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Catalytic activity of supported tungsten phenoxide complexes in olefin metathesis; XPS characterization; application of molecular modelling to surface organometallic chemistry

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Abstract

Heterogeneous catalysts with respect to the metathesis of olefins has been prepared by a controlled thermal reaction between $W(O-2,6-C_6H_3X_2)_2Cl_4$ ($X = t\text{-Bu, Me, Br, and Cl}$) or $W(MBPD)Cl_4$ and a silica support. Surface characteristics of the powder catalysts and a model catalyst have been determined by conventional XPS and Angle-Resolved XPS (AR-XPS). The catalytic activity has been related to the structure of the molecular entities on the surface of the precursor. Furthermore, a model for hydroxylated silica is described. The surface structure ($\equiv SiO$)₂ $W(O-2,6-C_6H_3X_2)_2Cl_2$ is modeled to determine the preferred arrangement of the tungsten diphenoxide species on the hydroxylated support.

Keywords: Metathesis; Silica; Tungsten phenoxide; Angle-resolved XPS; XPS; Model catalyst; Computer modelling; Surface organometallic chemistry

1. Introduction

During the last decade, tungsten(VI)phenoxides of the type $WCl_{6-x}(OAr)_x$ ($x = 0-4, 6$) or $W(O)Cl_{4-y}(OAr)_y$ ($y = 0-4$) have been reported. They are known to provide very active metathesis catalysts for linear, cyclic as well as functionalized olefins. These complexes require the addition of a cocatalyst, e.g., R_xAlCl_{3-x} , R_4Sn or an alkyltinhydride, to generate the active catalyst species in situ [1–9].

Complexes of the type $WCl_5(OAr)$ ($R =$ substituted phenyl) have been found to initiate ring opening polymerization of dicyclopentadi-

ene without any co-catalyst. Their activities are, however, lower than when they are associated with a reducing organometallic co-catalyst [10].

An improvement was made by alkylation of $WCl_4(OAr)_2$ complexes with R_2Mg which leads to $WCl(OAr)_2(CR^1R^2)R^3$ [11,12].

The phenoxide groups present in these tungsten catalysts increase the solubility and stability of the complexes, and more importantly, they can be used to influence the steric and electronic properties of the reaction site.

On the other hand Weis et al. [13] synthesized heterogeneous catalysts via protonation of the corresponding tungsten alkylidyne complexes by Brønsted acids. The electron withdrawing ligands, crucial for good catalytic activ-

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ity [14–16] would be provided by the surface siloxygroups.

In this paper we report on the synthesis, XPS characterization and catalytic activities of heterogeneous tungsten phenoxide complexes prepared by a surface reaction of $WCl_4(OAr)_2$ with a silica support.

Unfortunately, XPS spectra of insulating materials, e.g., WO_3/SiO_2 [17] suffer from signal distortion and broadening with loss of resolution due to inhomogeneous sample charging.

This prevents a straight forward analysis of the signal envelopes whereby much of the hidden information is not available for interpretation. However, detrimental charging can be avoided by using a model support consisting of a silicon or aluminium crystal covered by an oxide layer typically a few nanometers thick [17,18]. The active phase is usually deposited onto the support by the same procedure as for the powder catalysts.

In this way using a model catalyst for characterization, inhomogeneous sample charging is avoided producing spectra of a much better resolution and reliable peak shape.

Furthermore, a computer modelling study of surface tungsten phenoxide complexes has been performed. As an adjunct to experimental surface studies, computer models of organometallic species on surfaces that are based on structures of both molecular analogues and lattices parameters of oxides are potentially useful tools in considering factors that govern the accommodation of a molecular species on a relatively rigid surface.

Studies of such surface bound species can provide useful information leading to a better understanding of the elementary steps of heterogeneously catalyzed reactions.

2. Experimental section

Organometallic reactions were carried out under argon using standard anaerobic techniques.

2.1. Materials and reagents

2.1.1. Support

Silica Polypor SPG (surface area BET: 322 m^2/g , pore volume: 2.77 cm^3/g) is used as support.

2.1.2. Reagents

Chlorobenzene (Merck) is distilled twice from P_2O_5 in an argon atmosphere and stored on molecular sieves in an argon atmosphere.

iBAC = isobutylaluminiumdichloride (Ethyl Corporation) is diluted in chlorobenzene and stored in an argon atmosphere.

2-Pentene (Janssen Ch.) 71% *trans*, 29% *cis* is distilled and stored on molecular sieves in an argon atmosphere.

n-hexane is dried by distillation over Na-wire under argon and stored under argon over 5 Å molecular sieves.

WCl_6 (Aldrich) is purified by sublimation in vacuo, before use.

The substituted phenols (Aldrich) are used as received.

MBPD (5,5'-dimethoxy-3,3'-di-*t*-butyl-2,2'-diphenyldiol) has been provided by DSM, Geleen, and used as received.

The complexes $W(O-2,6-C_6H_3X_2)_2Cl_4$ (X = Me, *t*-Bu, Br, Cl) are prepared using well known procedures [19]. The $W(MBPD)Cl_4$ complex has been prepared in the same way.

2.1.3. Synthesis

Preparation of the $(\equiv SiO)_2W(O-2,6-C_6H_3X_2)_2(OH)_2$ precatalysts (Scheme 1).

