A study of the catalyst formed when reacting lithium-alkyls with Cr(II)/SiO$_2$: ethylene polymerisation, diffuse reflectance infrared fourier transform spectroscopy and gas chromatography results

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Abstract

The Cr(II)/SiO$_2$ catalyst modified by *tert*-butyl lithium and trimethylsilylsilylmethyl-lithium have been used in homopolymerisations of ethylene. Both catalysts produces branched polyethylene by incorporating oligomers formed in situ, but the number of branches are different for the two modifiers. The surface species formed in the reaction between the catalysts and the lithium-alkyl have been studied by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and by analyses of reaction products by gas chromatography. The lithium-alkyls react primarily with silanol groups and with siloxane bridges, but some also react with active chromium sites. For the *tert*-butyl lithium modified catalyst, isobutene π-bonded to chromium sites are observed, which is believed to be the result of a reaction between *tert*-butyl lithium and a chromium–oxygen bond followed by a β-hydrogen elimination. The reaction between lithium-alkyl and a chromium–oxygen bond is suggested to be responsible for the formation of oligomer producing sites for these catalysts, and the different behaviour of the two modified catalysts is a consequence of the different reactivities of the two lithium-alkyls. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The prereduced Phillips catalyst, Cr(II)/SiO$_2$, produces high density polyethylene with negligible amounts of branches [1]. However, in certain applications of polyethylene it is desirable to have a certain amount of short chain branches to ease the processability of the polymer. In most cases, a co-monomer, such as 1-hexene, is fed to the reactor to achieve this.

In a recent work it was shown that by modifying the catalyst with *t*-BuLi (*tert*-butyl lithium), one obtains linear low density polyethylene with a significant amount of branching (up to 20 to 40 branches/1000 C) [2]. The majority of the branches were ethyl and butyl

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groups, but also longer branches were present. In order to explain the results, two essentially different kinds of active sites were suggested on the *t*-BuLi modified $Cr(II)/SiO_2$ catalyst: (1) a site that produces α-olefins, mainly 1-butene and 1-hexene. The in situ production of low molecular weight 1-alkenes is only obtained when the contact time between *t*-BuLi and $Cr(II)/SiO_2$ is relatively long, i.e., hours. If *t*-BuLi is injected directly into the reactor just before the polymerisation, no oligomers are produced. These sites are therefore assumed to be a product of the reaction between *t*-BuLi and certain chromium sites. (2) A site that polymerises ethylene and co-polymerises the 1-alkenes produced on site 1. These sites are assumed to be similar to the unmodified $Cr(II)/SiO_2$ sites.

The structure of the polymerisation active chromium species on the Phillips catalyst has attained much attention [1]. Chromium species in oxidation state II [3–9] and III [10–12] have been proposed to be active precursors for ethylene polymerisation. Both mono or dinuclear [13] chromium sites have also been suggested. However, despite numerous investigations, mainly by spectroscopic methods, no general agreement on the structure of the active site(s) exists. According to the catalyst preparation used in the present study, which includes reduction with CO at 380°C, chromium in oxidation state $+II$ is most abundant before treatment with the lithium-alkyl [3]. As a basis for the present work, the structure of the prereduced catalyst before addition of RLi is assumed to be as shown in Scheme 1.

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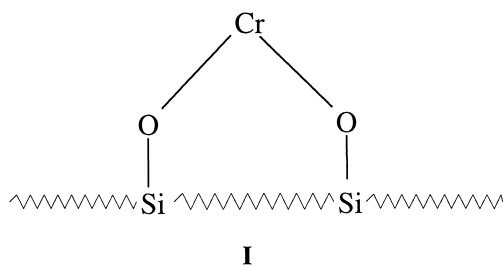
Scheme 1.

A main problem when studying this catalyst is that only a small fraction of the chromium is active, which may lead to erroneous conclusions. Observed properties of the inactive sites may be ascribed to the active sites and vice versa. When studying this catalyst system, this problem must be kept in mind.

The aim of the present investigation is to find how lithium-alkyls reacts with the chromium catalyst to make oligomer producing sites. Quantitative and qualitative analyses of the reaction products from the reaction between the lithium-alkyl and the catalyst have been carried out by using Gas Chromatography (GC) and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). Reactants such as H_2O, CO and C_2H_4 have been added to the modified catalysts and the resulting products have been analysed.

We have used *t*-BuLi (*tert*-butyl lithium) and Me_3SiCH_2Li (trimethylsilylmethyl-lithium) which differs in the presence or absence of hydrogen in the β-position. The different experiments were designed to reveal information on the reactions involved, and from the results of these experiments we have suggested structures of the different sites on the catalyst.

2. Experimental

2.1. General

All solvents and gases used in the present study were purified by standard methods, and all handling of the catalysts and air and moisture sensitive chemicals were carried out under argon atmosphere either in a glove-box or by using standard Schlenck techniques.

2.2. Chemicals

Silica (EP10 from Crosfield Chemicals) and CrO_3 (99.5%) from Strem Chemicals were used. A total of 1.6 M *t*-BuLi and 1.0 M Me_3SiCH_2Li in pentane solutions were purchased from

Aldrich. The concentrations of t-BuLi and Me_3-SiCH$_2$Li were measured to be 1.5 and 1.0 M by adding excess 1-butanol to the solutions at $-20°C$ followed by a measurement of the released isobutane and tetramethylsilane, respectively, with GC. Solid t-BuLi and Me_3SiCH_2Li were obtained by removing the pentane from the RLi solutions under reduced pressure. The final white powders were diluted in dry KBr before the DRIFT spectrum was recorded. Argon (99.999% from AGA), ethylene (polymerisation grade from Borealis) and CO (99.97% from Hydro gas) for the DRIFTS experiments were used without further purification.

2.3. Catalyst preparation

The catalyst preparation has been described in Ref. [2]. Silica was activated at 800°C in dry air for 16 h, while 1.0 wt.% Cr/silica was activated at 800°C in dry air overnight, then reduced to Cr(II) with 5% CO in N_2 at 380°C. RLi modification was carried out in a pentane slurry at temperatures between $-20°C$ and ambient. After about 1 h reaction between the lithium-alkyl and the carrier, the temperature is raised to ambient and the solvent was filtered off. The samples were washed two times with purified pentane and finally dried under vacuum. Only traces of pentane is left after this treatment. The polymerisation procedure as well as the characterisation of end groups by infrared spectroscopy are described in Ref. [2].

2.4. GC analysis

GC analyses were performed on two different GC's from Hewlett Packard. One was a HP 5880A equipped with a capillary column from HP and two FID detectors in parallel. A split after the column leads one line through an olefin adsorbent with a separate detector. This procedure differentiates between those peaks originating from olefins and those originating from paraffins. The other GC, also a HP 5880A Gas Chromatograph, was equipped with two thermal conduction detectors and a column system that can separate H_2, N_2, Ar, CO among others and different hydrocarbons up to C_5.

