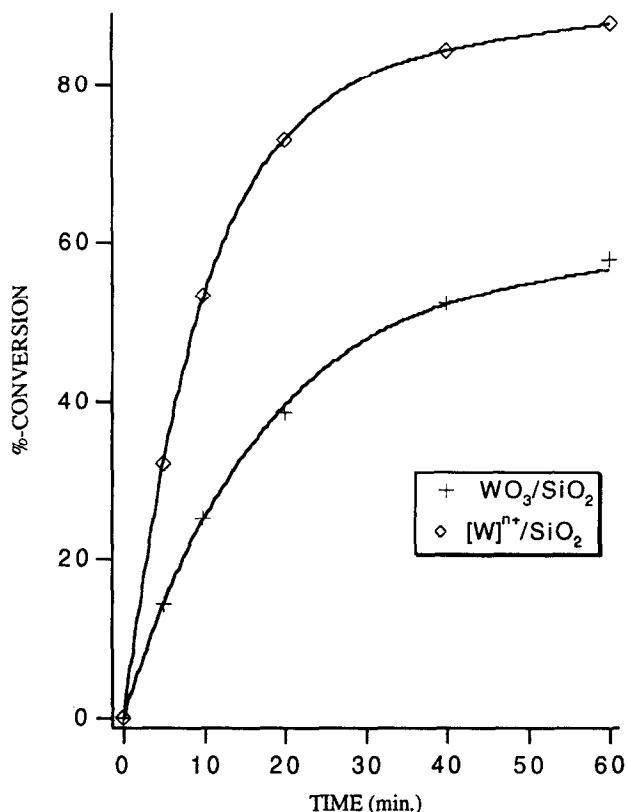


Fig. 2. % Conversion of 2-pentene vs. time in relation to the precursor: (+) WO_3/SiO_2 , (\diamond) WO_x/SiO_2 .

at 120°C for 12 h, then the temperature is raised by 1°C/min to 250°C. This temperature is maintained for 2 h and then raised by 3°C/min to 600°C. The end step is a calcination at 600°C for 8 h.

2.2. Activation procedures

2.2.1. Metathesis of 2-pentene based on precursor WO_x/SiO_2

All reactions are carried out in air and moisture free conditions in a Schlenk type equipment. An amount of 200 mg of the precursor is transferred to the Schlenk reactor, and is dried at 120°C for 2 h under reduced pressure to remove the physisorbed water. The Schlenk reactor is kept in a dry argon atmosphere and 20 ml of dry chlorobenzene is added by syringe. While vigorously stirring, the activator iBAC (0.2 ml: 2.56 M) is injected.

After an activation period of 10 min, 2-pentene (0.5 ml) is added to the reaction mixture. At time

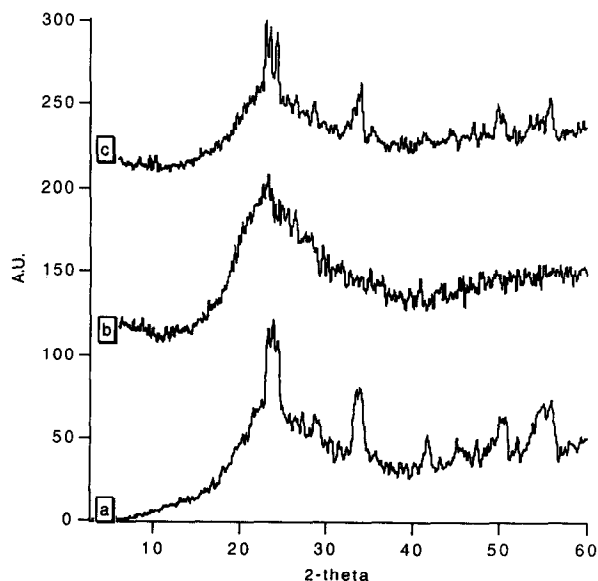


Fig. 3. X-ray diffraction patterns for: (a) WO_3/SiO_2 , (b) WO_x/SiO_2 , (c) calcinated WO_x/SiO_2 .