The precatalysts $(\equiv SiO)_2W(O-2,6-C_6H_3X_2)_2(OH)_2$ (X = Me, *t*-Bu, Br, Cl) and $(\equiv SiO)_2W(MBPD)(OH)_2$ has been prepared by a controlled thermal reaction between the tungsten complex and the silanol groups on the silica surface.

The silica (Polypor SPG) is preheated at 473 K for 2 h under vacuum to control the OH density concentration at about 5 OH nm^{-2} (nearly full monolayer). An amount of 40 ml of *n*-hexane is added to 5 g of silica (Polypor SPG)

in a Schlenk type reactor. Then a solution of 0.5 g $W(O-2,6-C_6H_3X_2)_2Cl_4$ in 40 ml of *n*-hexane is added within a period of 15 min. The mixture is stirred and refluxed for 4 h in a dry argon atmosphere. After separation of the residual solution, the modified SiO_2 is washed with *n*-hexane, under dry-argon atmosphere.

Removing the *n*-hexane under reduced pressure, the precatalysts are exposed to open air to convert the remaining Cl-ligands into hydroxyl groups. Afterwards, the catalysts are dried at 393 K for 2 h and stored in an argon atmosphere.

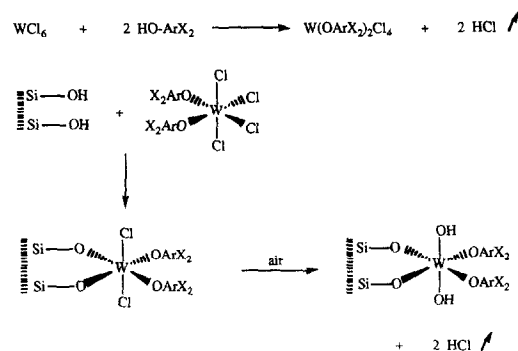
For the precatalyst ($\equiv SiO_2$)₂W(MBPD)(OH)₂, 0.5 g W(MBPD)Cl₄ in 40 ml of *n*-hexane is added to a suspension of 5 g of silica (Polypor SPG) and 40 ml of *n*-hexane in a Schlenk type reactor followed by the same procedure as for the ($\equiv SiO_2$)₂W(O-2,6-C₆H₃X₂)₂(OH)₂ precatalysts.

Preparation of the ($\equiv SiO_2$)₂W(O-2,6-C₆H₃Br₂)₂(OH)₂ model catalyst. The model support, a Si (100) single crystal (10 × 10 × 1 mm) was oxidized at 773 K in air for 12 h and cooled under argon atmosphere. Then a solution of 0.5 g W(O-2,6-C₆H₃Br₂)₂Cl₄ in 40 ml of *n*-hexane is added within a period of 15 min., followed by the same procedure as for the ($\equiv SiO_2$)₂W(O-2,6-C₆H₃X₂)₂(OH)₂ powder precatalysts.

2.2. Activation procedures

All reactions are carried out in air and moisture free conditions in a Schlenk type equipment. An amount of 100 mg of the precatalyst 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 dry chlorobenzene is added by syringe. While stirring, the activator iBAC (2.56 M) is injected.

After an activation period of 10 min, 2-pentene (0.275 ml) is added to the reaction mixture. At time intervals (5, 10, 20, 40 and 60 min) gas samples are analyzed by GC.



Scheme 1. Preparation steps of heterogeneous tungsten diphenoxide complexes.

In all experiments, 2-pentene is used as the olefinic feed. In a clean 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 gasphase.

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

XPS spectra were obtained with a Perkin Elmer PHI 5500 spectrometer equipped with a monochromatized AlKα source ($h\nu = 1486$ eV), a hemispherical analyzer connected to a multi channel detector and a manipulator which enables the variation of the take-off angle between 0 and 90°. XPS spectra of the model precursor were measured with 11.75 eV pass energy and those of the powder precursor, immobilised on an adhesive tape, at 48.50 eV pass energy. The C 1s or the Si 2p peak with a

Table 1

Bonding energy (eV) of the elements in the $W(O-2,6-C_6H_3t-Bu_2)_2Cl_4$ complex and in $(\equiv SiO)_2W(O-2,6-C_6H_3t-Bu_2)_2(OH)_2$ calibrated towards C 1s = 284.60 eV

Element	$WCl_4(O-2,6-C_6H_3t-Bu_2)_2$		$(\equiv SiO)_2W(OH)_2(O-2,6-C_6H_3t-Bu_2)_2$	
	B.E. (eV)	Assignment	B.E. (eV)	Assignment
C 1s	284.60	C (contamination)	284.60	C (contamination)
	285.53	C (phenyl)	285.68	C (phenyl)
O 1s	532.47	O of W–O–Ar	532.55	O^{2-} of [W]–OH, [W]–O–Ar
			533.88	O^{2-} of SiO_2 , Si–O–[W]
W 4f 7/2	36.26	W^{6+} (doublet)	37.34	$[W]^{n+}$ doublet
4f 5/2	38.35		39.44	
Cl 2p 3/2	198.87	Cl of W–Cl	–	–
2p 1/2	200.45			
Si 2p	–	–	104.65	Si^{4+} of SiO_2

Table 2

Bonding energy (eV) of the elements in the $W(O-2,6-C_6H_3Me_2)_2Cl_4$ complex and in $(\equiv SiO)_2W(O-2,6-C_6H_3Me_2)_2(OH)_2$ calibrated towards C 1s = 284.60 eV

