

# Vibrational spectra of silsesquioxanes impregnated with the metallocene catalyst bis( $\eta^5$ -cyclopentadienyl)zirconium(IV) dichloride

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## Abstract

FT-IR photoacoustic and Raman spectroscopy have been used to study the interactions between the metallocene catalyst,  $\text{Cp}_2\text{ZrCl}_2$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ), and two polyhedral oligomeric silsesquioxanes (POSS) supports. The first silsesquioxane support,  $\text{POSS}_h$ , contains ( $\beta$ -hydroxyl)-tertiary amine groups, while in the second one,  $\text{POSS}_u$ , these  $-\text{OH}$  groups have been converted into *N*-(*p*-toluyl) urethane groups. The vibrational spectra of the  $\text{Cp}_2\text{ZrCl}_2:\text{POSS}_h$  and  $\text{Cp}_2\text{ZrCl}_2:\text{POSS}_u$  samples show that the  $\text{Cp}_2\text{ZrCl}_2$  catalyst reacts with the C–OH groups of  $\text{POSS}_h$  and also interacts with N–H and  $>\text{C}=\text{O}$  groups of  $\text{POSS}_u$ . Furthermore,  $\text{Cp}_2\text{ZrCl}_2$  can react with the Si–OH groups of the POSS supports and also interact with the O atoms that are bonded to the benzene rings and the N atoms of the tertiary amines in both silsesquioxanes. As a result of the interactions between  $\text{Cp}_2\text{ZrCl}_2$  and the POSS supports, acidic species are generated. The  $\text{Cp}_2\text{ZrCl}_2:\text{POSS}_h$  mass ratio seems to be an important parameter in the formation of Zr–O bonds and the acidic species.

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## 1. Introduction

The title compound,  $\text{Cp}_2\text{ZrCl}_2$ , belongs to the organometallic class known as metallocenes which, together with a co-catalyst, form a versatile system for the (co)polymerization of ethylene, propylene and higher  $\alpha$ -olefins [1]. The main drawbacks for the industrial applications of metallocenes are the difficulties in controlling the polymer morphology and the large amount of co-catalyst needed to achieve and maintain high activity. Nowadays, in order to overcome these difficulties, the general direction of the industrial applications is to immobilize the metallocenes on inert supports. For instance, silica is one of the most suitable supports for metallocene catalysts. As the result of several factors, however, such as the silica activation temperature and the method of immobilization, inactive species can be generated on the catalytic surface that lead to a decrease

in activity. Previous studies have shown that catalytic activity can be improved when the metallocene catalyst is immobilized on methylaluminoxane or organosilanes-modified silicas when compared to immobilization on bare silica [2,3]. Moreover, immobilization of metallocenes on polyhedral oligomeric silsesquioxanes (POSS)-modified silicas [4] leads to an enhancement of the catalytic activity when compared with that resulting from immobilization solely on silica. The silsesquioxanes are polyhedral structures formed by the linkage of tetrahedral units (T), each unit containing a Si atom bonded to three O atoms and one R group. Furthermore, the silsesquioxanes can be either in a condensed form, displaying a perfect polyhedral structure, or in a non-condensed form with some broken Si–O–Si bonds [5].

As reported previously [4], the silsesquioxanes used in this study are formed as a mixture of octahedral,  $\text{T}_8$ , non-ahedral,  $\text{T}_9(\text{OH})$  and decahedral,  $\text{T}_{10}$ , condensed structures. The R groups of the  $\text{POSS}_h$  support contain ( $\beta$ -hydroxyl)-tertiary amine groups while, in the case of  $\text{POSS}_u$ , the C–OH groups have been functionalized by *p*-toluyl isocyanate leading to the formation of *N*-(*p*-toluyl) urethane groups [4]. The presence of

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the soluble R groups in the POSS structures facilitates the study of the interactions between the metallocene and the supports. In addition, Duchateau [6] has shown that the silsesquioxanes can be used as soluble models for silica when studying the interactions between different catalytic systems and their supports. This possibility arises because the silsesquioxanes contain bonds similar to those found in silica, such as Si–O–Si and Si–OH.

From our earlier X-ray photoelectron work [4], it appears that the Zr–O–C moiety can be obtained either by immobilization of (*n*-BuCp)<sub>2</sub>ZrCl<sub>2</sub> on POSS<sub>h</sub>-modified silica or by impregnation with POSS<sub>h</sub>. Therefore, it is reasonable to expect that a similar situation will exist when Cp<sub>2</sub>ZrCl<sub>2</sub> is immobilized on POSS<sub>h</sub>-modified silica or impregnated with POSS<sub>h</sub>. Since the compounds resulting from the reactions of Cp<sub>2</sub>ZrCl<sub>2</sub> with silsesquioxanes are soluble, their characterization using routine techniques is much easier, thus allowing a better understanding of the interactions between the catalyst and the supports. The organometallic compounds are complex molecules and undertaking an adequate vibrational treatment, *viz.*, a full normal-coordinate analysis and the associated force constant calculations, would be a challenge. The goal of this paper is to assign the photoacoustic IR and Raman modes of the Cp<sub>2</sub>ZrCl<sub>2</sub>:POSS compounds as much as possible in order to provide further evidence of any interactions. A deeper understanding of the interactions occurring in such catalytic systems is a key factor in the improvement of the resulting catalytic properties.