Table 1
Semi-quantitative XPS data of the WO_x/SiO_2 precursor

	Run 0	Run 4	Run 16	Residue
W 4f	0.20	0.20	0.20	0.001
Si 2p	1	1	1	1
Al 2s	-	0.10	1.1	0.14
Cl 2p	0.03	0.25	1.9	0.32
C 1s	0.14	1.1	14.1	14.3
O 1s	5.60	6.4	10.5	4.2

Run 0: WO_x/SiO_2 precursor before activation.

Run 4: WO_x/SiO_2 precursor after four runs.

Run 16: WO_x/SiO_2 precursor after sixteen runs.

Residue: after evaporation of the volatile components from the filtrate of Run 16.

intervals (of 5, 10, 20, 40 and 60 min) gas samples are analysed by CGC.

In all experiments, 2-pentene is used as the olefinic feed. In a clear metathesis reaction where equilibrium is reached the reaction mixture is composed of 50% 2-pentene, 25% 2-butene and 25% 3-hexene corresponding to a conversion of 50%. In our experiments a virtual conversion well above 50% can be reached due to the fact that all samples are taken in the gas phase.

2.2.2. Metathesis of 2-pentene based on precursor WO_x/SiO_2

Precursor WO_3 on silica (200 mg) is transferred to the Schlenk reactor and is dried at 120°C for 2 h under reduced pressure to remove the physorbed water. We follow the same procedure as the metathesis of 2-pentene based on precursor WO_x/SiO_2 .

2.3. Equipment and analysis procedures

2.3.1. Gas chromatography

GC analysis is performed using the following conditions: column: RSL 160; 30 m × 0.32 mm, *df*: 5 μm, temperature program: 40–128°C (4°C/min), 128–200°C (15°C/min), carrier gas: He, 100 kPa, detector: FID, gas chromatograph: Varian 4600, integrator: Vista 401.

2.3.2. XPS

The X-ray measurements are performed with a HP 5950 A ESCA spectrometer equipped with an Al $K\alpha$ X-ray source ($h\nu = 1486$ eV) and a hemispherical electron analyser. The X-ray source is operated at 12 kV and 5 mA. The samples are pumped down to 10^{-5} mbar before they are moved into the analyser chamber. The Si 2p peak with a binding energy of 103.6 eV [9] is taken as internal standard.

2.3.3. GC-MS equipment and analysis procedure

The GC-MS measurements are performed with a Varian 4600 gas chromatograph coupled with an ITD Finnigan-Matt mass detector. Silica 0.1 g (Polypor SPG) is mixed with 0.05 g $ClW(CO)_3Cp$ in dichloromethane, and after the evaporation of the solvent the sample is analysed using a self designed inlet system [10] by GC-MS. The inlet consists of a T tube in stainless steel with inside a capillary filled with the sample. The system is connected on one side by 0.2 m × 0.32 mm capillary column to the GC injector, the other side is coupled with 0.1 m × 0.32 mm empty capillary column to the transfer line of the mass detector. The whole is placed in the temperature programmed oven of the GC.

Temperature program: 40–100°C (6°C/min), 100–130°C (3°C/min), 130–160°C (2°C/min), 160–230°C (6°C/min) carrier gas: He, 100 kPa.

2.3.4. TGA-DTA

The samples are analysed with a Stanton Redcroft Thermal Analyser (STA-780 series). Gas: N_2 ; rate: 5°C/min.

2.3.5. XRD

Samples are analysed with an XRD Siemens Diffrac 5000. X-ray source: Cu $K\alpha$, operation conditions: 40 kV and 5 mA. The system has a coupled scan: $\theta/2\theta$.

3. Results and discussion

3.1. Catalytic activity

WO_x/SiO_2 precursor. Activation of the precursor, further described as WO_x/SiO_2 , by iBAC gen-