Element	$WCl_4(O-2,6-C_6H_3Me_2)_2$		$(\equiv SiO)_2W(OH)_2(O-2,6-C_6H_3Me_2)_2$	
	B.E. (eV)	Assignment	B.E. (eV)	Assignment
C 1s	284.60	C (contamination)	284.60	C (contamination)
	285.79	C (phenyl)	285.62	C (phenyl)
O 1s	532.86	O of W–O–Ar	532.79	O^{2-} of [W]–OH, [W]–O–Ar
				O^{2-} of SiO_2 , Si–O–[W]
W 4f 7/2	36.72	W^{6+} (doublet)	36.51	$[W]^{n+}$ doublet
4f 5/2	38.84		38.67	
Cl 2p 3/2	199.05	Cl of W–Cl	–	–
2p 1/2	200.67			
Si 2p	–	–	103.95	Si^{4+} of SiO_2

Table 3

Bonding energy (eV) of the elements in the $W(MBPD)Cl_4$ complex and in $(\equiv SiO)_2W(MBPD)(OH)_2$ calibrated towards C 1s = 284.60 eV

Element	$WCl_4(MBPD)$		$(\equiv SiO)_2W(OH)_2(MBPD)$	
	B.E. (eV)	Assignment	B.E. (eV)	Assignment
C 1s	284.60	C (contamination)	284.60	C (contamination)
	285.71	C (biphenyl)	285.67	C (biphenyl)
O 1s	531.88	O^{2-} of W–O–Ar	532.63	O^{2-} of [W]–OH, [W]–O–Ar,
	533.08	O^{2-} of Ar–OMe		O^{2-} of SiO_2 , Si–O–[W]
W 4f 7/2	36.34	W^{6+} (doublet)	36.81	$[W]^{n+}$ doublet
4f 5/2	38.49		39.00	
Cl 2p 3/2	199.05	Cl of W–Cl	–	–
2p 1/2	200.64			
Si 2p	–	–	104.60	Si^{4+} of SiO_2
H NMR of $WCl_4(MBPD)$ in C_6D_6			δ 6.84 (d, $J = 3$ Hz, 2H, 2 ArH)	
			δ 6.40 (d, $J = 3$ Hz, 2H, 2 ArH)	
			δ 3.31 (s, 6H, 2 –OC H_3)	
			δ 1.58 (s, 18H, 2 –C(CH_3) $_3$)	

Table 4

Bonding energy (eV) of the elements in the $W(O-2,6-C_6H_3Br_2)_2Cl_4$ complex and in $(\equiv SiO)_2W(O-2,6-C_6H_3Br_2)_2(OH)_2$ calibrated towards C 1s = 284.60 eV

Element	$WCl_4(O-2,6-C_6H_3Br_2)_2$		$(\equiv SiO)_2W(OH)_2(O-2,6-C_6H_3Br_2)_2$	
	B.E. (eV)	Assignment	B.E. (eV)	Assignment
C 1s	284.60	C (contamination)	284.60	C (contamination)
	285.69	C (phenyl)	285.68	C (phenyl)
O 1s	532.62	O of W–O–Ar	532.55	O^{2-} of [W]–OH, [W]–O–Ar
			533.88	O^{2-} of SiO_2 , Si–O–[W]
W 4f 7/2	36.61	W^{6+} (doublet)	37.34	$[W]^{n+}$ doublet
	38.81		39.44	
Br 3d 5/2	70.73	Br of $HOC_6H_3Br_2$	70.50	Br of $HOC_6H_3Br_2$
	71.72		71.50	
Cl 2p 3/2	199.35	Cl of W–Cl	–	–
	200.94			
Si 2p	–	–	104.65	Si^{4+} of SiO_2

binding energy of respectively 284.6 eV and 103.60 eV is taken as internal standard. The spectra were accumulated, smoothed, and integrated with the PHI-ACCESS program. Constraints suited to impose the spin doublet character of the line pairs, e.g., ratios of line widths and intensities, binding energy splitting, had to be imposed by the user.

3. Results and discussion

3.1. Characterization of the tungsten complexes

In all cases of precatalyst preparation, HCl is evolved, indicating that the chloride ligands of

the tungsten phenoxide complexes are replaced by oxygen's from the surface hydroxyls, generating grafted surface organometallic complexes.

Van Roosmalen et al. [20] have previously studied the reactions between WCl_6 and $WOCl_4$ and silica gels, and suggest that two hydroxyls react with one tungsten species. In accordance, the mole ratio HCl evolved/ $WCl_4(OArX_2)_2$ amounts to two, indicating also that two hydroxyls react with one tungsten phenoxide complex.

