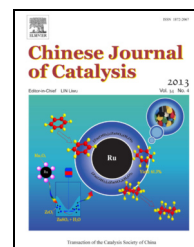


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## Article

# In situ FTIR study of low-pressure hydroformylation of 1-hexene catalyzed by ultrafine cobalt nanoparticles

WANG Hang, CAI Zhipeng, ZHONG Mengqi, YAO Siyu, KOU Yuan \*

PKU Green Chemistry Center, Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

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## ABSTRACT

The hydroformylation of 1-hexene in syngas ( $\text{CO}:\text{H}_2 = 1$ ) under 2–3 MPa at 100 °C was catalyzed using 2.8 nm ultrafine cobalt nanoparticles and investigated by in situ Fourier transform infrared spectroscopy (FTIR). A group of bands observed in the in situ FTIR spectra at 2071, 2041, and 2022  $\text{cm}^{-1}$  are assigned to terminal CO adsorptions distributed over different Co sites. A band at 2054  $\text{cm}^{-1}$  is attributed to the intermediate,  $\text{RCH}_2\text{CH}_2\text{COCO}$ , which has been observed for the first time. Through this intermediate, the catalytic reaction proceeds via the elimination of  $\text{RCH}_2\text{CH}_2\text{COCO}$  to leave a single H atom on the surface of each 2.8-nm Co nanoparticle.

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## 1. Introduction

Hydroformylation, which adds a formyl group and a hydrogen atom to a carbon-carbon double bond, is an important industrial process for the production of aldehydes. The most widely used catalysts for this reaction include rhodium and cobalt carbonyl complexes, and more recently, water-soluble rhodium catalysts [1,2]. The homogeneous hydroformylation of olefins catalyzed by cobalt carbonyl molecules has long been an excellent example for understanding the mechanism of this reaction [3,4]. Based on a study of the hydroformylation reaction involving  $\text{Co}_2(\text{CO})_8$  as a catalyst, it was concluded that [5,6] the real effective catalytic species is not  $\text{Co}_2(\text{CO})_8$ , but rather  $\text{HCo}(\text{CO})_4$ , which is derived from  $\text{Co}_2(\text{CO})_8$  under high pressure syngas ( $\text{CO}+\text{H}_2$ ). A mechanistic cycle for the CO migratory insertion during the hydroformylation reaction is shown in Scheme 1, i.e., after the conversion of alkyl into an acetyl ligand

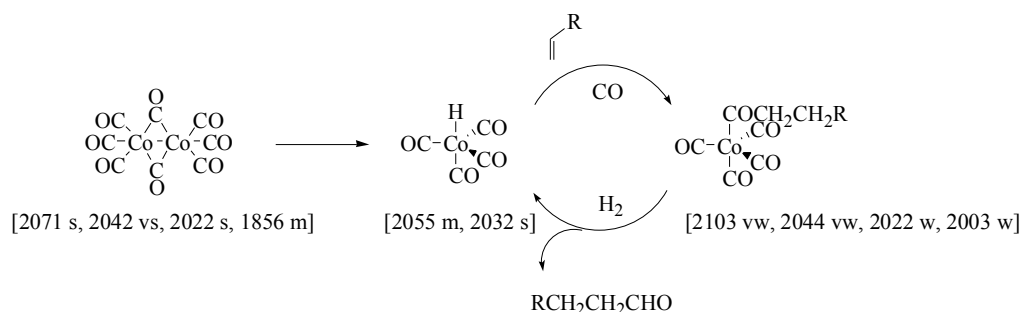
in the presence of CO, the  $\text{HCo}(\text{CO})_4$  is recycled, whilst an aldehyde is formed with the reductive elimination by a single H atom.

For the determination of this mechanism, in situ IR spectroscopy has played a key role. Whyman et al. [7–9] demonstrated the existence of the  $\text{HCo}(\text{CO})_4$  and  $\text{RCH}_2\text{CH}_2\text{COCO}(\text{CO})_4$  intermediate species under hydroformylation reaction conditions by using in situ IR. The CO adsorption bands reported for these important intermediates are summarized in Scheme 1. They also pointed out that when conducting a cobalt carbonyl complex catalyzed hydroformylation reaction under normal conditions, high pressure was needed as the effective catalytic species,  $\text{HCo}(\text{CO})_4$ , is unstable under mild conditions. It was reported that a turnover frequency (TOF) of 35  $\text{h}^{-1}$  was obtained from the hydroformylation of 1-octene when catalyzed by  $\text{Co}_2(\text{CO})_8$  at 120 °C, under a syngas pressure of 5 MPa [10]. For the hydroformylation of 1-hexene in  $[\text{BMIM}][\text{NTf}_2]$ , the activity of the  $[\text{Co}_2(\text{CO})_8]/\text{pyridine}$  system could be as high as

\* Corresponding author. Tel: +86-10-62757792; Fax: +86-10-62751708; E-mail: [yuankou@pku.edu.cn](mailto:yuankou@pku.edu.cn)

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**Scheme 1.** Mechanism of CO migratory insertion in a hydroformylation reaction. The in situ IR bands ( $\text{cm}^{-1}$ ) reported for each species are indicated in brackets.

