

In situ-DRIFTS investigations of the gas phase polymerisation of 1,3-butadiene on supported Nd and La allyl complexes

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Abstract

DRIFT spectroscopy was successfully used to investigate interactions of allyl lanthanide complexes with aluminium organic cocatalysts and for in situ studies of the insertion/polymerisation of gaseous 1,3-butadiene on the ‘adducts’ of both catalyst components as well as on silica-supported allyl complexes/cocatalysts. Shifts of characteristic bands revealed electronic interactions between the allyl species and the Lewis-acidic methylaluminoxane (MAO) as well as the trialkyl aluminium compounds. It was found, that only trialkyl aluminium compounds with steric-demanding alkyl groups enable a polymerisation of 1,4-polybutadiene corresponding to a π -allyl insertion mechanism. Start and progress of the heterogeneous catalytic polymerisation could be semi-quantitatively followed by means of in situ-DRIFTS, recording the appearance and the changes of characteristic vibration bands of the allyl species and the formed polymer.

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1. Introduction

Synthetic rubber is usually produced by homogeneous catalytic liquid phase polymerisation of 1,3-butadiene to 1,4-*cis*-polybutadiene using Ziegler–Natta catalysts. However, this reaction can also be carried out as heterogeneous catalytic gas phase process with supported neodymium Ziegler catalysts [1–3] or with allyl lanthanide complexes using methylaluminoxane (MAO) as cocatalyst [4].

In previous papers results of DRIFT spectroscopy, NIR Raman spectroscopy, NMR spectroscopy, and temperature-programmed reaction spectroscopy

(TPRS) were presented, characterising the structure, bonding properties and stability of Nd and La triallyl complexes as well as the changes of their properties upon supporting on silica (WITCO) modified with methylaluminoxane (MAO) as cocatalyst [5,6]. Details of the identification of the characteristic allyl vibrations are given in [6]. π -Allyl ligands were suggested as catalytic active sites for the polymerisation of 1,3-butadiene, or they are the sites where π -coordinated heptadienyl species are formed by insertion of butadiene molecules. These heptadienyl neodymium complexes are recently assigned to be the genuine active sites of unsupported $\text{Nd}(\text{C}_3\text{H}_5)_3$ used as catalyst in the liquid phase polymerisation of 1,3-butadiene [7,8].

The present work is aimed at following objectives. Firstly, Nd pentamethylcyclopentadienyl-diallyl ($\text{NdCp}^*(\text{C}_3\text{H}_5)_2$) as another potential catalyst is

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compared with $\text{Nd}(\text{C}_3\text{H}_5)_3$ concerning the binding properties, stability and activity. Secondly, the interactions of various aluminium organic compounds (potential cocatalysts) with Nd triallyl complexes are investigated to better understand the function of the cocatalyst, being necessary to achieve a high activity (TOF) and predominantly *cis*-selectivity of the polybutadiene formation [9,10]. Thirdly, the adsorption/reaction of 1,3-butadiene at the catalysts should be investigated by in situ-DRIFTS studies, i.e. the start of the polymerisation, as well as the growing of the polymer should be followed.

2. Experimental

2.1. Samples

Syntheses of the complexes were performed by project partners and has been described for $\text{Nd}(\text{C}_3\text{H}_5)_3$ elsewhere [7,8], the first synthesis of the $\text{NdCp}^*(\text{C}_3\text{H}_5)_2$ has been reported in [11]. Supporting of the allyl lanthanides on MAO-modified silica (WITCO) was carried out by another partner and has been described in detail in [4]. Usually, the allyl lanthanide complex was added to a toluene solution of methylaluminoxane with a molar Al/Nd or Al/La ratio of 30:1 at temperatures down to -70°C . Afterwards, this solution was added to a suspension of the WITCO support (silica modified by MAO) in toluene. The pre-treatment of the complexes with MAO has been proved as promisingly to protect the metal complexes against reaction with residual hydroxyl groups on the silica support.

Model samples for investigation of interactions between potential cocatalysts with the allyl lanthanide complexes were prepared by adsorption/reaction of various aluminium organic compounds from a toluene solution on the powdered allyl complexes. The aluminium organic compounds used in several times excess to the Nd complexes are summarised in Table 1. The solids dried under anaerobic conditions are called 'adducts' in this paper. A survey on all samples studied by DRIFTS is given in Table 2.