The nature of the grafted molecular entities on the silica surface has been studied by XPS. The XPS data for each tungsten complex are collected in Tables 1–5. No chlorine signal is

Table 5

Bonding energy (eV) of the elements in the $W(O-2,6-C_6H_3Cl_2)_2Cl_4$ complex and in $(\equiv SiO)_2W(O-2,6-C_6H_3Cl_2)_2(OH)_2$ calibrated towards C 1s = 284.60 eV

Element	$WCl_4(O-2,6-C_6H_3Cl_2)_2$		$(\equiv SiO)_2W(OH)_2(O-2,6-C_6H_3Cl_2)_2$	
	B.E. (eV)	Assignment	B.E. (eV)	Assignment
C 1s	284.60	C (contamination)	284.60	C (contamination)
	285.98	C (phenyl)	285.62	C (phenyl)
O 1s	532.43	O of W–O–Ar	532.79	O^{2-} of [W]–OH, [W]–O–Ar O^{2-} of SiO_2 , Si–O–[W]
			36.51	$[W]^{n+}$ doublet
W 4f 7/2	36.43	W^{6+} (doublet)	36.51	$[W]^{n+}$ doublet
	38.57		38.67	
Cl 2p 3/2	198.85	Cl of W–Cl	–	–
	200.40			
Cl 2p 3/2	200.15	Cl of $HOC_6H_3Cl_2$	200.28	Cl of $HOC_6H_3Cl_2$
	201.70		201.83	
Si 2p	–	–	103.24	Si^{4+} of SiO_2

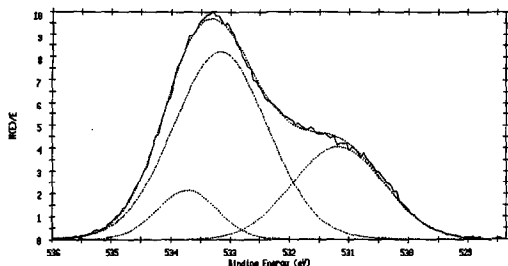


Fig. 1. XPS spectra of the O 1s region of the (\equiv SiO_2) $_2$ W(OH) $_2$ (O-2,6-C $_6$ H $_3$ Br $_2$) $_2$ /Si(100) model catalyst.

detected confirming the complete hydrolysis of the tungsten complexes.

3.2. Characterization of the model catalyst

In earlier work [17,18] we have proved that spectra of the model precatalyst shows a much better resolution than the powder precatalyst.

The XPS spectrum of O 1s photoelectrons (Fig. 1) is characterized by a strong asymmetry indicating multiple band structure. The O1s band was resolved and satisfactory approximation of the signal envelope is obtained on superposition of a minimum of three bands: at 533.74 eV, at 533.18 eV and at 531.30 eV. The peak at 533.74 eV is assigned to O $^{2-}$ of the W–O–Ph bonding. The peak at 533.18 eV coincides with the O 1s electron peak for SiO $_2$ since the oxygen atom in the silica matrix produce the basic contribution to the spectrum. The peak at 531.30 eV is assigned to O $^{2-}$ of the W–OH bonding.

A satisfactory approximation of the C1s band (Fig. 2) is obtained on superposition of a mini-

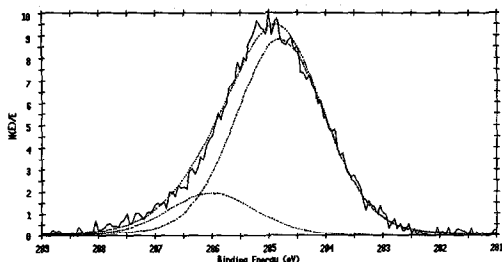


Fig. 2. XPS spectrum of the C 1s region of the (\equiv SiO_2) $_2$ W(OH) $_2$ (O-2,6-C $_6$ H $_3$ Br $_2$) $_2$ /Si(100) model catalyst.

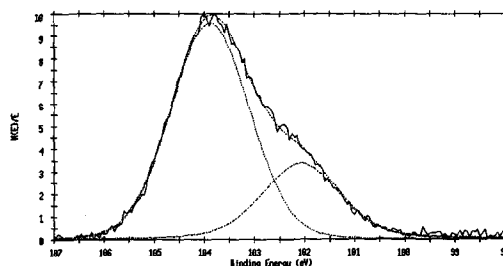


Fig. 3. XPS spectrum of the Si 2p region of the (\equiv SiO_2) $_2$ W(OH) $_2$ (O-2,6-C $_6$ H $_3$ Br $_2$) $_2$ /Si(100) model catalyst.

num of two bands: at 286.00 eV and at 284.80 eV. The latter is assigned to physisorbed carbon contamination. The peak at 286.00 eV is assigned to carbon of the phenyl group.

During deconvolution of the Si2p envelope (Fig. 3) a very good approximation is reached on superposition of a minimum of two bands. Each band represents a not resolved 2p $_{3/2}$ –2p $_{1/2}$ doublet. The photoelectron peak with an E_b = 103.88 eV is assigned to Si $^{4+}$ of the SiO $_2$ matrix, which is consistent with results in literature [17,18]. The second peak with an E_b = 102.08 eV is assigned to Si $^{4+}$ of Si–O–W units [21].