In most experiments, a 0.3-g sample of the RLi modified silica or Cr/silica catalyst was divided into stopcock-equipped 40 ml flasks
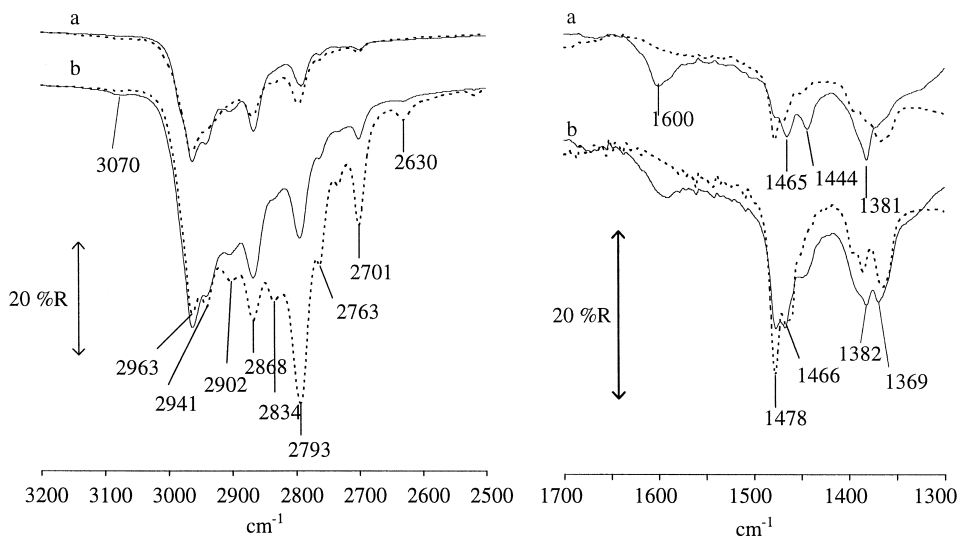

Fig. 1. Diffuse reflectance IR-spectra of the t-BuLi modified catalyst (solid line) and t-BuLi modified silica (broken line). The samples are diluted with CaF_2 in weight ratio sample: CaF_2 = 1:2 to obtain acceptable signal to noise ratio in the 1300–1700 region. (a) And (b) refer to samples with low t-BuLi content (0.19 mmol/g support) and high t-BuLi content (0.53 mmol), respectively. The spectra are ratioed against a spectrum of silica calcined at 800°C mixed up with CaF_2 in the same weight ratio.
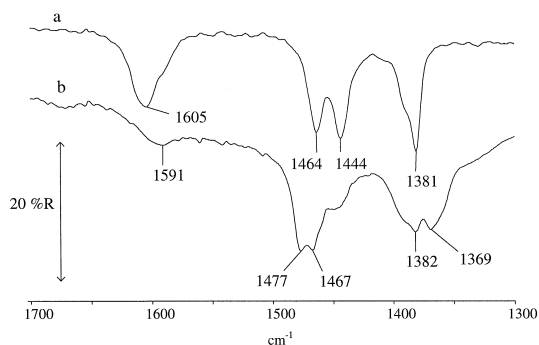
Fig. 2. DRIFT difference-spectra of the Cr(II)/SiO$_2$ catalyst exposed to isobutene at room temperature (a) and the *t*-BuLi modified catalyst (b) with high *t*-BuLi content (0.53 mmol). The samples are diluted with CaF$_2$ in a weight ratio sample: CaF$_2$ = 1:2 to obtain acceptable signal to noise ratio. The spectra are ratioed against a spectrum of silica calcined at 800°C mixed up with CaF$_2$ in the same weight ratio.

under argon atmosphere. Water or different reacting gases were introduced at room temperature by using a syringe, and gas samples for the GC were taken from the flask after a desirable reaction time. For the Me$_3$SiCH$_2$Li modified samples, the amount of tetramethylsilane released were either determined in the gas phase after heating the flask to 50°C, or by extraction of tetramethylsilane by using 1.5 g pentane at

0°C, followed by a GC analysis of the resulting solution.

2.5. DRIFTS study

DRIFTS measurements were performed on a Perkin-Elmer 2000 instrument fitted with a diffuse reflectance accessory equipped with a vacuum cell (both from Harrick Scientific). This allows spectra of the samples in granular form to be recorded. The DRIFTS cell was filled with approximately 100 mg of the sample in a glovebox and closed under argon atmosphere, then aligned in the FTIR instrument. The cell was connected to a flow system with argon, and through a septum on this line, other gases such as ethylene could be injected by using a syringe. A set-up in which the gas flow just passes through the cell was used. In this case, only a fraction of the injected gas comes in contact with the catalyst sample. The rest of the gas just passes through the cell without getting in contact with the catalyst. All DRIFTS experiments in this work were carried out at room temperature under atmospheric pressure of argon. The spectra were recorded with a resolution of 4/cm on a liquid nitrogen cooled MCT detector.
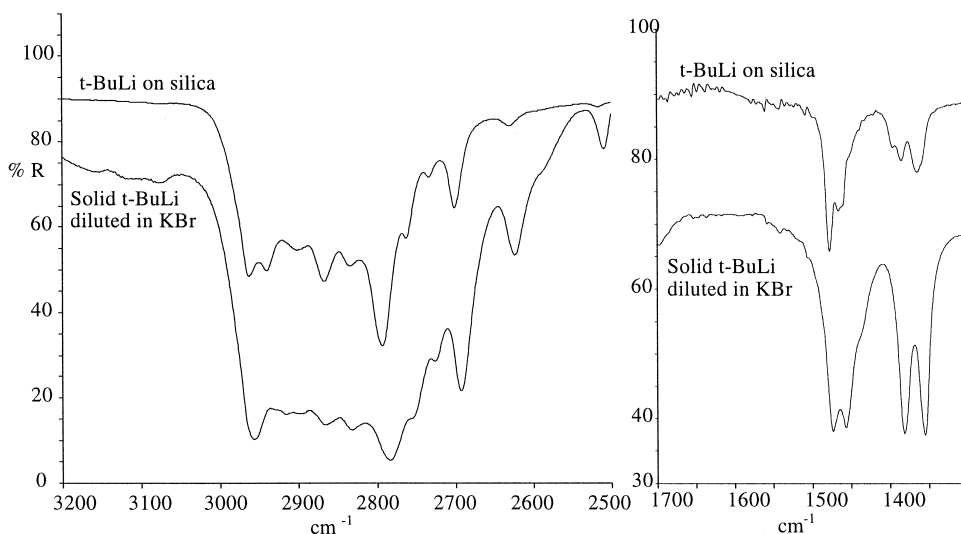

Fig. 3. A comparison between silica reacted with 0.53 mmol *t*-BuLi per gram support (identical to Fig. 1) and pure *t*-BuLi diluted in KBr-powder. The spectrum of *t*-BuLi/KBr is ratioed against a spectrum recorded of pure KBr.
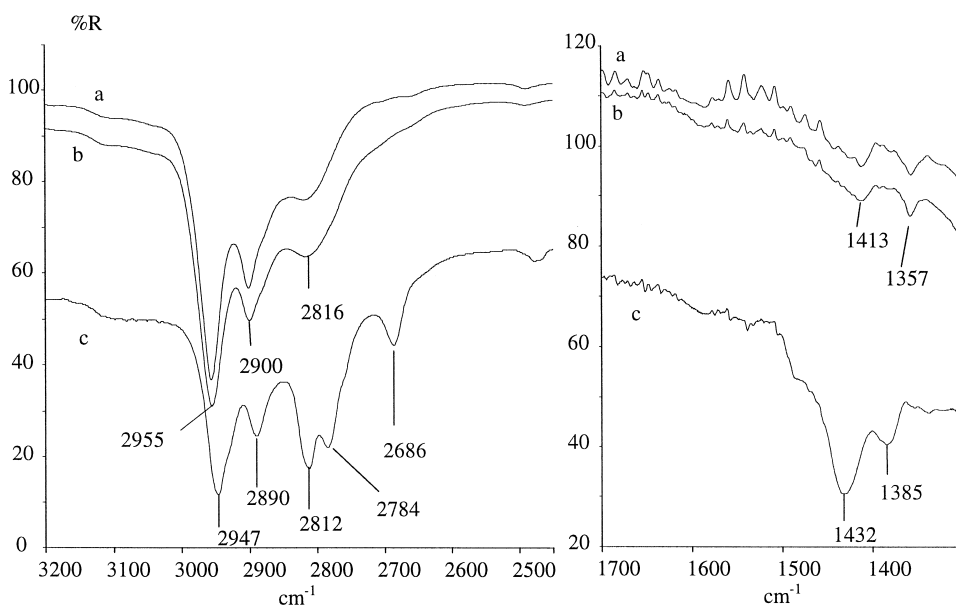
Fig. 4. DRIFT spectra of Me_3SiCH_2Li/SiO_2 (a) and $Me_3SiCH_2Li/Cr/SiO_2$ (b). The spectra are recorded on samples mixed up with CaF_2 in weight ratio sample: CaF_2 = 2:1. The backgrounds used are similar samples without RLi treatment. Solid Me_3SiCH_2Li diluted in KBr (spectrum c) is ratioed against a spectrum of pure KBr.