## 2. Experimental

### 2.1. Materials

The silsesquioxanes were synthesized according to the procedure reported in the literature [4]. The Cp<sub>2</sub>ZrCl<sub>2</sub> (99% purity) catalyst was purchased from Strem Chemicals (USA) and was used without further purification. *Purum*-grade toluene, purchased from EMD (USA), was dried by standard techniques prior to utilization.

### 2.2. Samples preparation

The POSS<sub>h</sub> and POSS<sub>u</sub> supports were impregnated with the Cp<sub>2</sub>ZrCl<sub>2</sub> catalyst in the following mass ratios: Cp<sub>2</sub>ZrCl<sub>2</sub>:POSS<sub>h</sub> (1:1), Cp<sub>2</sub>ZrCl<sub>2</sub>:POSS<sub>h</sub> (3:1) and Cp<sub>2</sub>ZrCl<sub>2</sub>:POSS<sub>u</sub> (1:1). The catalyst and the silsesquioxane were dissolved separately in distilled toluene in Schlenk tubes. The catalyst solution was then added to the Schlenk tube containing the solubilized silsesquioxane. After 1 h stirring at room temperature, the solvent was removed under vacuum. The resulting solid was dried under vacuum for 8 h. All the procedures were performed under a N<sub>2</sub> atmosphere.

### 2.3. FT-IR photoacoustic spectroscopy (FT-IR-PAS)

The compounds were characterized using a Bio-Rad-FTS6000 spectrometer equipped with a MTEC 300 photoacoustic detector. The PA spectra were collected in rapid-scan mode

at room temperature in absorbance units, co-adding 64 scans at a resolution of 4 cm<sup>-1</sup> in the 4000–400 cm<sup>-1</sup> range. All spectra were measured at 2.5 kHz optical path difference velocity. Under these conditions, the positions of the main bands were reproducible and are considered to be accurate to about ±1 cm<sup>-1</sup>. No spectral band fitting was employed.

### 2.4. Raman spectroscopy

Raman measurements were performed at room temperature using an inVia Renishaw spectrometer equipped with a NIR diode laser (785 nm), a charge-coupled detector, a 1200 lines/mm diffraction grating and an edge filter. The samples were mounted on an XYZ manual stage of a Leica microscope and the laser beam was focused onto the samples through a 20× long-working distance objective. The spectra were recorded using a laser power adjusted between 15 and 300 mW and a slit width of 50 μm. Several scans were co-added to improve the signal-to-noise ratio. The acquisition time was varied from sample to sample in the range of 10–60 s. The Raman spectrometer was calibrated prior to the measurements by exciting a Si wafer placed under the microscope and by performing an automatic offset correction. The data acquisition and analysis were accomplished using WiRE<sup>TM</sup> software [7]. The wavenumbers are estimated to be accurate to at least ±1 cm<sup>-1</sup>. The samples were loaded in capillary tubes and analyzed under a N<sub>2</sub> atmosphere.

## 3. Results and discussion

### 3.1. Vibrational spectra of the catalyst, Cp<sub>2</sub>ZrCl<sub>2</sub>

Maslowsky and Nakamoto [8] have reported that molecules of type Cp<sub>2</sub>MCl<sub>2</sub>, where M = Zr, Ti and Hf, have C<sub>2v</sub> local symmetry (Fig. 1), displaying 14 normal vibration modes, of which 11 are both IR- and Raman-active and three are Raman active only. Balducci et al. [9] have reported that the normal modes of the cyclopentadienyl (Cp) ring are not affected significantly by the number of Cp rings present or the nature of the metal M, because the Cp vibrations appear in a different region than do those of the M-ligand with one exception, the Cp tilt modes. Despite the fact that some of the vibrational modes of the Cp rings should be active only in the Raman or the IR or even inactive, these modes are observed by both techniques. It was reported [9] that the vibrational spectrum is more complex when the Cp rings are not parallel. On the other hand, the presence of two voluminous Cp rings leads to the distortion of the tetrahedral

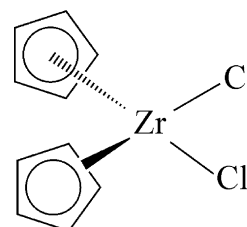


Fig. 1. Structure of the metallocene catalyst, Cp<sub>2</sub>ZrCl<sub>2</sub>.

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