Finally, applying the Scofield W 4f $_{5/2}$:W 4f $_{7/2}$ intensity ratio of 0.78 and E_b splitting of 2.1 eV [22], the deconvolution of the W 4f envelope (Fig. 4) leads to a satisfactory approximation by using two bands. Each band consist of a W 4f $_{5/2}$ –W 4f $_{7/2}$ doublet. For the (\equiv SiO_2) $_2$ W(O-2,6-C $_6$ H $_3$ Br $_2$) $_2$ (OH) $_2$ model catalyst the W 4f $_{7/2}$ binding energies, resp. 35.56 eV and 33.76 eV, indicate two different Si–O–W units showing a low energy shift of respectively

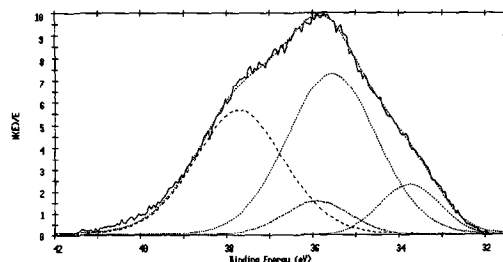
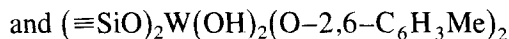
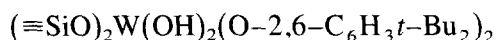


Fig. 4. XPS spectrum of the W 4f region of the (\equiv SiO_2) $_2$ W(OH) $_2$ (O-2,6-C $_6$ H $_3$ Br $_2$) $_2$ /Si(100) model catalyst.

1.23 eV and 3.03 eV with respect to the $\text{WO}_3/\text{SiO}_2/\text{Si}$ (100) system [17]. This means that the effective charge on tungsten in the $(\equiv \text{SiO})_2\text{W}(\text{O}-2,6\text{-C}_6\text{H}_3\text{Br}_2)_2(\text{OH})_2$ model catalyst is lower than in $\text{WO}_3/\text{SiO}_2/\text{Si}$ (100) system.

3.3. Catalytic activity

3.3.1.



Activation of $(\equiv \text{SiO})_2\text{W}(\text{OH})_2(\text{O}-2,6\text{-C}_6\text{H}_3\text{t-Bu}_2)_2$ by iBAC generates a catalyst with an excellent activity for the metathesis of 2-pentene with a high initial rate. On addition, after equilibration, of a new amount of 2-pentene, further catalytic activity is observed indicating a long-term stability of the system. When after the third addition of 2-pentene, the catalytic activity is drastically decreased, the system can be reactivated by a repeated treatment with iBAC. The catalytic activity as function of time for different amounts of iBAC is given in Table 6.

Increasing the iBAC/complex ratio results in a decreasing initial rate of the reaction (Fig. 5). These results supports the hypothesis [23] that high amount of Lewis acids can act as poisons for the metathetic active sites of the catalyst.

A poor catalytic activity (conversion $\leq 5\%$) is observed with Et_2AlCl or Et_3Al as a cocatalyst.

Table 6

Catalytic activity towards 2-pentene of the $(\equiv \text{SiO})_2\text{W}(\text{OH})_2(\text{O}-2,6\text{-C}_6\text{H}_3\text{t-Bu}_2)_2$ /iBAC system using a variable amount of cocatalyst

Time (min.)	0.1 ml iBAC	0.2 ml iBAC	0.4 ml iBAC
5	50.76	37.10	20.45
10	59.34	50.96	39.22
20	61.16	61.69	52.44
40	64.44	61.83	62.55
60	65.77	69.30	66.05
120	66.80	72.05	69.16
180	67.77	71.51	71.13

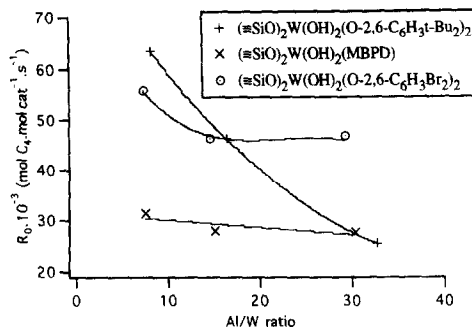
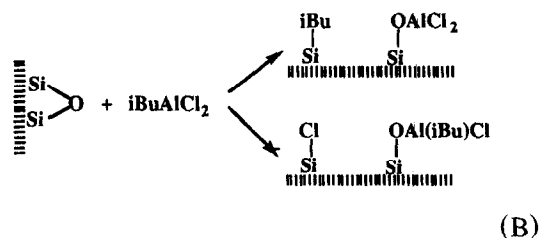
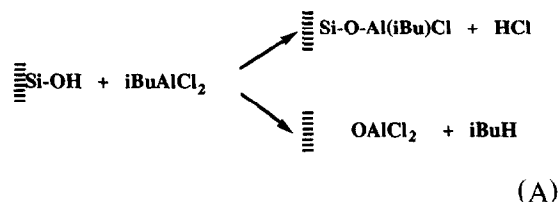
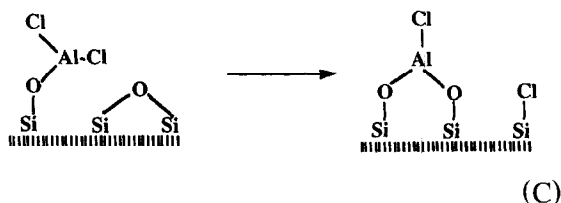


Fig. 5. Initial rate of the 2-pentene metathesis versus the Al/W ratio.

The $(\equiv \text{SiO})_2\text{W}(\text{OH})_2(\text{O}-2,6\text{-C}_6\text{H}_3\text{Me}_2)_2$ system gives analogous results (Fig. 6). Furthermore, chemisorption of organo aluminium species on silica is a known phenomenon [24] 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).