Preparation and handling of all the oxygen and moisture sensitive samples needs application of extremely anaerobic conditions. Preparation of DRIFTS samples was carried out in a glove box (Ganuk

Table 1

Survey on the aluminium organic compounds used as potential cocatalysts

Abbreviation	Compound/reagent ^a
TMA	Trimethylaluminium, 2.0 M solution in toluene
TEA	Triethylaluminium, 1.9 M solution in toluene
TIBA	Triisobutylaluminium, 1.0 M solution in toluene
MAO	Methylaluminoxane, 10 wt.% solution in toluene

^a Aldrich reagents.

GmbH) under purified Ar. DRIFTS investigations were performed in a modified reaction chamber (Graseby Specac) which allowed a sample loading under inert conditions in the glove box and subsequently a connection of the reaction chamber to a gas manifold.

2.2. Temperature-programmed reaction spectroscopy (TPRS)

A conventional TPX micro-flow system equipped with a thermal conductivity detector (TCD) was used to study the thermal decomposition of the allyl lanthanide complexes in a flow of highly purified/dried helium (6.0). Analysis of the desorbed gaseous products occurred by a quadrupole mass spectrometer QMG 420-C (Balzers) using the multi-ion detection mode. The quartz reactor of the TPX apparatus was filled with the samples (unsupported or supported complexes) under inert condition in a glow box.

Table 2

Survey on the used allyl lanthanide 'adducts' with cocatalysts and allyl lanthanide/support catalysts

Samples	Active component	Cocatalyst	Support
$[\text{Nd}(\text{C}_3\text{H}_5)_3]_2$	–	–	–
$\text{Nd}(\text{C}_3\text{H}_5)_3 \cdot$ dioxane	–	–	–
$\text{NdCp}^*(\text{C}_3\text{H}_5)_2$	–	–	–
$\text{Nd}(\text{C}_3\text{H}_5)_3$ -MAO	$\text{Nd}(\text{C}_3\text{H}_5)_3$	MAO	–
$\text{Nd}(\text{C}_3\text{H}_5)_3$ -TIBA	$\text{Nd}(\text{C}_3\text{H}_5)_3$	TIBA	–
Cat.1	$\text{Nd}(\text{C}_3\text{H}_5)_3$ -dioxane	MAO	MAO-SiO ₂
Cat.2	$\text{La}(\text{C}_3\text{H}_5)_3$ -dioxane	MAO	MAO-SiO ₂
Cat.3	$\text{NdCp}^*(\text{C}_3\text{H}_5)_2 +$ 2,3-Me ₂ -butadiene ^a	MAO	MAO-SiO ₂

Cp*, pentamethylcyclopentadienyl.

^a 2,3-Me₂-butadiene added to the metal complex solution to stabilise the Nd complex prior supporting.

2.3. DRIFT spectroscopy (DRIFTS)

Infrared spectra of the allyl lanthanide complexes were recorded on a Mattson research spectrometer RS-1 with a ‘Selector’ equipment (Graseby Specac/L.O.T.). The heatable reaction chamber has been modified for extremely anaerobic sample loading and enhanced optical transmission (KCl instead ZnSe window).

Special sample holders were used for unsupported and supported metal complexes. A ‘diamond pad’ with a sample volume of 1 μl was utilised for metal complexes and their ‘adducts’ with cocatalysts. The metal complexes and also the ‘adducts’ were placed between diamond splinters. In this way a sufficient ‘optical dilution’ and high dispersing power was achieved. The catalysts were placed in a ‘conned hole’ with a volume of 28.3 μl to investigate ‘optical undiluted’ the relative small amounts of supported metal complexes. A MCT detector (Analytik Jena GmbH) cooled with liquid nitrogen allowed to collect a spectrum in only 1 min, accumulating two hundred scans to obtain a sufficient signal to noise ratio. Resolution amounted to 8 or 4 cm^{-1} . A gas manifold system enabled DRIFTS investigations under inert gas atmosphere as well as in situ adsorption/polymerisation during exposure of gaseous butadiene to the samples. 1,3-butadiene was purified from ‘stabilisers’ by molecule sieve 5A and basic alumina.