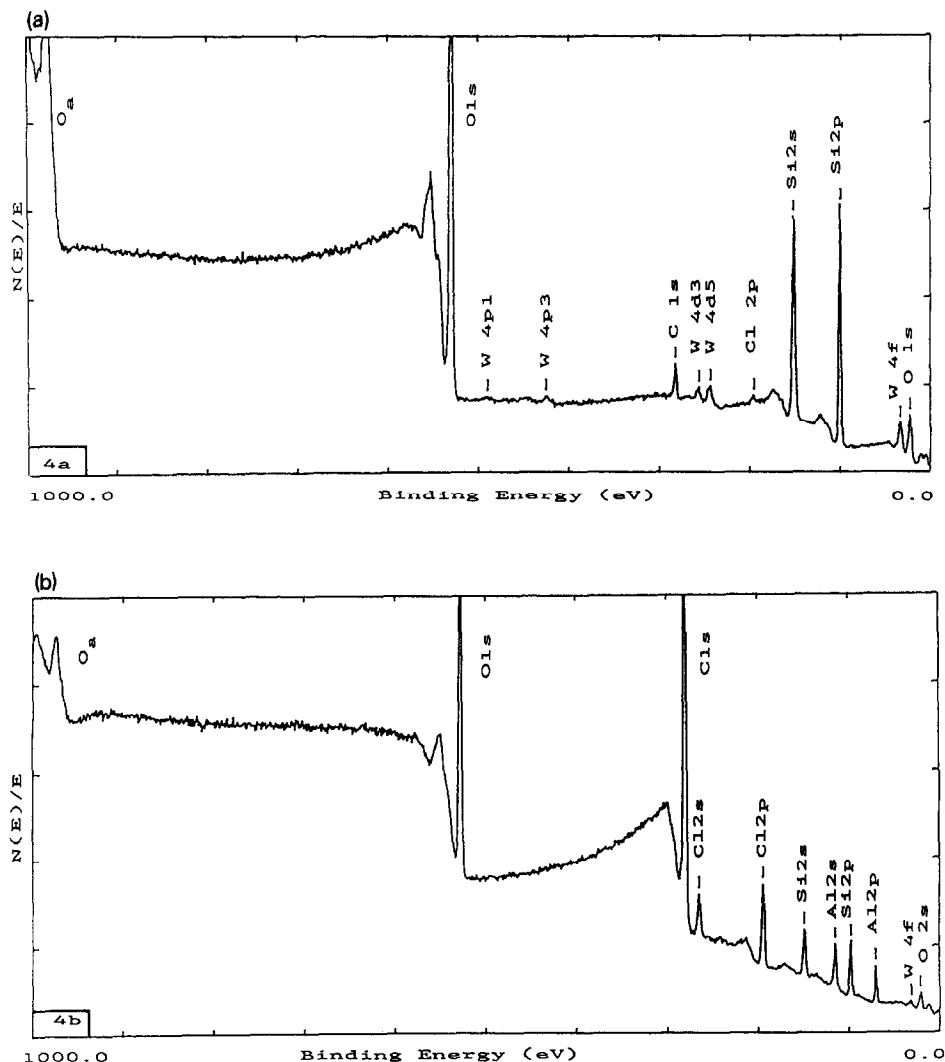


Fig. 4. XPS spectra of WO_x/SiO_2 : (a) before activation, (b) after 16 runs.

erates a catalyst with a very high activity for the metathesis of 2-pentene. However on addition, after equilibration, of a new amount of 2-pentene, no further catalytic activity is observed indicating a short-term stability of the system. Nevertheless the system can be reactivated by a repeated treatment with iBAC. In this way, several (actually 16) successive runs have been carried out without any substantial loss of activity. Only when the system has been perturbed by sampling the solid for XPS investigation, a drop in the activity is observed, however followed by an remarkable activity redress in the subsequent runs (Fig. 1).

WO_3/SiO_2 precursor. The classic WO_3/SiO_2 [11] precursor can be activated by the olefinic substrate at elevated temperatures ($T > 300^\circ\text{C}$). However chemical activation of WO_3/SiO_2 by iBAC generates an active catalytic system at room temperature. The %-conversion of 2-pentene based on the WO_3/SiO_2 and WO_x/SiO_2 precursors, respectively, is depicted in Fig. 2. The initial rate and conversion is markedly higher for the WO_x/SiO_2 system. The performance of the WO_x/SiO_2 based catalyst is undoubtedly superior to the WO_3/SiO_2 analogue.

