

Determining the pure component spectra of trace organometallic intermediates by combined application of in situ Raman spectroscopy and band-target entropy minimization analysis



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ABSTRACT

Trace organometallic intermediates arising from complex organic syntheses are usually quite difficult to detect spectroscopically. In situ FTIR and in situ NMR are the only techniques that are used with any regularity for such studies. In this contribution, high-pressure in situ Raman spectroscopic measurements were performed for the rhodium catalyzed hydroformylation of 3,3-dimethylbut-1-ene using $\text{Rh}_4(\text{CO})_{12}$ as catalyst precursor at 298 K – a reaction extensively studied previously by more sensitive in situ FTIR. The Raman spectroscopic measurements were analyzed using the band-target entropy minimization (BTEM) algorithm. As expected, the pure component spectra of dissolved CO, 3,3-dimethylbut-1-ene, and 4,4-dimethylpentanal were easily recovered. In addition, the pure component spectra of the precursor $\text{Rh}_4(\text{CO})_{12}$ and the intermediate $\text{RCORh}(\text{CO})_4$ ($\text{R} = (\text{CH}_3)_3\text{CCH}_2\text{CH}_2-$) were successfully reconstructed – even though the mean concentrations of both species were on the order of 150 ppm. The BTEM estimate of the Raman spectrum of $\text{RCORh}(\text{CO})_4$ is reported for the first time. This Raman spectrum is consistent with the DFT predicted spectrum. This study represents the first combined application of Raman spectroscopy and BTEM analysis to a homogeneously catalyzed metal-mediated reaction. The potential and limitations of this general approach are discussed.

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1. Introduction

Due to both academic and industrial interest, there has been a considerable increase in the use of in situ spectroscopic techniques for metal-mediated homogeneous catalysis for complex organic syntheses, i.e. bulk chemicals, speciality chemicals and pharmaceuticals [1]. Since typical organometallic concentrations are on the order of 100 ppm, the in situ spectroscopic methods used are almost exclusively restricted to FTIR or NMR (where measurements are normally confined to high susceptibility nuclei like ^1H and ^{31}P) [2,3]. In contrast, in situ Raman measurements of such systems in order to identify intermediates are nearly non-existent.

The hydroformylation reaction, i.e. the addition of H_2 and CO to an alkene to make aldehydes is one of the largest liquid-phase homogeneous catalyzed reactions, responsible for circa 10^7 tons product per year [4]. The unmodified rhodium catalyzed hydroformylation of alkenes [5,6] has been the subject of numerous in situ FTIR spectroscopic studies. In particular, the intermediate $\text{RCORh}(\text{CO})_4$ has been repeatedly observed during reaction [7–9].

Moreover, the in situ spectroscopic measurements have allowed the determination of instantaneous concentrations and this has led to considerably enhanced kinetic and mechanistic understanding of the reaction [10–12].

The band-target entropy minimization (BTEM[®])¹ algorithm has played a crucial role in the interpretation of these complex FTIR reaction spectra [9,11,12], since it is capable of reconstructing the pure component spectra of the individual constituents without recourse to any a priori information (i.e. spectral libraries) [13]. Subsequently, BTEM spectral estimates can be compared to DFT spectral predictions in order to positively identify non-isolatable intermediates. For example, the infrared BTEM spectral estimates and DFT spectral predictions in the infrared for species such as $\text{HRh}(\text{CO})_4$ and $\text{RCORh}(\text{CO})_4$ have been shown to be quite consistent in terms of both relative intensities and spectral patterns [14].

Raman spectroscopy is being increasingly used to monitor various types of reactions [15]. It is particularly useful for the monitoring of gas-solid heterogeneous catalyzed reactions [16], and to a

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¹ BTEM[®] is a registered trademark (since 2006) of the Institute of Chemical and Engineering Sciences (ICES) as well as the Agency for Science Technology and Research (A*STAR), Singapore.

much lesser extent liquid-phase homogeneously catalyzed metal-mediated reactions [17] (in the latter, only the organics can be observed by Raman – not the organometallics). The latter situation is complicated by the considerable scatter due to the large quantity of solvent and other organic solutes present, and the considerably weaker signals due to the dilute organometallics present. In the present contribution, Raman spectroscopy and BTEM analysis are applied to the rhodium catalyzed hydroformylation reaction. Since Raman spectroscopy is usually considerably less sensitive than FTIR to trace levels of organometallic complexes, the ability of combined Raman and BTEM to reconstruct the pure component Raman spectra of intermediates is not immediately obvious. In the following, the pure component Raman spectrum of $\text{RCORh}(\text{CO})_4$ is reported for the first time.