3. Results and discussion

3.1. TPRS investigations

Previous TPRS studies of Nd and La triallyl have shown that propylene is released at 390 and 417 K, respectively. DRIFTS investigations of the solid residues of the thermally decomposed complexes showed the formation of hydrogen poor compounds such as allenylidene [5]. In the case of $\text{Nd}(\text{C}_3\text{H}_5)_3$ -dioxane the donor ligand dioxane is desorbed at ca. 345 K. A comparison with the decomposition behaviour of $\text{NdCp}^*(\text{C}_3\text{H}_5)_2$ is shown in Fig. 1. Propylene desorption from $\text{NdCp}^*(\text{C}_3\text{H}_5)_2$ takes place at significantly higher temperature (ca. 428 K) than from $\text{Nd}(\text{C}_3\text{H}_5)_3$ -dioxane. Nearly two molecules propylene were released from one triallyl complex,

whereas only one propylene molecule was obtained per $\text{NdCp}^*(\text{C}_3\text{H}_5)_2$. Methane releasing from the pentamethyl group was observed only at higher temperatures (above 450 K). Obviously, $\text{NdCp}^*(\text{C}_3\text{H}_5)_2$ is more thermally stable than $\text{Nd}(\text{C}_3\text{H}_5)_3$.

3.2. DRIFTS investigations

DRIFT spectra of unsupported and supported $\text{Nd}(\text{C}_3\text{H}_5)_3$ as well as $\text{La}(\text{C}_3\text{H}_5)_3$ were previously presented in [5,6]. The main results of this study are briefly summarised here. The spectra of the complexes showed characteristic absorption bands at 1545–1550 and 1008–1024 cm^{-1} which could be assigned to anti-symmetric and symmetric stretching vibration of the CCC chain of π -allyl ligands. A complete π -charge equilibration in the CCC chain is the reason that only one $\nu_{\text{as}}(\text{C}\cdots\text{C}\cdots\text{C})$ and also one $\nu_{\text{s}}(\text{C}\cdots\text{C}\cdots\text{C})$ band appears. The spectra of all the supported complexes were similar to the spectra of the unsupported complexes showing a characteristic vibration absorption at 1536–1538 cm^{-1} . The $\nu_{\text{s}}(\text{C}\cdots\text{C}\cdots\text{C})$ band is superimposed by strong IR absorption of the silica support. The absence of a σ -allyl band ($\nu(\text{C}=\text{C})$ between 1620 and 1650 cm^{-1}) indicated that the equilibrated π -charge distribution in the CCC chain coordinated to the neodymium cation is retained after supporting. However, the shift of the $\nu_{\text{as}}(\text{C}\cdots\text{C}\cdots\text{C})$ band for ca. 10 cm^{-1} to lower wave numbers points to interactions with the MAO loaded silica support. Presumably, the electron density in the CCC chain is slightly decreased by the interaction with the Lewis-acidic MAO, i.e. the ‘electron cloud’ at the allyl species is slightly shifted to the metal cation by an interaction with the electrophilic MAO-SiO₂ support. Now we obtained similar bands for the π -allyl ligands with unsupported as well as with supported $\text{NdCp}^*(\text{C}_3\text{H}_5)_2$. Calculation of the structure and binding parameters using the previously developed structural model [6] confirmed that the π -bonded allyl ligands in $\text{Nd}(\text{C}_3\text{H}_5)_3$ and $\text{NdCp}^*(\text{C}_3\text{H}_5)_2$ have quite similar binding properties.

3.2.1. DRIFT spectra of ‘adducts’

The investigation of the interaction of allyl complexes with potential aluminium organic cocatalysts were exemplary carried out with $\text{Nd}(\text{C}_3\text{H}_5)_3$ and

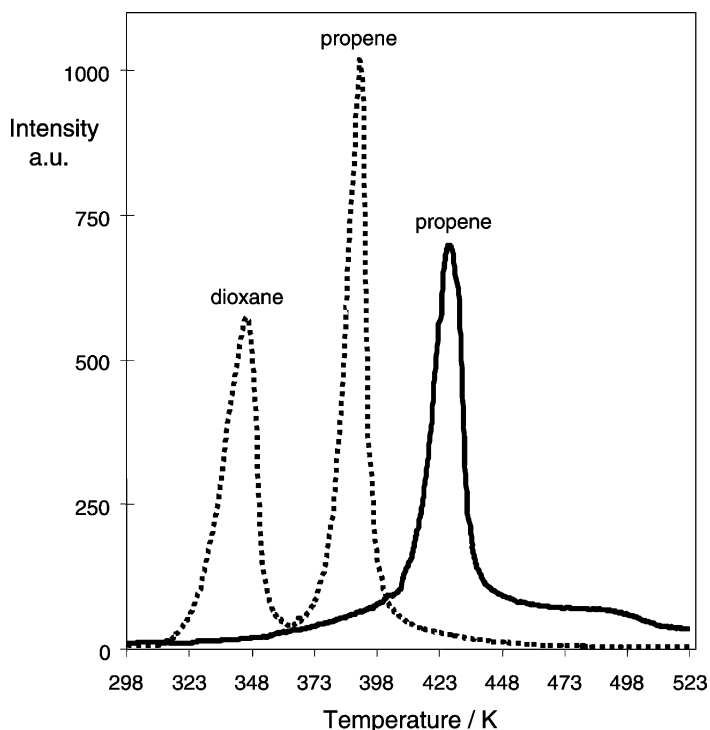


Fig. 1. TPRS profiles of thermal decomposition of $\text{Nd}(\text{C}_3\text{H}_5)_3$ -dioxane (broken line) and $\text{NdCp}^*(\text{C}_3\text{H}_5)_2$ (full line), respectively, in a He flow.