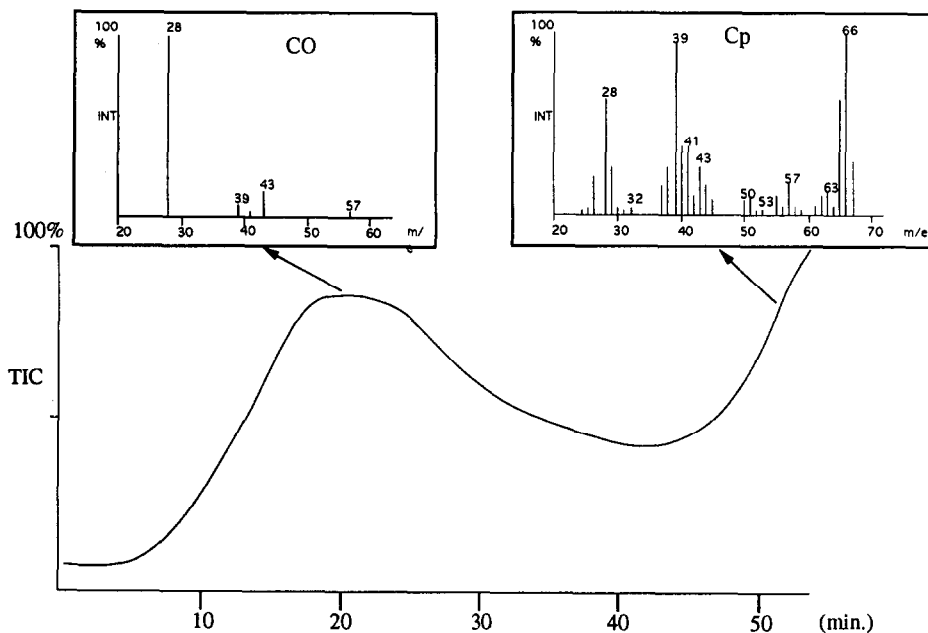


Fig. 5. Temperature programmed GC-MS of the solid state reaction between $\text{ClW}(\text{CO})_3\text{Cp}$ and silica (TIC = total ion current).

With reference to the characteristics of the precursors (see following section) the catalytic performance of the two systems can be related to the dispersion and physical state of the tungsten oxide species on the silica surface. The high dispersive monolayer structure of the WO_x species promotes the generation of a highly active catalyst.

3.2. Characteristics of precursors and activated systems

3.2.1. XPS and XRD characterization

From the XPS spectra can be deduced that the structural unit on the silica surface is probably only composed of tungsten and oxygen. However the XPS carbon region is obscured by adventitious undefined adsorbed carbonaceous species [12], the complete absence of carbonyls and cyclopentadiene in the coordination sphere of tungsten can only be definitely proved by a combination of the GC-MS, TGA-DTA and XPS results. Furthermore in a separate angle resolved and depth profiling XPS study [13] the silica surface has been characterized as composed of structural units of



with [O] = oxo or hydroxo.

The high uniform dispersion of tungsten on the silica surface indicates a monolayer structure. This has been confirmed by X-ray diffraction measurements (Fig. 3b). No crystallites are detected proving the amorphous character of the layered structure.

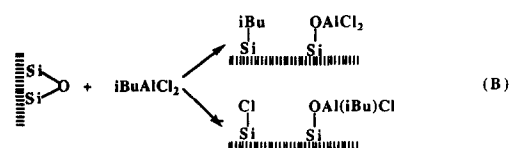
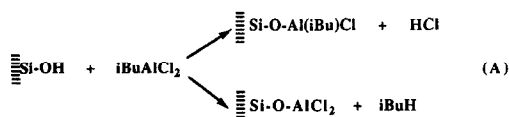
This is in marked contrast to the WO_3/SiO_2 precursor prepared by the wet impregnation method. From the XRD spectrum can be deduced that the silica surface is covered by WO_3 microcrystallites (average diameter of 20 nm) [14] with an orthorhombic crystal structure (Fig. 3a).

Calcination of precursor WO_x/SiO_2 above 500°C results in a condensation and probably migration of the tungsten structural units. The XRD spectrum clearly shows that by this thermal treatment, the initial amorphous tungsten monolayer on silica is transformed in a crystalline WO_3 phase with triclinic microcrystallites (Fig. 3c).

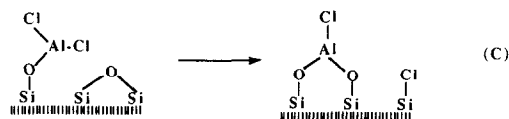
A semi-quantitative XPS analysis of the WO_x/SiO_2 samples after a defined number of runs (Table 1) indicates no substantial leaching of tungsten from the surface. Furthermore an XPS analysis of the residue after evaporation of the reaction mixture detects only traces of tungsten confirming the firm anchoring of the tungsten species to the silica support.