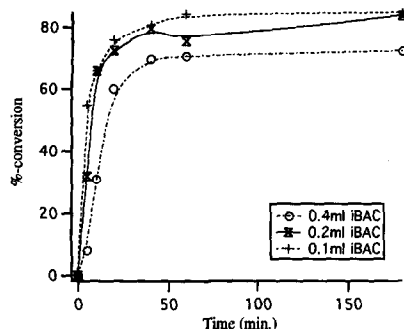
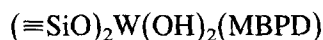


Fig. 6. %-conversion towards 2-pentene of the $(\equiv \text{SiO})_2\text{W}(\text{OH})_2(\text{O}-2,6-\text{C}_6\text{H}_3\text{Me}_2)_2$ /iBAC system using a variable amount of cocatalyst.

This means that the given Al/W ratio (Fig. 5) are formal ratios, since a part of the iBAC reacts with the support and is in this way not available for activation of the catalyst.

3.3.2.



Activation of $(\equiv \text{SiO})_2\text{W}(\text{OH})_2(\text{MBPD})$ by iBAC generates a catalyst with a medium activity for the metathesis of 2-pentene. When the amount of iBAC is increased, no influence on the initial rate is observed, Table 7.

The latter has also no impact on the catalytic activity (Fig. 5). An explanation for this behaviour can be found in the sterical hindering of the active sites by the MBPD ligand. An important observation is that when the amount of the olefinic feed is doubled, the catalyst retains its initial rate.

Table 7

Catalytic activity towards 2-pentene of the $(\equiv \text{SiO})_2\text{W}(\text{OH})_2(\text{MBPD})$ /iBAC system using a variable amount of cocatalyst

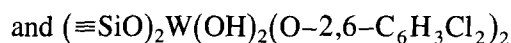
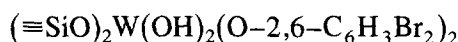
Time (min)	0.1 ml iBAC	0.2 ml iBAC	0.4 ml iBAC	0.1 ml iBAC/ 0.5 ml 2-P
5	37.43	23.09	23.74	25.81
10	48.03	39.23	38.95	46.24
20	61.23	48.51	47.69	–
40	59.45	52.25	54.37	59.89
60	70.46	54.36	57.48	–
180	70.47	–	62.47	55.79

Table 8

Catalytic activity towards 2-pentene of the $(\equiv \text{SiO})_2\text{W}(\text{OH})_2(\text{O}-2,6-\text{C}_6\text{H}_3\text{Br}_2)_2$ /iBAC system using a variable amount of cocatalyst

Time (min)	0.1 ml iBAC	0.2 ml iBAC	0.4 ml iBAC	0.1 ml iBAC/ 0.5 ml 2-P
5	50.14	41.42	41.91	31.43
10	67.68	63.77	65.45	50.38
20	81.60	73.33	75.79	61.90
40	83.17	81.28	73.71	71.85
60	82.68	80.12	80.45	75.09
180	84.09	82.25	81.05	79.73

3.3.3.



Activation of $(\equiv \text{SiO})_2\text{W}(\text{OH})_2(\text{O}-2,6-\text{C}_6\text{H}_3\text{Br}_2)_2$ by iBAC gives a highly active metathesis catalyst. Using Et_2AlCl or Et_3Al as a cocatalyst only small conversions (less than 5%) are obtained. Increasing the amount of iBAC decreases the initial rate (Fig. 5) and slows down the conversion Table 8.

These results clearly indicate that too high amounts of Lewis acids can act as an inhibitor for the metathetical activity.

The $(\equiv \text{SiO})_2\text{W}(\text{OH})_2(\text{O}-2,6-\text{C}_6\text{H}_3\text{Cl}_2)_2$ /iBAC system gives analogous results.

3.4. Modelling

3.4.1. Modelling of the support

Although hydroxylated silica is amorphous, its structure seems to be similar to that of β -cristobalite and related phases [25].

The surface of hydroxylated silica is constructed with regions similar to the (100) face and the partially hydroxylated (111) face of β -cristobalite, with the degree of hydroxylation being a function of the pretreatment of the silica [26]. Hydroxylation of the (100) surface leads to geminal $\text{Si}(\text{OH})_2$ groups (Fig. 7A) which form hydrogen bonded chains (Fig. 7B) through interaction with neighbouring geminal groups [27].

Hydroxylation of the (111) surface gives isolated silanol groups (Fig. 7C).

Dehydroxylation of the (100) surface is believed to occur readily by the reaction of hydroxyl groups on neighbouring silicon atoms (Scheme 2) which result in the formation of siloxane bridges. Dehydroxylation of the (111) plane, under the conditions in which the surface bound cluster is formed, is unlikely [27].

To construct our model the known structure of β -cristobalite [25] was used. Welberry et al. recently described the structure of β -cristobalite as one in which the oxygen atoms are disordered [25]. The oxygen atoms are distributed uniformly around an annulus which encircles the 16(c) sites of the Fd3m space group.

Based on this structure, a model for the silica surface was built.

3.4.2. The (100) surface

Modelling of the local regions on the (100) plane involve first generating, by means of INSIGHT II [28], a β -cristobalite lattice consisting of 3×2 units cells along the b and c axes. From this structure only the surface site ($a = 1/2$) has been minimized using the E.S.F.F. force field. Fully optimization (charge compensation) of the surface site is obtained by adding hydride ions to the silicon atoms which contains less than four bondings. Hydroxylation was accomplished by adding hydrogen atoms to surface oxygens to form geminal silanol groups that were oriented to allow hydrogen bonded 'chains' consistent with spectroscopic results [29].