$\text{Nd}(\text{C}_3\text{H}_5)_3$ -dioxane. Prior the investigation of their 'adducts' with aluminium organic compounds of different structures, the IR spectra of toluene solutions of the Al compounds were recorded using a cuvette with KBr windows. No other bands in the range of the vibration absorption of the allyl species were observed apart from the vibration bands of the toluene at 1604 and 1495 cm^{-1} . Thus, interactions between the neodymium allyl complexes and the Al compounds could be studied without any superimposition.

DRIFT spectra of the 'adducts' of $\text{Nd}(\text{C}_3\text{H}_5)_3$ and $\text{Nd}(\text{C}_3\text{H}_5)_3$ -dioxane with MAO and TIBA (Fig. 2) showed bands at 1575 and 1520 cm^{-1} instead of the characteristic bands of the allyl species of the $\text{Nd}(\text{C}_3\text{H}_5)_3$ ca. 1550 and 1490 cm^{-1} [5]. Comparable spectra obtained for the 'adducts' of $\text{Nd}(\text{C}_3\text{H}_5)_3$ and $\text{Nd}(\text{C}_3\text{H}_5)_3$ -dioxane with the aluminium organic compounds indicate a displacement of dioxane as donor ligand upon formation of the 'adducts'. Similar IR spectra as shown in Fig. 2 were obtained with TMA and TEA.

Three possibilities for the interactions of the co-catalysts with the triallyl neodymium complexes from metal organic view can be discussed:

- (i) Only an adduct is formed between Nd triallyl and Al trialkyl. Two alkyl groups are coordinated as electron donors to the Nd and consequently, the electron density in the π -bonded allyls would be increased.
- (ii) The aluminium alkyl act as Lewis acid and therefore, one allyl is transferred from the Nd triallyl to the aluminium organic compound. The formed $[\text{AlR}_3(\text{C}_3\text{H}_5)]^-$ anion is coordinated to the $[\text{Nd}(\text{C}_3\text{H}_5)_2]^+$ cation by two alkyl groups to the Nd^{3+} cation. The allyl in the aluminate anion would be σ -bonded to the aluminium.
- (iii) $[\text{AlR}_3]_2$ react with $\text{Nd}(\text{C}_3\text{H}_5)_2$ corresponding to Eq. (1) where also one allyl is transferred from the Nd complex, but this allyl would be π -bonded in the formed dialkyl-allyl aluminium. The formed aluminate anion $[\text{AlR}_4]^-$ is coordinated to the

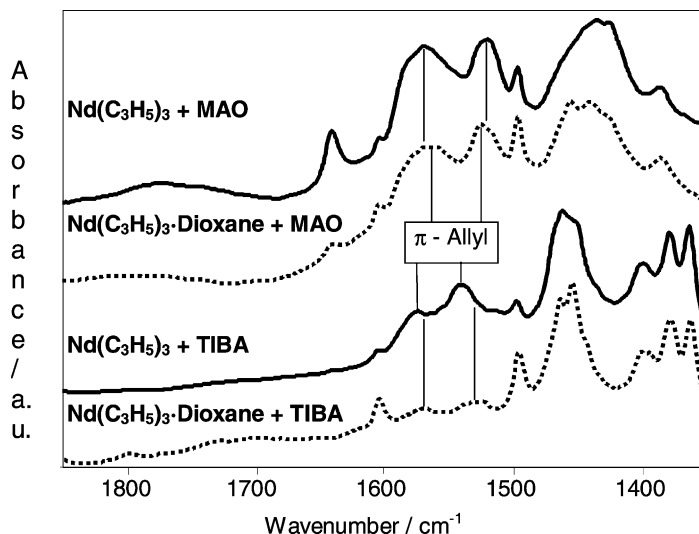
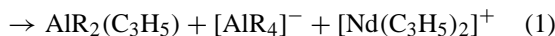


Fig. 2. DRIFT spectra of 'adducts' of $\text{Nd}(\text{C}_3\text{H}_5)_3$ -dioxane and $\text{Nd}(\text{C}_3\text{H}_5)_3$, respectively, formed with MAO or TIBA.