A steep fall in reflectance intensity below ca. 2000/cm causes a low signal to noise ratio in the region 1300–1700/cm. However, the S/N in this region is increased if the catalyst samples are diluted with dry CaF_2 powder. The spectra presented in Figs. 1–4 were recorded on samples mixed up with a given amount of CaF_2. No changes in the C–H stretch region are found between spectra recorded on diluted samples and spectra recorded without diluent. Neither are changes in catalytic properties observed when adding CaF_2 to the catalyst samples studied in this work. Below 1300/cm, there is a complete blackout of signal due to strong silica absorbency, except for a window in a region around 900/cm.

3. Results and discussion

First, the behaviour of alkyl-lithium modified catalysts in homopolymerisation of ethylene is described, then the results from the different experiments on the catalyst have been presented together with possible assignments and discus-

sions. The final conclusions are summarised in Section 4.

3.1. Effect of the lithium-alkyl on the polymer product

Results from homopolymerisations of ethylene with unmodified $Cr(II)/SiO_2$, t-BuLi/Cr/SiO_2 and $Me_3SiCH_2Li/Cr/SiO_2$, are shown in Table 1.

Table 1
Activities and concentration of end groups from IR analyses [2] in the polymers produced with unmodified $Cr(II)/SiO_2$, and for the t-BuLi and Me_3SiCH_2Li modified versions, respectively

Catalyst type:	Activity	-CH₃	R‿	R‿R	R⫫
	$\frac{g_{polymer}}{g_{cat.} \cdot h}$	/1000C	/1000C	/1000C	/1000C
$Cr(II)/SiO_2$	430	0.85	0.6	0.01	0.02
t-BuLi/ $Cr(II)/SiO_2$.	1173	27	1.9	0.08	0.22
$Me_3SiCH_2Li/Cr(II)/SiO_2$.	564	4	1.1	0.02	0.04

Slurry polymerisation at 90°C and 30 bar total pressure in a stirred autoclave with isobutane diluent. Ethylene homo-polymerisation without hydrogen.

Table 2

Results from GC analyses of reaction products when reacting RLi with calcined silica and calcined and prereduced Cr(II)/SiO$_2$ in pentane

Type of support	Type of RLi	RLi added (mmol)	Release of *t*-BuH (mmol)	Release of SiMe$_4$ (mmol)
SiO$_2$[a]	*t*-BuLi	0.19	0.07	–
Cr(II)/SiO$_2$[a]	*t*-BuLi	0.19	0.05	–
SiO$_2$[a]	*t*-BuLi	0.53	0.19	–
Cr(II)/SiO$_2$[a]	*t*-BuLi	0.53	0.15	–
Cr(II)/SiO$_2$[a]	Me$_3$SiCH$_2$Li	0.53	–	0.05
SiO$_2$[b]	Me$_3$SiCH$_2$Li	0.53	–	0.15
Cr(II)/SiO$_2$[b]	Me$_3$SiCH$_2$Li	0.53	–	0.12

[a] Reaction performed at −20°C.
[b] Reaction performed at 5°C.
A total of 1.0 g silica or 1.0 g 1.0 wt.% Cr(II)/SiO$_2$ catalyst (0.192 mmol Cr per gram catalyst) was used in each run.

With the *t*-BuLi modified catalyst, GC-analyses of the liquid phase in the reactor after 30 min polymerisation time showed concentrations of 3.3, 0.9 and 0.2 mole% of 1-butene, 1-hexene and 1-octene, respectively. The concentration of other isomers than the linear 1-alkenes were negligible. The concentration of 1-butene and 1-hexene measured when polymerising at the same conditions with the trimethylsilylmethyl-lithium modified catalyst were 0.23 and 0.07 mol%, respectively. The branching content in polymer, the reduction in polymer density and the concentration of α-olefins in the isobutane diluent are much less pronounced with Me$_3$SiCH$_2$Li as modifier as compared to *t*-BuLi [1]. No oligomers were detected in the liquid phase when polymerising with the unmodified Cr(II)/SiO$_2$ catalyst at these conditions.

From these polymerisations, we conclude that both *t*-BuLi and Me$_3$SiCH$_2$Li modify the Cr(II)/SiO$_2$ in such a way that the oligomers are produced in situ, but in different extents. As both catalysts produce oligomers, we can not ascribe the oligomerisation property solely to the different ability of the two alkyl groups to undergo β-hydrogen elimination. Other factors, such as different reactivities of the two lithium-

alkyls with the catalyst precursor must be considered as well. This will be further discussed in the following sections.

3.2. Preparation of catalysts

The modification with lithium-alkyl is typically carried out at −20°C to ambient temperature in a pentane slurry. Different reactions often lead to different reaction products. Analyses of the soluble products formed in the reaction between lithium-alkyl and the carrier may therefore give indirect information about the major reactions that take place on the catalyst surface during preparation. In Table 2, the quantitative analyses of the soluble reaction products formed when reacting *t*-BuLi and Me$_3$SiCH$_2$Li with pure SiO$_2$ and with Cr(II)/SiO$_2$ are given.

When *t*-BuLi reacts with the support, the GC analyses show that isobutane is the sole detectable soluble product. Isobutane is formed when *t*-BuLi reacts with silanol groups on the surface according to reaction Scheme 2 below [2].

The values presented in Table 2 are lower than the previously reported amount of available silanol groups left on silica after calcination at 800°C, in the range 0.30–0.45 mmol/g [1,14]. Tetramethylsilane, SiMe$_4$, is the sole product formed when Me$_3$SiCH$_2$Li reacts with calcined

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[1] Polymerisation with catalysts modified by *sec*-BuLi and *n*-BuLi gave the same oligomer composition as for *t*-BuLi, within experimental accuracy (Bade, O.M. and Blom, R., unpublished results).

[2] Li∗ may either represent a single lithium atom or the remainder of a tetrameric cluster (see Section 3.3), namely Li$_4$(*t*-Bu)$_3$.
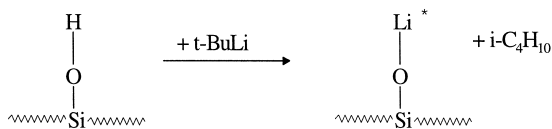
Scheme 2.

silica. When reacting 0.53 mmol Me_3SiCH_2Li with the $Cr(II)/SiO_2$ catalyst at $-20°C$, only 0.05 mmol of $SiMe_4$ is obtained. When the same experiment is carried out at 5°C, 0.15 and 0.12 mmol of $SiMe_4$ are released in the reaction with pure silica and on $Cr(II)/SiO_2$, respectively.

From DRIFTS analyses of several of the $Me_3SiMeLi$ samples, we found that longer reaction time, and/or higher reaction temperature had to be used in the catalyst preparation in order to obtain as low a concentration of silanol groups (observed by intensity reduction of the O–H stretch band at 3747/cm) as observed when using t-BuLi modifier. If the reaction between Me_3SiCH_2Li with $Cr(II)/SiO_2$ is carried out at ambient temperature over several days, most of the silanol groups are removed. However, the polymer produced with the resulting catalyst contains the same amount of short chain branches as the $Me_3SiCH_2Li/Cr/SiO_2$ catalyst prepared at 5°C for shorter time. This indicates that the oligomer producing properties of the catalyst is not connected to the amount of OH groups present.

In the following sections, the t-BuLi and Me_3SiCH_2Li modified samples used were those prepared at -20 and 5°C, respectively.

3.3. DRIFTS study of catalysts

The spectra of t-BuLi/SiO_2 and t-BuLi/Cr/SiO_2 with different amounts of t-BuLi added are shown in Fig. 1.

The spectra show a high number of bands in the region from 2600 to 3000/cm. When comparing the pure silica samples with the chromium containing catalysts, three main differences are observed; only the chromium containing catalyst show bands at 1444, and at approximately 1600/cm. These two bands are similar to bands found for isobutene on $Cr(II)/SiO_2$, which is shown for the C–H deformation and C=C stretch region in Fig. 2 together with the spectrum of t-BuLi/Cr/SiO_2 [15]. Isobutene form stable π-complexes with the surface Cr-atoms on the prereduced Phillips catalyst, and does not undergo polymerisation or other reactions at room temperature.