2. Materials and methods

2.1. General

All solutions preparations and transfers were carried out under purified argon (99.9995%, Saxol, Singapore) atmosphere using standard Schlenk techniques. The argon was further purified before use by passing it through a de-oxy and zeolite packed column. Carbon monoxide (research grade, 99.97%, Saxol, Singapore), hydrogen (99.9995%, Saxol, Singapore), were also further purified through de-oxy and zeolite columns before they were used in the hydroformylation experiments. Purified air was used to purge the Bruker Vertex70 FT-IR spectrometer system.

The chemicals used in the present study include n-hexane (99.5% Fluka puriss), $\text{Rh}_4(\text{CO})_{12}$ (98% Strem) and 3,3-dimethylbut-1-ene (99%, Fluka). The n-hexane was purified by distillation from NaK under argon. The organometallic $\text{Rh}_4(\text{CO})_{12}$ was used without further purification.

2.2. Apparatus

Hydroformylations were performed in an in-house designed 100 ml high-pressure SS316 reactor, which was connected with an injection block, and a high-pressure magnetically driven gear pump (Model GAH-X21, Micro pump, USA). One high-pressure infrared cell was situated in a Bruker Vertex-70 FT-IR spectrometer and the spectral resolution was 2 cm^{-1} with an interval of 0.12 cm^{-1} for the range $1000\text{--}2500\text{ cm}^{-1}$. The other high-pressure Raman cell was situated in the ChiralRamanTM (BioTools, USA) spectrometer using a 532 nm green laser, where the optical components, specifically the fiber optic cable and CCD camera were upgraded to increase the resolution from 7 cm^{-1} to circa 3.5 cm^{-1} . A detailed description of the reactor, pump, injection block and mass transfer issues can be found elsewhere [18]. In addition, a high-pressure syringe pump (PHD 4400, Harvard Apparatus) was used for injecting n-hexane solutions of $\text{Rh}_4(\text{CO})_{12}$ (see Fig. 1).

2.3. High-pressure Raman cell

A high-pressure Raman flow-through cell was specially designed and constructed for the small compartment of the ChiralRamanTM. The materials of construction for the cell were SS 316, Kalrex o-rings and sapphire windows (Korth Monokristalle, Germany). The flow-through cell was positioned using a x-y-z micrometer (Kohzu, Japan) in order to optimize positioning and hence maximize the signal intensity. The micromachining was provided by a local workshop, Integrated Motion (Singapore) (see Fig. 2).

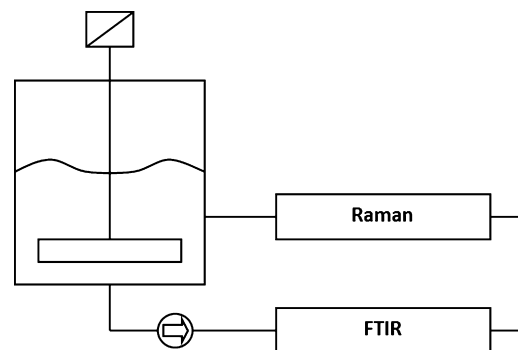


Fig. 1. A schematic diagram of the batch reactor and connected FTIR and Raman spectrometers.

2.4. Design of experiments

The experimental design is shown in Table 1. It has been repeatedly demonstrated that multiple perturbation experiments provide excellent sets of spectroscopic measurements for BTEM analysis since a large variation in signals can be surveyed quickly [19].

3. Theory and calculations

3.1. Data preprocessing

Despiking is often necessary for Raman spectra [20]. For the present in situ Raman spectra an in-house developed algorithm was used.

3.2. Band-target entropy minimization (BTEM) analysis

The pre-processed Raman data was analyzed using the band-target entropy minimization (BTEM) algorithm in order to reconstruct the pure component spectra of the underlying constituents from the sets of mixture spectra. This algorithm has been repeatedly shown to be able to reconstruct the individual pure component spectra from complex mixtures without any a priori information (such as libraries etc.) [9,13]. It is also very suitable for reconstructing the pure component spectra of trace components with high signal-to-noise levels. The main equation in the BTEM algorithm is shown in Eq. (1), where \mathbf{a} is a spectral estimate, \mathbf{T} is an unknown transformation vector, \mathbf{V}^T is the set of right singular vectors used, ν is the index for the channels of data in each spectrum and j is the index for the number of right singular vectors. For further details the reader is referred to Refs. [9,13].

$$\mathbf{a}_{1 \times \nu} = \mathbf{T}_{1 \times j} \mathbf{V}_{j \times \nu}^T \quad (1)$$

3.3. Density functional theory

DFT calculations were performed to optimize the geometries of $\text{Rh}_4(\text{CO})_{12}$ and $\text{RCORh}(\text{CO})_4$ and predict their Raman spectra from first principles. The calculations were performed at PBEPBE/DGTZVP level of theory. This is the same level of theory that has been used previously to reliably model organorhodium complexes [14]. The solvation calculations were performed on all the compounds using the IEFPCM model which is the Polarizable Continuum Model (PCM) using the integral equation formalism variant.

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