$[\text{Nd}(\text{C}_3\text{H}_5)_2]^+$ cation and influences the binding properties in similar way as suggested under (i) and (ii).



We prefer the third mode of interaction because only it can properly explain the appearance of two bands for π -allyl species. The band at 1575 cm^{-1} can be attributed to the allyl species of the $[\text{Nd}(\text{C}_3\text{H}_5)_2]^+$ cation and we assume that the band at ca. 1520 cm^{-1} can be attributed to the allyl of the $\text{AlR}_2(\text{C}_3\text{H}_5)$. A formation of a trialkyl-allyl aluminate $[\text{AlR}_3(\text{C}_3\text{H}_5)]^-$ corresponding to (ii) can be excluded because we did not observe any IR band in the range for σ -allyl between 1620 and 1650 cm^{-1} .

3.2.2. DRIFTS studies of 1,3-butadiene interaction with 'adducts'

Next, the interaction of the 'adducts' of Nd tri-allyl and selected Lewis-acidic aluminium organic compounds with 1,3-butadiene was studied by in situ-DRIFTS experiments. Gaseous butadiene was introduced into the IR cell for 1 min and then DRIFT spectra were recorded after butadiene exposure at

room temperature under static conditions for 10, 30 and 60 min.

Results of the investigations with $\text{Nd}(\text{C}_3\text{H}_5)_3$ -MAO are shown in Fig. 3, similar results were obtained with $\text{Nd}(\text{C}_3\text{H}_5)_3$ -TIBA. The bands of allyl ligands (1545 cm^{-1}) and the bands of gaseous butadiene decreased, whereas bands at 1641 and 1655 cm^{-1} appeared. The band at 1641 cm^{-1} can be attributed to a butadiene insertion into the allyl-neodymium bond, forming heptadienyl species ($\text{C}_3\text{H}_4-(\text{CH}_2)_2-\text{CH}=\text{CH}_2$) in the initiating period and to a subsequent formation of a polybutadiene chain by repeated butadiene insertion. The heptadienyl species and the polybutadienyl chain are similarly π -coordinated to the Nd^{3+} cation as the parent allyl species [8,10]. The growing of a polymer chain is reflected by the rising bands at 1655 cm^{-1} ($\nu(\text{C}=\text{C})$ of *cis*- $\text{CH}=\text{CH}-$) and at about 1455 cm^{-1} ($\delta(\text{CH})$ of *cis*- $\text{CH}=\text{CH}-$) [12].

In the case of TMA and TEA only butadiene insertion was observed, but not a growing of polybutadiene chains. Following explanation for this different behaviour is suggested from coordination chemical view [13].

At first, all three aluminium trialkyls (TIBA, TMA, TEA) can insert two times into the two allyl of the $\text{Nd}(\text{C}_3\text{H}_5)_2[\text{AlR}_4]$ complex, forming heptadienyl species. In this way a maximum coordination