The isobutene fragments of this kind typically show three strong bands at 1464, 1444 and 1381/cm, respectively, in the deformation region, together with a broad, strong band at 1605/cm. The latter is assigned to the (C=C) stretching mode. The assignments are mainly based on related work on isobutene adsorbed on different metal oxides by Busca et. al. [16]. The peak at 1591/cm in the spectrum of the t-BuLi/Cr/SiO_2 catalyst which we assign to C=C of a π-coordinated isobutene, is somewhat broader and the peak maximum is slightly displaced compared to that of the isobutene/$Cr(II)/SiO_2$ sample. Chromium–isobutene fragments can be formed in a two step reaction sequence as shown in Scheme 3.

The primary reaction product in Scheme 3 is assumed to be a Cr(II)-(t-Bu) fragment. However, the Cr atom of this fragment is electronically very unsaturated and might for this reason extract a β-hydrogen from the alkyl group. The result of the β-hydrogen elimination is the formation of a Cr-hydride and the alkyl group is transferred into an isobutene fragment π-bonded to the chromium, formally a 12-electron species. Species III is not the same as the complex formed when isobutene adsorbs on the prereduced $Cr(II)/SiO_2$ catalyst. This difference may explain the differences observed in the two spectra in Fig. 2.

However, we also have to consider the formation of isobutene by thermal decomposition of t-BuLi according to the reaction:

$$t\text{-BuLi} \rightarrow H_2C=CMe_2 + LiH. \tag{i}$$
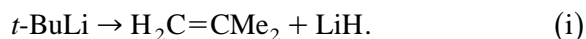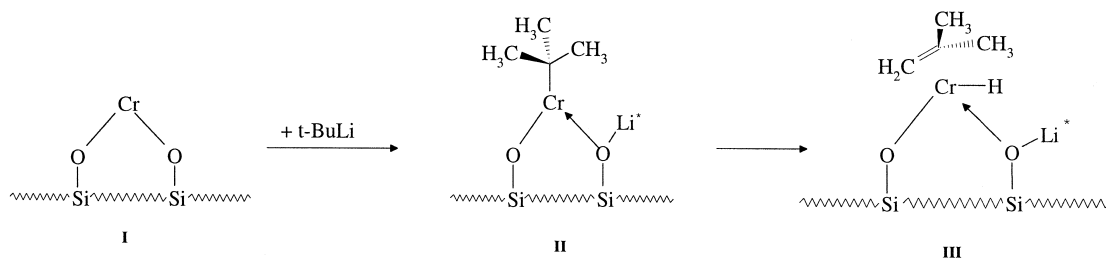
Scheme 3.

The isobutene released by reaction (i) can bind to unmodified Cr(II) sites (Scheme 1).

Dent and Kokes [17] have studied the interaction of propylene on dehydrated zinc oxide, and found that the chemisorption was dissociative. Formation of O–H groups was confirmed spectroscopically, and the remaining hydrocarbon species was shown to form allylic species in a trihapto bonding mode. One might therefore argue that species III could be transformed into an allylic species (IV) by a second hydrogen abstraction as shown in Scheme 4.

We have recently recorded the DRIFTS spectra of (2-methyl-allyl)$_3$Cr deposited on silica dehydrated at 400 and 800°C [18]. The Cr(2-methyl-allyl)$_3$/SiO$_2$(800) sample exhibits bands at 3058 and 1493/cm assigned to $\nu_{as}(CH_2)$ and $\nu_{as}(C\text{⋯}C\text{⋯}C)$ of η^3-coordinated allyls. These bands are not present in spectra of the *t*-BuLi/Cr/SiO$_2$ samples. However, we can not rule out the presence of small amounts of allylic species. From the DRIFT spectra, and in particular from the band at about 1600/cm, we conclude that a significant number of π-isobutene–chromium fragments are present, and that these are stable at the conditions used.

t-BuLi is tetrameric both in the solid state and in hydrocarbon solutions [19]. In the crystal, and presumably also hydrocarbon solutions, the lithium atoms form a tetrahedron with the butyl groups centred over each face of the tetrahedron. The butyl groups are bonded through a 4-centre-2 electron bonding to the three lithium atoms on the triangular face, and each of the methyl groups on the butyl are centred over one of the lithium atoms respectively, indicating interactions between lithium and hydrogen on the methyl groups. This interactions give rise to low frequency C–H stretch modes in the range 2800 to 2600/cm.

The DRIFT spectrum of solid *t*-BuLi is shown in Fig. 3 together with the spectrum of *t*-BuLi/SiO$_2$ with high *t*-BuLi content. The similarity between these two spectra, specially in the C–H stretch region below 2800/cm suggest that a significant amount of unreacted *t*-BuLi is present on the silica sample and that the tetrameric structure is largely maintained. Some-
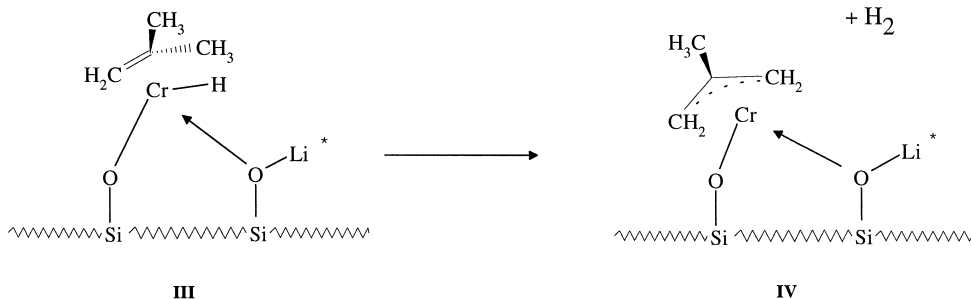
Scheme 4.

what less unreacted *t*-BuLi is left on the high content *t*-BuLi/Cr/SiO$_2$ catalyst as shown in Fig. 1, while only traces of unreacted lithium-alkyl is present on the two low content samples. This will be further discussed in Section 3.4.

DRIFT spectra of silica and Cr(II)/SiO$_2$ after reaction with trimethylsilylmethyl-lithium are illustrated in Fig. 4, spectra (a) and (b). These spectra are very similar. The two strong modes at 2955 and 2900/cm are typical C–H stretch bands of a Me$_3$Si fragment [20]. The several bands in the lower C–H stretch region below 2800/cm found for the *t*-BuLi modified catalyst are not present for the Me$_3$SiCH$_2$Li modified samples. However, a broad band at about 2816/cm is observed on both the silica and the Cr/SiO$_2$ samples.

Also included in Fig. 4 is the spectrum of solid Me$_3$SiCH$_2$Li diluted in KBr (spectrum c). Trimethylsilylmethyl-lithium has a hexameric ring structure in the solid state [21]. The DRIFT spectrum shows typical bands at 2947 and 2890/cm that can be assigned to the asymmetric and symmetric C–H stretches of the methyl groups. Also, three bands are observed at 2812, 2784, and 2686/cm. These can tentatively be assigned to the methylene or methyl groups interacting with Li. Such interactions have been suggested by Tecle et al. [21], although direct evidences were missing. The pattern of these three bands is different when Me$_3$SiCH$_2$Li is added to SiO$_2$ or Cr(II)/SiO$_2$, and may be attributed to a change from hexameric units to smaller clusters or even monomers. If the sam-

ples are oxidised in air, the bands below 2850/cm disappear, while the other bands remain unchanged. This supports an assignation of the low frequency C–H stretch bands to methyl or methylene groups interacting with lithium.

3.4. Hydrolysis

The dry lithium-alkyl modified silica samples were hydrolysed directly in closed bottles and the volatile products were analysed by GC. The results are presented in Table 3.

When hydrolysing the silica modified by small amounts of *t*-BuLi (0.096 mmol), negligible amounts of gaseous species are detected. This indicates that all *t*-BuLi has reacted with silanol groups (Scheme 2) or with siloxane bridges (Scheme 5 below) during the preparation and that no unreacted *t*-BuLi is adsorbed on the surface.