Since Sindorf et al. [26,30] has shown that there is a relatively low concentration of gemi-

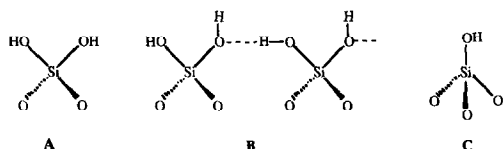
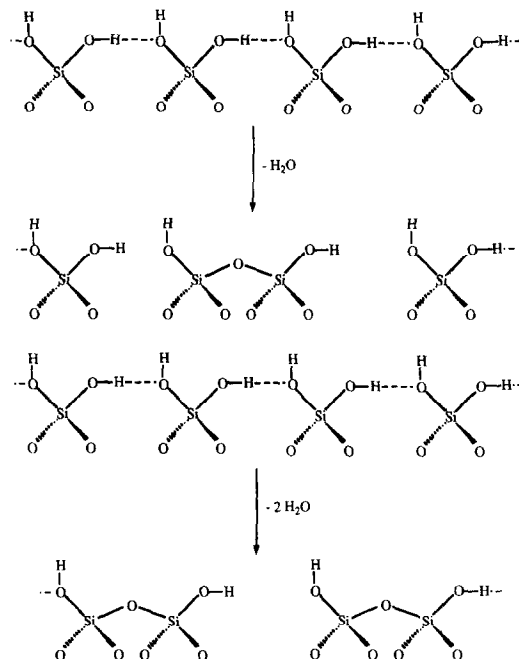


Fig. 7. Surface hydroxyl groups by hydroxylation of various faces of silica.



Scheme 2. Dehydroxylation of the (100) silica surface resulting in the formation of siloxane bridges.

nal $\text{Si}(\text{OH})_2$ units, there is probably a significant concentration of local dehydroxylated surface which contains adjacent siloxane bridges. Such a region was obtained by removing two H_2O molecules from the fully hydroxylated (100) plane (Scheme 2) forming two adjacent siloxane bridges. The pretreatment of silica at 473 K under vacuum results in a OH-density concentration of about 5 OH nm^{-2} , a nearly full monolayer coverage [31]. This means that with this pretreated silica some Si–O–Si bridges are present at the surface (Fig. 8).

3.4.3. Modelling of surface species on SiO_2 support

Molecular modelling is used to gain insight in the various modes of grafting a tungsten diphenoxide complex onto the support surface.

Surface complexes were modeled by fitting a $\text{WCl}_3(\text{O}-2,6\text{-ArX}_2)_2$ fragment to local regions of the support surface. A hydrogen atom was removed from a hydroxyl group of a particular site, and the fragment $\text{WCl}_3(\text{O}-2,6\text{-ArX}_2)_2$ was anchored to that oxygen.

For silica as a support, there are different possible configurations, given in Fig. 9. Molecular modelling attempts indicate that the $WCl_3(O-2,6-ArX_2)_2$ fragment could be accommodated on the (100) silica surfaces sites A and B (Fig. 7).

In case of a fully hydroxylated silica, it is obvious, that a Cl-ligand of the $WCl_3(O-2,6-ArX_2)_2$ fragment anchored on the (100) surface, will react with a second hydroxyl group of the support. This reaction is probably possible since the distance between the Cl-ligand and the OH group is of the same order of magnitude.

This results in the attachment of $WCl_2(O-2,6ArX_2)_2$ entities on a (fully) hydroxylated silica support, to give structures I and II (Fig. 9).

Accommodation of a $WCl_3(O-2,6ArX_2)_2$ fragment on the (111) silica surface sites C (Fig. 7) gives structure III (Fig. 9).

Since amorphous silica is constructed with regions similar to the (100) face and the (111) face, most complexes anchored to a fully hydroxylated silica will have structures I and II.

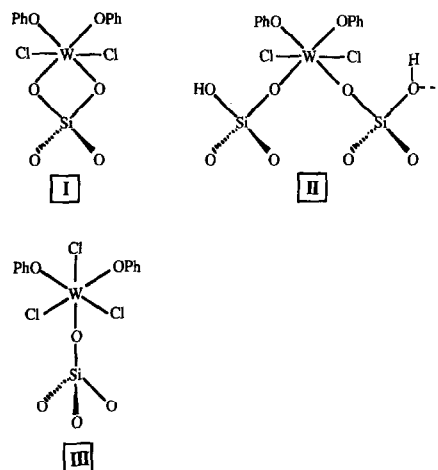


Fig. 9. Possible configurations of $(\equiv SiO)_2WCl_2(O-2,6-C_6H_3X_2)_2$ on hydroxylated silica.

When the pretreatment temperature of the silica increases, resulting in effective dehydroxylation the relative amount of structure III will increase.