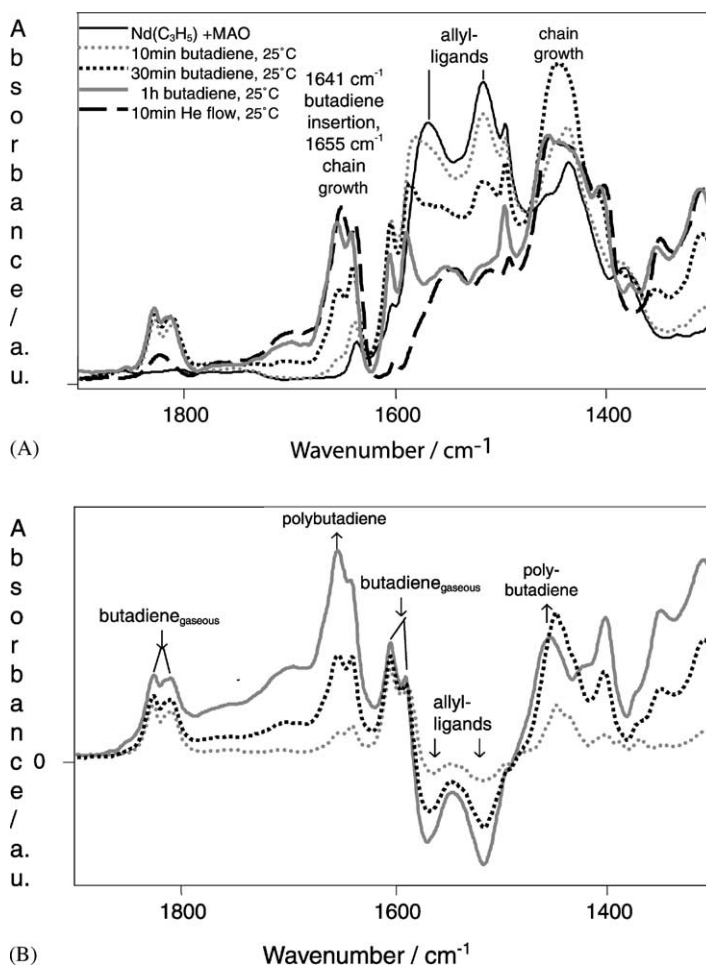


Fig. 3. (A) DRIFT spectra recorded during exposure of $\text{Nd}(\text{C}_3\text{H}_5)_3\text{-MAO}$ to gaseous 1,3-butadiene. (B) Corresponding difference spectra = spectra after butadiene exposure subtracted by the initial spectrum before 1,3-butadiene treatment.

number of eight is achieved for the Nd^{3+} . However, in the case of the unwieldy isobutyl groups of TIBA the bond of the $[\text{AlR}_4]^-$ species to the $[\text{Nd}(\text{C}_3\text{H}_4-(\text{CH}_2)_2-\text{CH}=\text{CH}_2)_2]^+$ species should be weak only. Therefore, the coordination of another 1,3-butadiene molecule to the Nd^{3+} cation by its π -electrons (η^4 -*cis*-coordination) is not hindered and butadiene insertion into a heptadienyl group occurs subsequently. Repeated intermediate butadiene anchoring and insertion into the polybutadienyl neodymium bond result in a polymer chain growth.

In contrast, the alkyl-bridge formation should be much stronger in the case of TMA and TEA 'adducts'.

Therefore, butadiene insertion is restricted (two times only), polymerisation does not take place.

3.2.3. *In situ*-DRIFTS studies of 1,3-butadiene polymerisation on supported allyl lanthanides

Catalyst samples located in the 'conned hole' was exposed to gaseous 1,3-butadiene at 25 °C. First, the spectrum of the supported allyl lanthanide was recorded under inert atmosphere. The area of the bands (integral absorbance) of the π -allyl species was determined as a measure for the amount of allyl species in the various samples in order to calculate