Reactive Si–O–Si bridges are formed when dehydroxylation of the silica is carried out at high temperature. Hydrolysis of the samples with larger amounts of *t*-BuLi (0.19 or 0.53 mmol) releases isobutane as the major component. The isobutane is most probably formed in the reaction between water and unreacted *t*-BuLi:

$$H_2O + t\text{-BuLi} \rightarrow t\text{-BuH} + LiOH. \qquad (ii)$$
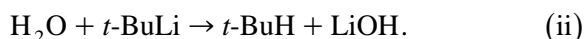
Traces of hydrogen and isobutene are detected as well. When the hydrolysis was performed on a catalyst sample of the same batch

Table 3
GC analyses of the gaseous products released when reacting 5.7 mmol of water with a fresh RLi modified silica

t-BuLi added (mmol)	Me$_3$SiCH$_2$Li added (mmol)	H$_2$ (mmol)	*t*-BuH (mmol)	SiMe$_4$ (mmol)	Me$_2$C=CH$_2$ (mmol)
0.096	–	0	0	–	0
0.19	–	0.005	0.054	–	0
0.53	–	0.017	0.180	–	0.004
–	0.53	0.000	–	0.131	–

A total of 1.00 g of RLi/SiO$_2$ was used in each analysis.
t-BuLi and Me$_3$SiCH$_2$Li samples prepared at −20 and 5°C, respectively.
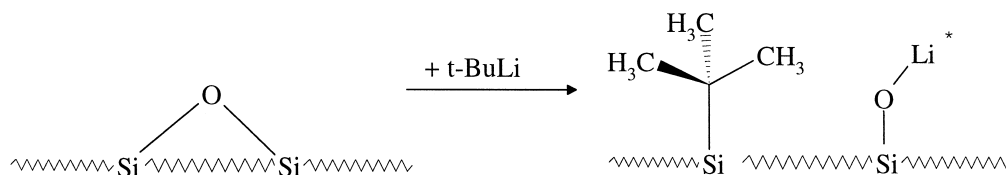
Scheme 5.

after a few weeks of storage in a glove-box, we found that less isobutane but more hydrogen was produced. This shows a slow decomposition of unreacted *t*-BuLi on silica according to reaction (i). DRIFT spectra recorded after 2 weeks storage also show a reduction in the concentration of organic species, mostly in the C–H stretch region below 2800. When hydrolysing the Me_3SiCH_2Li/SiO_2 samples, $SiMe_4$ is the sole product. DRIFT spectra show no decomposition of this sample with time if stored under argon, consistent with a higher stability of Me_3SiCH_2Li as compared to *t*-BuLi due to the lack of labile β-hydrogens in the former.

The results of the GC analyses of the reaction products formed when hydrolysing the chromium-containing catalysts are given in Table 4.

When hydrolysing the $t\text{-BuLi}/Cr/SiO_2$ samples, both isobutene, isobutane and hydrogen are observed. As found for the silica samples in Table 3, the concentration of isobutane is only significant with high *t*-BuLi loading where unreacted tetrameric *t*-BuLi is present. However, isobutene is also found, and the amount is steadily increasing with *t*-BuLi loading. The chromium sites must play a role in formation of isobutene since no isobutene was observed when hydrolysing the modified silica

samples. However, isobutene is the expected product when hydrolysing both π-isobutene–chromium species and 2-methyl-allyl-chromium species. Also, a significant amount of hydrogen is observed, which is the expected product from hydrolysation of chromium- and lithium-hydrides.

The sum of released isobutane and isobutene for the 0.53 mmol $t\text{-BuLi}/Cr/SiO_2$ sample is less than the amount of isobutane released when hydrolysing the $t\text{-BuLi}/SiO_2$ sample. This indicates that the decomposition of adsorbed *t*-BuLi (reaction (i)) is more pronounced for the chromium containing sample, thus chromium seems to accelerate the decomposition of *t*-BuLi.

When hydrolysing the Me_3SiCH_2Li modified catalyst, traces of hydrogen is detected along with the expected tetramethylsilane. However, small amounts of hydrogen is also observed when hydrolysing the unmodified $Cr(II)/SiO_2$ catalyst, and is most probably formed through the redox reaction (iii) [22]:

$$2Cr(II) + H_2O \rightarrow 2Cr(III) + H_2 + O^{2-}. \quad \text{(iii)}$$
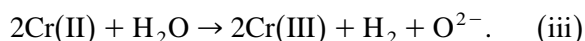
The oxidation is followed by a colour change from blue to green.

The amount of $SiMe_4$ when hydrolysing the $Me_3SiCH_2Li/Cr/SiO_2$ sample is almost twice

Table 4

Results of GC analyses of the volatile products formed when hydrolysing $RLi/Cr/SiO_2$ catalysts with 5.7 mmol water

Li/Cr	RLi	RLi added (mmol)	H_2 (mmol)	*t*-BuH (mmol)	$SiMe_4$ (mmol)	$Me_2C{=}CH_2$ (mmol)
0.5	*t*-BuLi	0.096	0.046	0.005	–	0.032
1.0	*t*-BuLi	0.19	0.063	0.016	–	0.052
2.8	*t*-BuLi	0.53	0.293	0.045	–	0.078
2.8	Me_3SiCH_2Li	0.53	0.002	–	0.238	–

A total of 1.00 g of catalyst was used.

t-BuLi and Me_3SiCH_2Li samples prepared at -20 and 5°C, respectively.

as high as found when hydrolysing Me_3SiCH_2Li/SiO_2 (Table 3). It is reasonable to assume that more siloxane bridges are present on dehydrated silica than on dehydrated Cr/silica, because chromium oxide, when preparing the catalyst, is believed to react with two silanol groups, thus reducing the number of such. Without chromium, more siloxane bridges will be present that can react with the lithium-alkyl. The surface Si–R groups formed (Scheme 5) are expected to survive hydrolysation [23], and their presence were confirmed by DRIFT spectra of the modified samples after being hydrolysed by water. The spectra showed that considerable amounts of organic species remain on the samples after hydrolysation and thermal treatment at 105°C in dry air over 3 days, both for the Me_3SiCH_2Li and *t*-BuLi modified samples.

The amount of surface Si–R groups left after hydrolysis is difficult to estimate exactly. However, from mole balance considerations, the sum of RH released during preparation, the amount of RH (and H_2 in the case of *t*-BuLi) released during hydrolysation, and the remaining Si–R groups should constitute for the amount of added RLi. A calculation carried out on the basis of the GC data shown in Tables 2–4 for the samples added 0.53 mmol RLi is shown in Table 5.

The amounts of Si–R groups are estimated at 0.14, 0.04, 0.25 and 0.17 mmol/g for *t*-BuLi/ SiO_2, *t*-BuLi/Cr/SiO_2, Me_3SiCH_2Li/SiO_2 and $Me_3SiCH_2Li/Cr/SiO_2$, respectively. We find that approximately 0.09 mmol less Si–R groups is formed on the Cr containing samples as compared to the pure silica samples, consis-

tent with the lower number of reactive siloxane bridges on the former. The intensities of the C–H stretch bands in the DRIFT spectra of the hydrolysed and dried samples also give the same relative order. Me_3SiCH_2Li seems to be more reactive towards siloxane bridges than *t*-BuLi.

3.5. Reaction with ethylene

3.5.1. Reaction under argon atmosphere in closed bottles

When ethylene is reacted with the unmodified Cr(II)/SiO_2 catalyst in a sealed bottle with an ethylene/chromium molar ratio of 12, no organic species are detected in the gas phase after a few minutes. When subsequently hydrolysing the sample, ethylene and traces of higher α-olefins are detected in the gas phase. This is consistent with the earlier work reported by Hogan [6].