In our study, only the physisorbed water is removed, during pretreatment, so a fully hydroxylated silica support is obtained. In general

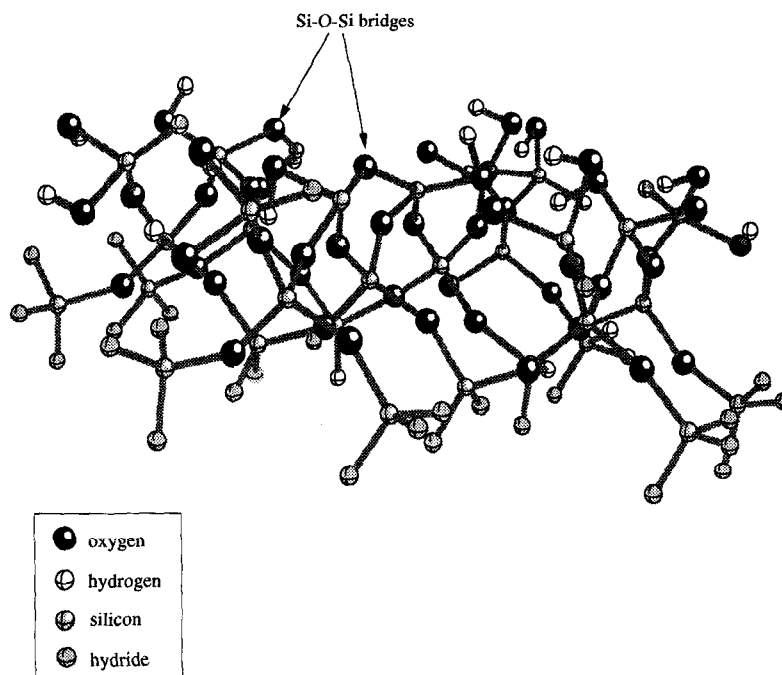


Fig. 8. Computational model of local surface sites of silica using the INSIGHT II program.

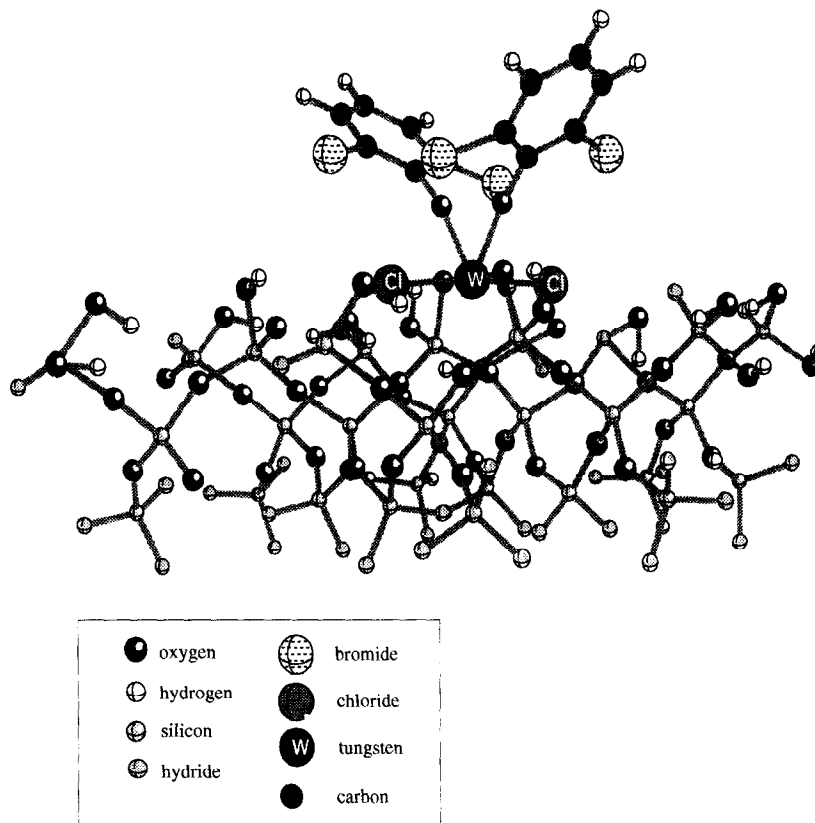


Fig. 10. A ball-and-stick representation of surface complex II using $W(O-2,6-C_6H_3Br_2)_2Cl_4$ as organometallic complex.

the attachment of the tungsten complex to the surface will occur by two Si–O–W bonds.

Fig. 10 is a ball-and-stick representation of surface structure II with $W(O-2,6-C_6H_3Br_2)_2Cl_2$ as organometallic entity.

It is remarkable that on attachment on the surface, the original CIS configuration of the phenoxide complex is transformed into a TRANS configuration.

4. Conclusion

By a controlled thermal reaction of $W(O-2,6-C_6H_3X_2)_2Cl_4$ ($X = t\text{-Bu, Me, Br, Cl}$) or $W(\text{MBPD})Cl_4$ with silica tungsten phenoxide species are anchored on the surface. On chemi-

cal activation, the $(\equiv SiO)_2W(OH)_2(O-2,6-C_6H_3X_2)_2/iBAC$ system shows a significantly higher initial rate and conversion for the metathesis of 2-pentene than the classic $WO_3/SiO_2/iBAC$ system [32] and they can be repeatedly reactivated without loss of tungsten moieties. This can be directly related to the surface structure of the precursors, ‘molecular’ tungsten units compared to orthorhombic WO_3 micro crystallites. XPS characterization indicates that the effective charge on tungsten in the $(\equiv SiO)_2W(O-2,6-C_6H_3Br_2)_2(OH)_2$ model catalyst is lower than in the $WO_3/SiO_2/Si(100)$ system.

The use of computer modelling techniques can be useful in gaining insight into the configuration of organometallic surface entities.

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