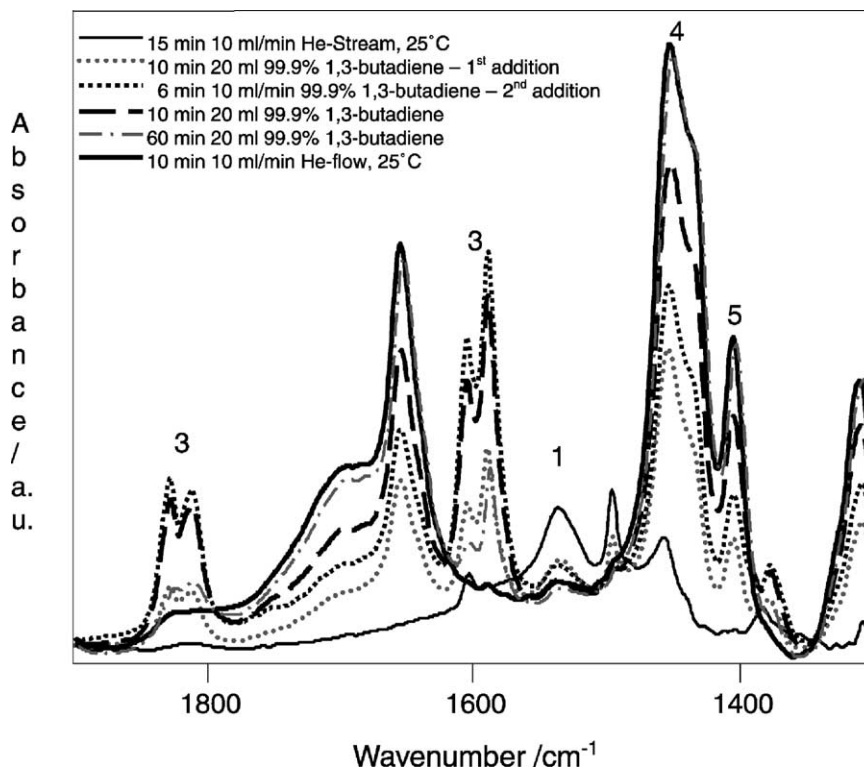


Fig. 4. DRIFT spectra recorded during in situ study of the interaction of Cat.1 with 1,3-butadiene at 25°C. Assignments of the IR vibration bands: (1) 1536 cm⁻¹, π -allyl species; (2) 1655 cm⁻¹, polybutadiene ν (CC); (3) 1828, 1811, 1605 and 1588 cm⁻¹, gaseous 1,3-butadiene; (4) 1451 cm⁻¹, polybutadiene δ (CH); (5) 1408 cm⁻¹, 1,4-*cis*-polybutadiene δ (CH) of –HC=CH).

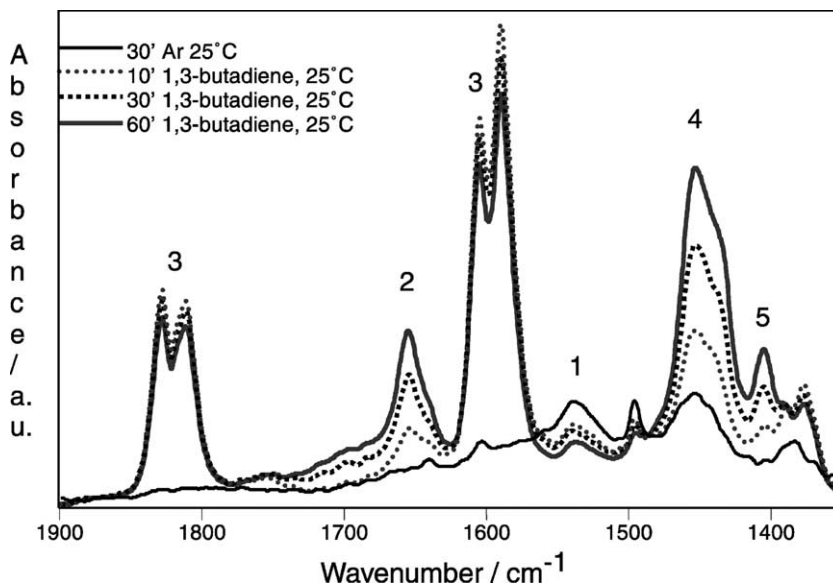


Fig. 5. DRIFT spectra recorded during in situ study of the interaction of Cat.3 with 1,3-butadiene at 25°C. Assignments of the IR vibration bands: (1) π -allyl species; (2) polybutadiene ν (CC); (3) gaseous 1,3-butadiene; (4) polybutadiene δ (CH); (5) 1,4-*cis*-polybutadiene δ (CH) of –HC=CH).

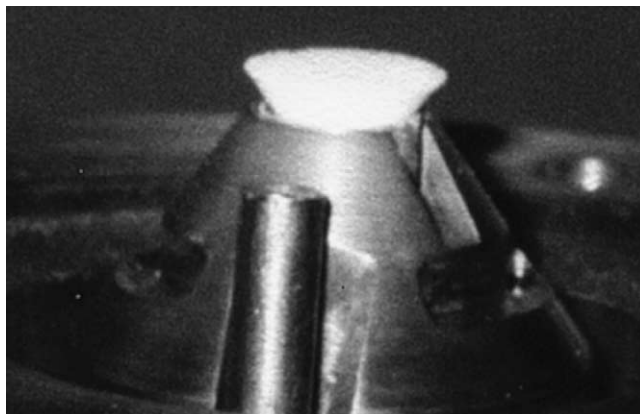


Fig. 6. Picture of the 'conned hole' sample holder of the IR cell with the growing white polymer/catalyst composite.

specific activities (see below). Afterwards, the He flow was switched to butadiene for 1 min, then the cell was closed and the polymerisation process was observed under static conditions, i.e. under decreasing butadiene atmosphere.

Spectra recorded after different butadiene exposure periods are shown in Fig. 4 for a Nd triallyl catalyst (Cat.1) and in Fig. 5 for a Nd pentamethylcyclopentadienyl-diallyl catalyst (Cat.3).

In the case of the more active Cat.1 the 1,3-butadiene addition into the cell was repeated because of the fast butadiene consumption which was advisable by the strongly decreased bands of gaseous 1,3-butadiene.