When *t*-BuLi/Cr/SiO_2 (Li/Cr = 2.8) is reacted with ethylene in the same manner, all linear butene-isomers are immediately observed together with small amounts of ethylene, ethane, *n*-butane and higher hydrocarbons. This illustrates the difference in behaviour of the unmodified and modified catalysts; the former form stable ethylene–chromium species and produces long Cr-alkyl chains which probably do not terminate at ambient temperature before hydrolysation. The *t*-BuLi modified sites show much higher reactivity towards the propagating chain, and a number of products are observed as a result of rapid β-hydrogen transfer to coordinated monomer or to the chromium sites. The

Table 5
A calculation carried out on the basis of the GC data shown in Tables 2–4 for the samples added RLi

Sample	Added RLi (mmol)	Released during preparation *t*-BuH or SiMe$_4$ (mmol)	Released when hydrolysing the samples		Sum released (mmol)
			H_2 (mmol)	*t*-BuH or SiMe$_4$ (mmol)	
t-BuLi/SiO$_2$	0.53	0.19	0.017	0.180	0.39
t-BuLi/Cr/SiO$_2$	0.53	0.15	0.293	0.045	0.49
Me$_3$SiCH$_2$Li/SiO$_2$	0.53	0.15	0.000	0.131	0.28
Me$_3$SiCH$_2$Li/Cr/SiO$_2$	0.53	0.12	0.002	0.238	0.36

The difference between the amount added and the sum released should represent the amount of Si–R groups formed. See text for details.

primary products are the 1-alkenes. In absence of additional ethylene monomers, the 1-alkenes recoordinates to active sites and undergoes iso-merisation and dimerisation processes, which explain the increasing amounts of *cis-* and *trans-*2-butene and higher hydrocarbons with increasing reaction time. After 2 h, no more 1-butene is observed.

The presence of small amounts of saturated hydrocarbons indicates that additional hydrogen is available. This hydrogen could be formed by the reaction shown in Scheme 3.

t-BuLi/SiO_2 does not show any reaction with ethylene. This shows that *t*-BuLi itself, or on the SiO_2 support, is not active in this kind of polymerisation or oligomerisation reactions at the chosen conditions.

3.5.2. Polymerisation with ethylene in the DRIFTS cell

The DRIFT spectra of *t*-BuLi/Cr/SiO_2 with different numbers of ethylene doses added are shown in Fig. 5. Ethylene doses of 0.20 ml were added to the steady 50 ml/min argon flow through the DRIFTS cell. With the flow system used, only a part of the injected ethylene comes in contact with the catalyst sample. Polymerisation is observed by growing methylene bands at about 2925 and 2854/cm. In addition, two smaller bands which also seem to be steadily
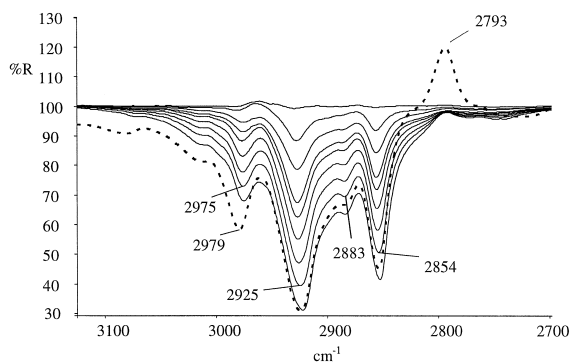
Fig. 5. DRIFT difference spectra of early stages of polymerisation on *t*-BuLi/Cr/SiO_2. The broken line shows the spectrum of the oxidised sample. A spectrum of the *t*-BuLi modified catalyst recorded before ethylene exposure is used as background.

growing with the amount of ethylene added are observed at 2975 and 2883/cm. The two latter bands are assigned to methyl groups of side branches. The side branches are probably formed by incorporating low molecular weight α-olefins formed on oligomerising sites, but the α-olefins themselves could also contribute to the methyl bands if adsorbed on the catalyst surface. This, however, does not seem to appear to any large extent as the spectra show no evidence for vinyl end groups. π-Coordinated ethylene on Cr(II)/SiO_2 is found to give bands at 2998, 3079 and 3098/cm [15], but no such bands are found in these spectra.

A shoulder is observed at ca. 3016/cm, which is the same frequency as Kantcheva et al. [24] ascribed to carbene groups on active polymeri-sation sites on the Cr(II)/SiO_2 catalyst. This assignment is unlikely in the present work, be-cause the mode is still present after oxidation of the sample.

Ethylene polymerisation with Me_3SiCH_2-Li/Cr/SiO_2 in the DRIFTS cell was carried out in a similar manner as for *t*-BuLi/Cr/SiO_2 described above. The spectra are shown in Fig. 6. While the *t*-BuLi modified catalyst show significant amounts of methyl, and the unmodi-fied Cr(II)/SiO_2 catalyst give no methyl bands at all [8], the spectra obtained with Me_3-$SiCH_2Li/Cr/SiO_2$ show small amounts of methyl groups together with strong methylene bands. Some π-coordinated ethylene is observed (by the band at 3003/cm) when ethylene gas is introduced, in a similar manner as observed for the Cr(II)/SiO_2 catalyst and in contrast to the *t*-BuLi modified catalyst.

The DRIFTS spectra thus give direct infor-mation about the catalyst behaviour. The spectra shown in Figs. 5 and 6 together with previous published spectra using the unmodified Cr(II)/SiO_2 [8,15,24] reflect the behaviour of these three catalysts under realistic polymerisa-tion conditions as shown in Table 1. The DRIFTS method therefore appears to be an efficient tool for investigating these catalyst sys-tems.
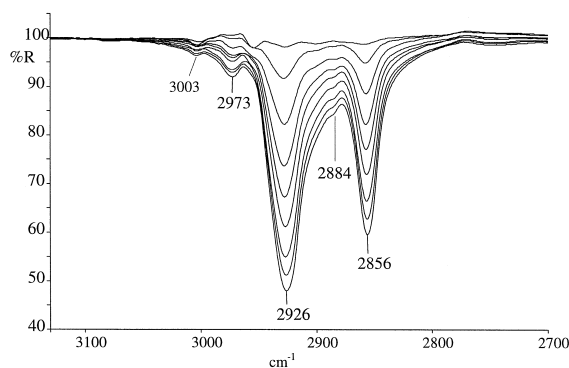
Fig. 6. DRIFT difference spectra of early stages of polymerisation on the $Me_3SiCH_2Li/Cr/SiO_2$ catalyst. A spectrum of the catalyst recorded before ethylene exposure is used as background.

3.6. Addition of carbon monoxide

Carbon monoxide has been used thoroughly as a probe molecule to identify different sites on the $Cr(II)/SiO_2$ catalyst [9,25]. When CO is added to t-BuLi/Cr/SiO_2, one might expect that CO coordinates to chromium and saturate the metal. However, chemical reactions such as replacement of isobutene by CO and insertion of CO into a Cr–C bond must also be considered. The latter possibility would give an aldehyde when hydrolysed.

When CO is added to t-BuLi/Cr/SiO_2 catalyst in sealed bottles, we detect no C_4 species in the gas phase. Neither is aldehyde detected when hydrolysing the CO-treated catalyst, even when the bottle is heated to 100°C to remove potentially adsorbed species. Only isobutane and isobutene are observed, and in approximately the same amounts as if hydrolysing the sample without CO added. However, the hydrolysation is slower when CO is present, which indicate that CO saturates the chromium sites and makes them less available for incoming H_2O molecules.

The stability of the organic ligands towards CO shows that the chromium–isobutene bond is stable with CO present. This is consistent with previous suggestions by Ghiotti et al. [26] where they assign a specific CO stretch band to a

species in which CO is bonded to the same chromium as a π-coordinated ethylene.

DRIFTS spectra of CO adsorbed on t-BuLi modified catalyst with Li/Cr = 2.8 are shown in Fig. 7. After the last CO injection, two bands with maxima at about 1959 and 1784/cm are observed. At least, the band with maximum at 1784/cm consists of overlapping bands at lower frequency. With additional CO injections, the intensity growth rapidly declines, which indicates that the catalyst becomes saturated. A broad band at 1747/cm is detected at low coverage.