Furthermore in the course of the catalytic activity experiments an enrichment of the surface with aluminium, chlorine and carbon is observed.

At the end (after 16 runs) a Si:Al ratio of 1:1 is obtained together with a substantial loading of the surface with chlorine and carbon derivatives (Fig. 4). Chemisorption of organo aluminium species on silica is a known phenomenon [15] where silanol (A) as well as siloxane (B) groups are involved.



In addition structural changes on the surface are induced in the neighbourhood of adsorbates by cleaving siloxane bonds with formation of O–Al–O bridges (C).



The composition of the gas phase (see further) in the catalytic activity experiments can be related to the presence of the above defined surface species. The fragmentation of isobutane to methane and ethane is an indication for the superacid character of certain surface centres (aprotic superacids). Saturated organic derivatives known as extremely weak bases only interact with superacids by an attack of the strong electrophilic Lewis

acid centres on the C–H and C–C σ bonds [16,17].

3.2.2. GC–MS and TGA–DTA

In the thermogram and chromatogram of the WO_x/SiO_2 precursor only the escape of adsorbed water has been observed in the temperature range 50–250°C. This indicates that in the course of the preparative procedure all carbonyls and cyclopentadiene are removed.

As a supplementary check, the solid state reaction between silica and $ClW(CO)_3Cp$ has been monitored by the same techniques. In the temperature range 100–150°C the carbonyl groups are progressively split off, while the cleavage of the cyclopentadiene group starts at about 165°C (Fig. 5). This observations firmly confirm the XPS results.

Furthermore a GC–MS study of the volatile reaction products formed in the activation of WO_x/SiO_2 with iBAC reveals the presence of iC_4H_{10} , C_2H_6 , CH_4 and HCl , in addition to the metathesis products.

Following the evolution of the gas phase components (Table 2) in the course of the catalytic activity runs we notice that :

- the relative concentrations of CH_4 and C_2H_6 are related to the concentration of iC_4H_{10} ;
- the amount of iC_4H_{10} decreases in the metathesis series;
- the amount of iC_4H_{10} is related to the catalytic activity.

Methane and ethane are the result of the fragmentation of iC_4H_{10} caused by the action of the superacid centres on the silica surface (see above).

Observation b leads to the conclusion that reaction A forms a considerable contribution to the iC_4H_{10} amount in the initial runs. However at the end of the series, a second mechanism directly related the catalytic activity, becomes the almost exclusive source of iC_4H_{10} .

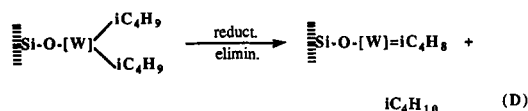
This can be related to the activation cycle of the WO_x/SiO_2 precursor where reductive elimination in an isobutylated species generates catalytically

Table 2
Relative ^a amounts CH₄, C₂H₆, iC₄H₁₀ in the gas phase vs. time

Compounds	Relative amount (%)								
	Run 1 times (min)			Run 3 times (min)			Run 16 times (min)		
	5	10	20	5	10	20	5	10	20
CH ₄	21	25	26	11	12	16	8	11	11
C ₂ H ₆									
iC ₄ H ₁₀									

^a Calibration with respect to [2-pentene] + [2-butene] + [3-hexene].

active tungsten isobutene with the joint elimination of isobutane (D).



4. Conclusion

A tungsten oxide species is chemisorbed on the surface by a controlled thermal reaction of ClW(CO)₃Cp with silica. The structural tungsten units are anchored to the surface by Si–O–W bonds in a monolayer arrangement. On chemical activation, the WO_x/SiO₂/iBAC system shows a significant higher initial rate and conversion for the metathesis of 2-pentene than the classic WO₃/SiO₂/iBAC system.

This can be directly related to the surface structure of the precursors, ‘molecular’ WO_x units compared to orthorhombic WO₃ microcrystallites.

Furthermore the WO_x/SiO₂/iBAC catalytic system can be reactivated unrestrictedly since no leaching of tungsten from the surface has been observed in the course of the numerous runs.

Acknowledgements

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