The characteristic bands of polybutadiene at 1655 cm^{-1} and in the range between 1400 and 1470 cm^{-1} [13] increased with rising exposure period, whereas the band of catalytic-active π -allyl species at 1536 cm^{-1} decreased. The decrease of the

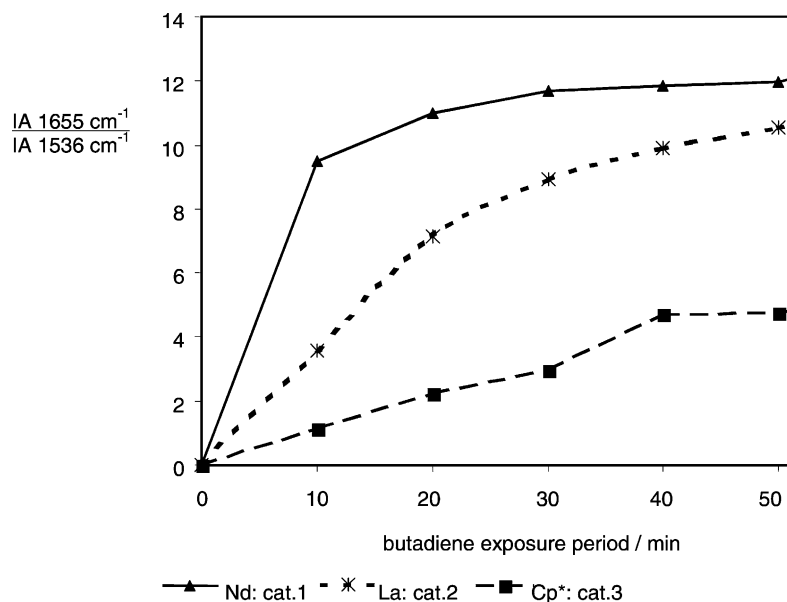


Fig. 7. Comparison of the polymer formation rate on selected allyl lanthanide catalysts, based on an increase of the $IA_{1655\text{ cm}^{-1}}$ (polymer chain), ratio $IA_{1655\text{ cm}^{-1}}/IA_{1536\text{ cm}^{-1}}$ vs. polymerisation period.

characteristic bands of allyl groups coordinated to neodymium does not mean that the active sites are lost but the decrease is caused by increasing dilution of the catalyst by the formed polymer. Fig. 6 show the polymer/catalyst composite growing out of the ‘conned hole’.

The comparison of the spectra series in Figs. 4 and 5 indicates that the formation of polybutadiene occurs significantly more slowly on Cat.3 than on Cat.1. Obviously, a steric shielding of the active sites (allyl and heptadienyl species, respectively), by the methyl-cyclopentadienyl ligand results in a significantly lower activity of Cat.3.

A semi-quantitative comparison of the intrinsic polymerisation activity of different catalyst is possible, when the integral absorbance (IA) of the rising band of the $\nu(\text{C}=\text{C})$ vibration of polybutadiene at 1655 cm^{-1} is referred to the IA of the band of the allyl species in the untreated catalyst. The latter band should be proportional to the concentration of catalytic active sites in the various samples. The results of this evaluation is shown in Fig. 7. The following activity ranking of the catalysts can be stated clearly:

Cat.1 > Cat.2 > Cat.3

4. Conclusions

Using in situ-DRIFTS it was possible for the first time to study the interaction of butadiene with supported allyl lanthanide complexes under conditions which come nearby the heterogeneous catalytic gas phase polymerisation of 1,3-butadiene to 1,4-polybutadiene.

In detail following different interactions of 1,3-butadiene with the allyl complex in absence and presence of aluminium organic cocatalysts were observed. Interaction of 1,3-butadiene with the unsupported complexes resulted only in an insertion of one 1,3-butadiene into the π -allyl-neodymium bond revealed by the appearance of a band at ca. 1640 cm^{-1} , no polymer formation was observed. A further 1,3-butadiene insertion into the π -heptadienyl neodymium bond took place only, if a suitable cocatalysts such as MAO and TIBA was present (growth of the band at 1655 cm^{-1}). Investigation of ‘adducts’ of $\text{Nd}(\text{C}_3\text{H}_5)_3$ with various aluminium trialkyls showed

that only compounds with steric-demanding alkyl groups enables a repeating butadiene insertion, i.e. a polymer formation.

A semi-quantitative comparison of the specific polymerisation activities is possible using the ratio of the integral absorbance (IA) of the increasing band of the polymer chain to the IA of the band of the π -allyl species. The latter IA value is a measure for the concentration of the π -allyl species and should be proportional to the concentration of the primary formed heptadienyl species which are suggested as the genuine active sites for the chain growth.

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