Adsorbed CO on the $Cr(II)/SiO_2$ catalyst at room temperature gives rise to a triplet of carbonyl bands at 2192–2188, 2181–2186 and 2177–2182/cm [8,26,27]. The near complete absence of carbonyl stretch bands in the region 2170–2200/cm in Fig. 7 shows that undetectable amounts of the original, unsaturated Cr(II) sites exist after modification with t-BuLi. Only when gas phase CO is present in the cell, right after CO injection (spectrum not shown), weak carbonyl bands at 2181 and 2170/cm are observed. These are, however, much more labile than CO adsorbed on the original Cr(II) sites. On the latter, the intensity of the carbonyl bands are only slowly reduced when pure argon flows through the cell. However, we found that the
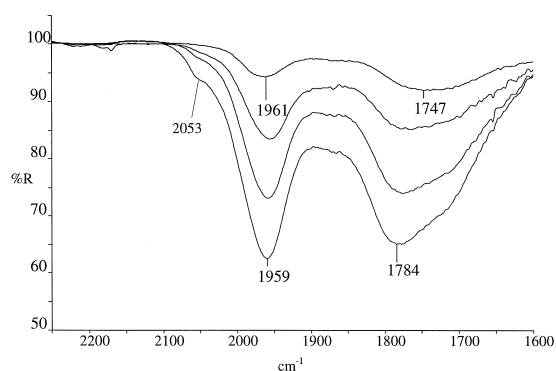

Fig. 7. DRIFT spectra of the t-BuLi/Cr/SiO_2 catalyst exposed to successive pulses of CO in an argon flow of 50 ml/min, which steadily flows through the cell. The first two batches consist of 0.1 ml, the next two of 0.2 ml. Each spectrum is recorded 3 min after each injection of CO, when no CO is observed in the gas phase. The spectrum of the catalyst before admitting CO is used as background.

unmodified $Cr(II)/SiO_2$ catalyst, which first was exposed to isobutene and then to CO, also exhibit reversible carbonyl bands at 2170 and 2181/cm [15]. The band at 2170/cm is most likely assigned the carbonyl stretch on a mixed CO/isobutene chromium complex. Isobutene may act as an electron donor, which results in increased back-donation to CO. Persistence of the (C=C) band at about 1600/cm after introduction of CO shows that the π-coordinated isobutene species is not replaced by CO.

When the CO exposed *t*-BuLi modified sample shown in Fig. 7 is oxidised by air, the bands disappear, indicating that they are real carbonyl bands and not originating from reaction products between CO and organic species. Instead, after oxidation, bands at 1669/cm and 1580/cm are observed which can be ascribed to oxidised species. A spectrum recorded of t-BuLi/SiO$_2$ exposed to CO (not shown), shows only a very weak band at 2066/cm which may be assigned to CO adsorbed on *t*-BuLi clusters adsorbed on the silica surface. Spectra recorded of silica alone after exposure to CO show no carbonyl bands at the present conditions.

The spectra recorded when carrying out the same experiment on Me_3SiCH_2Li modified catalyst are presented in Fig. 8. The strong bands at 2179/cm and 2187/cm are assigned to CO on Cr(II) sites, and illustrates that many of the original sites still exist after the treatment with
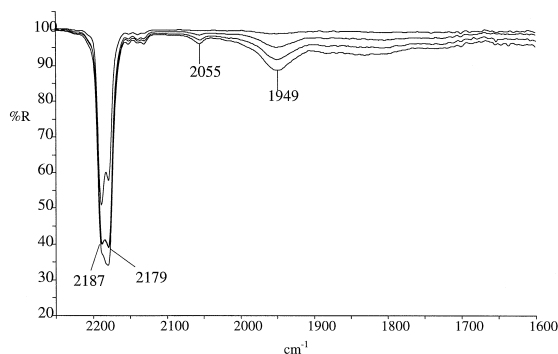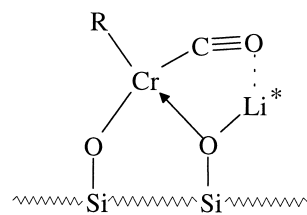

Scheme 6.

Me_3SiCH_2Li. However, two bands with lower intensity at 2055 and 1949/cm are not observed for the unmodified $Cr(II)/SiO_2$ catalyst. These are more like carbonyl bands similar to those observed for the *t*-BuLi modified catalyst shown in Fig. 7. As for the *t*-BuLi modified catalyst, with additional CO injections, saturation of these bands is achieved.

No carbonyl bands are observed when pure silica reacted with Me_3SiCH_2Li are exposed to CO.
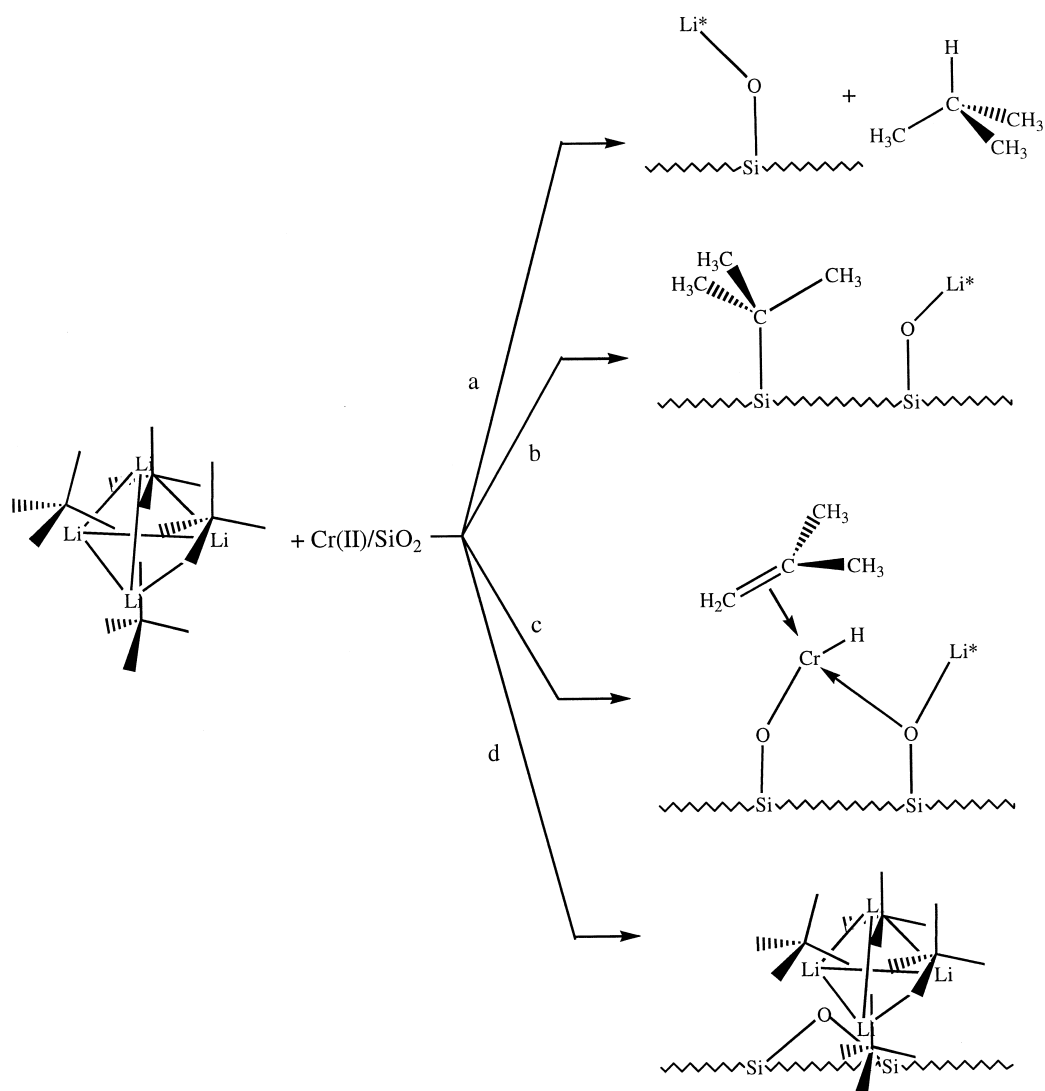
Carbonyl bands at low wavenumbers are often assigned to bridging carbonyl groups. However, the negative charge in the oxygen end of CO enables CO to interact with electrophiles such as lithium ions [28]. As a result, the CO stretching frequency is lowered to various degrees. A possible structure of a modified site after CO coordination, and responsible for the 1747–1784/cm band(s) in Fig. 7, is illustrated in Scheme 6.

The bands at about 2055/cm and in the region 1949–1960/cm may then be assigned to terminal CO adsorbed on chromium without interaction between CO and neighbouring lithium atoms. The bands are observed on both modified catalysts, but they are clearly more dominant for the *t*-BuLi modified sample.

4. Conclusions

Scheme 7 summarises what we have found to be the main surface species on the $Cr(II)/SiO_2$ catalyst modified by *t*-BuLi. They are discussed below.

(a) Si–O–Li from reactions between Si–O–H groups and *t*-BuLi. These sites are not observed

Fig. 8. DRIFT difference spectrum of the $Me_3SiCH_2Li/Cr/SiO_2$ catalyst exposed successive injections of CO as described in the caption of Fig. 7. A spectrum of the catalyst before admitting CO is used as background.

Scheme 7.

directly, but they reveal themselves through the formation of isobutane combined with a reduction of the Si–O–H bands in the DRIFTS spectrum.

(b) Si–R groups from reaction between reactive Si–O–Si bridges and *t*-BuLi. Organic species, detected by DRIFTS, are still present on the supports after hydrolysis and subsequent thermal treatments.

(c) Formation of an isobutene–chromium surface complex. This site is suggested from the DRIFT spectrum which reveal coordinated

isobutene, and where differences to spectra of isobutene on $Cr(II)/SiO_2$ can be attributed to the hydride ligand and/or modification of the Cr–O bond.

(d) Tetrahedral clusters of *t*-BuLi seem to be present, in particular for catalysts with high content of *t*-BuLi.

The only chromium species identified are the isobutene–chromium complexes. However, we know that when *t*-BuLi is added to a $Cr(II)/SiO_2$ catalyst, a site is formed that produces low molecular weight oligomers. We also

know that the number of, or the relative activity of the oligomer producing sites are lower if Me_3SiCH_2Li is used as a modifier. As addition of isobutene does not make a $Cr(II)/SiO_2$ catalyst produce oligomers [15], other factors must be responsible for the modification.

Chromium–isobutene fragments can be formed by two different routes: isobutene formed by decomposition of *t*-BuLi according to reaction (i) can bind to unmodified $Cr(II)$ sites, and, secondly, chromium–isobutene sites can be formed according to the two-step reaction shown in Scheme 3. The latter route leads to a chromium-hydride species which in principle should be possible to detect by infrared spectroscopy by a Cr–H stretch mode in the range 1800 to 1830/cm [29,30]. We observed no such band in our spectra, but this mode might be weak and therefore difficult to observe. We did observe a significant increase in hydrogen formation upon hydrolysis of the *t*-BuLi/Cr/SiO$_2$ catalyst as compared to *t*-BuLi/SiO$_2$, indicating the presence of large amounts of hydride species. We also observed a shift in the C=C stretching band of π-coordinated isobutene to lower wavenumbers indicating stronger metal–isobutene interaction. This shift is in the direction expected for species III in which one covalent chromium–oxygen bond is transferred into a dative bond, resulting in a weaker anti effect and thus a stronger chromium–olefin interaction. Based on these factors, we therefore suggest that species III is present on the *t*-BuLi/Cr/SiO$_2$ catalyst.

The $Me_3SiCH_2Li/Cr/SiO_2$ catalyst also produces oligomers, although to a much lesser extent. Me_3SiCH_2Li have no β-hydrogens and is therefore not able to form a double bond that can π-coordinate to the surface sites. The formation of the π-complexes is therefore not the crucial part of the modification that makes the catalyst produce oligomers.

We have found that the reactivity of the two different lithium-alkyls are different; *t*-BuLi is much more reactive towards silanol groups than Me_3SiCH_2Li. On the other hand, Me_3SiCH_2Li

is the most reactive towards siloxane bridges. The reason for the tendency to produce oligomers might therefore be a consequence of the different abilities of the two lithium-alkyls towards rupture or modification of one of the Cr–O bonds. *t*-BuLi clearly changes the chromium sites more than Me_3SiCH_2Li, which is reflected in the polymerisation results and in the DRIFT spectra, in particular those showing the effect of adding CO. We therefore conclude that *t*-BuLi is more reactive towards the Cr–O bond than Me_3SiCH_2Li, and this difference is the cause for the higher ability of the *t*-BuLi modified catalyst to produce oligomers.

Acknowledgements

References

[1] M.P. McDaniel, Adv. Catal. 33 (1985) 47.
[2] O.M. Bade, R. Blom, Appl. Catal. 161 (1997) 249.
[3] H.L. Krauss, H. Stach, Inorg. Nucl. Chem. Lett. 4 (1968) 393.
[4] A. Zecchina, E. Garrone, G. Ghiotti, C. Morterra, E. Borello, J. Phys. Chem. 79 (1975) 966.
[5] A. Zecchina, E. Garrone, G. Ghiotti, S. Coluccia, J. Phys. Chem. 79 (1975) 972.
[6] J.P. Hogan, J. Polym. Sci., Part A-1 8 (1970) 2637.
[7] C. Groeneveld, P.P.M. Wittgen, H.P.M. Swinnen, A. Wernsen, G.C.A. Schuit, J. Catal. 83 (1983) 346.
[8] G. Ghiotti, E. Garrone, A. Zecchina, J. Mol. Catal. 46 (1988) 61.
[9] A. Zecchina, G. Spoto, G. Ghiotti, E. Garrone, J. Mol. Catal. 86 (1994) 423.
[10] D.L. Myers, J.H. Lunsford, J. Catal. 92 (1985) 260.
[11] B. Rebenstorf, Z. Anorg. Allg. Chem. 571 (1989) 148.
[12] P. Zielinski, J.A. Szymura, I.G. Dalla Lana, Catal. Lett. 16 (1992) 117.
[13] B. Rebenstorf, Acta Chem. Scand. 43 (1989) 413.
[14] L.H. Little, Infrared Spectra of Adsorbed Species, Academic Press, New York, 1966, p. 275.
[15] O.M. Bade, R. Blom, I.M. Dahl, A. Karlson, J. Catal. (in press).
[16] G. Busca, G. Rasmis, V. Lorenzelli, J. Chem. Soc., Faraday Trans. 1 85 (1989) 137.

[17] A.L. Dent, R.J. Kokes, J. Am. Chem. Soc. 92 (1970) 6709.
[18] O.M. Bade, R. Blom, M. Ystenes, Organometallics (submitted).
[19] T. Kottke, D. Stalke, Angew. Chem. 105 (1993) 619.
[20] J.Z. Nyathi, J.M. Ressner, J.D. Smith, J. Organomet. Chem. 70 (1974) 35.
[21] B. Tecle, M. Rahman, J. Oliver, J. Organomet. Chem. 317 (1986) 267.
[22] W.K. Jozwiak, I.G. Dalla Lana, R. Fiedorow, J. Catal. 121 (1990) 183.
[23] D.J.C. Yates, G.W. Dembinski, W.R. Kroll, J.J. Elliot, J. Phys. Chem. 73 (1969) 911.

[24] M. Kantcheva, I.G. Dalla Lana, J.A. Szymura, J. Catal. 154 (1995) 329.
[25] B. Rebenstorf, J. Polym. Sci., Part A: Polym. Chem. 29 (1991) 1949.
[26] G. Ghiotti, E. Garrone, A. Zecchina, J. Mol. Catal. 65 (1991) 73.
[27] B. Rebenstorf, J. Catal. 117 (1989) 71.
[28] C.P. Horwitz, D.F. Shriver, Adv. Organomet. Chem. 23 (1984) 219.
[29] H.P. Fritz, Adv. Organomet. 1 (1964) 239.
[30] T.A. Markova, S.A. Smirnov, I.A. Oreshkin, B.A. Dolgoplosk, Kinet. Katal. 28 (1986) 1229.