$110 \text{ h}^{-1}$  at 10 MPa and  $130 \text{ }^\circ\text{C}$  [11].

Although many heterogeneous hydroformylation studies, both experimental [12,13] and theoretical [14], have been published, the nature of how the hydroformylation reaction proceeds, namely, whether it involves a homogeneous or heterogeneous mechanism, is still debatable. We have previously reported that the hydroformylation of 1-hexene by using 2.8-nm ultrafine Co nanoparticles as a catalyst can be realized at a relatively low pressure [15]. The system was performed under 2.0 MPa at  $100 \text{ }^\circ\text{C}$ , giving an average TOF of  $130 \text{ h}^{-1}$ , which, after 18 h running time, resulted in a TTO of 2380. The catalyst was very stable under the reaction conditions, and after the hydroformylation reaction was complete, the catalyst could be separated almost completely using high-speed centrifugation. It was suggested that this reaction system is heterogeneous in nature. By using in situ IR, we found from a comparative investigation of the 1-hexene hydroformylation process conducted in the presence of a cobalt carbonyl complex (homogeneous part) and in the presence of Co ultrafine nanoparticles (heterogeneous part) [16,17], that the ultrafine Co nanoparticles are much more active than the cobalt carbonyl complex, which may be due to the different reaction routes they follow.

## 2. Experimental

### 2.1. Catalyst preparation

Preparation of precursory and ultrafine Co nanoparticles was performed according to a previously reported method [15], in which ultrafine Co nanoparticles were obtained from the pretreatment of the precursory Co nanoparticles. After the pretreatment, the ultrafine Co nanoparticles were well-dispersed in the toluene phase, while the residual nanoparticles remained in the lower solid layer. The average particle sizes of the precursory, residual and ultrafine nanoparticles, as characterized by high-resolution transmission electron microscopy (HR-TEM), are 20, 10, and 2.8 nm, respectively. The substrates were all obtained from commercial sources and used without further purification. All of the solvents used for the reactions were of analytical reagent (A.R.). 1-Hexene (97%) and  $\text{Co}_2(\text{CO})_8$  (99%) were provided by Alfa Aesar.  $\text{RhCl}(\text{PPh}_3)_3$  (99%) was provided by Sigma Aldrich. The preparation and transfer of Co nanoparticles and  $\text{RhCl}(\text{PPh}_3)_3$  to the autoclave were operated under an  $\text{N}_2$  atmosphere, while  $\text{Co}_2(\text{CO})_8$  was

handled in a glove box under an  $\text{N}_2$  atmosphere.

### 2.2. In situ FTIR spectroscopy

Figure 1(a) shows a schematic diagram of our home-designed in situ transmission FTIR system. The system comprises a stainless steel autoclave (I), an FTIR spectrometer (III), an in situ cell (II) configured for mounting within the spectrometer (III), a thermocouple (B), two high-precision pressure gauges (C), and a magnetic stirrer (D). The in situ cell (II) is operably coupled to the autoclave via a first stainless steel pipe of 3 mm diameter, in which a terminal end (E) of the pipe is a liquid inlet that extends through the lid of the autoclave (I) into the chamber thereof. The magnetic stirrer (D) is operably mounted within the chamber of the autoclave (I), and the thermocouple (B) and one of the two high-precision pressure gauges (C) are mounted within the lid of the autoclave (I). A second stainless steel pipe is mounted in the lid of the autoclave (I) for purging the autoclave (I) with a gas via the pipe inlet (A). The autoclave (I) and the in situ cell (II) are operably coupled to a gas supply by virtue of a third stainless steel pipe having a gas inlet (G), which is used to release abundant gas from the system. The third pipe comprises a gas outlet (F) at a terminal end thereof that extends through the lid of the autoclave (I) into the chamber thereof, and a gas inlet (H) at an opposing end thereof. The third pipe is operably connected to the first pipe at a junction generally midway between the gas outlet (F) and the gas inlet (H). H is connected to a high-pressure gas supply. The second of the two high-precision pressure gauges (C) is operably mounted at the gas inlet (G). The system further comprises five valves, as represented by numbers, 1, 2, 3, 4, and 5, which are operably mounted to the corresponding pipes.

Reaction mixtures can be transferred between the stainless steel autoclave (I) and the in situ cell (II) by purging the system with a gas pulse from A or H.

In a typical experiment, the autoclave is loaded with the reaction mixture and gas ( $\text{H}_2$ , syngas or CO) at a pressure of 2 MPa and heated to a desired temperature under vigorous stirring (600 r/min) with all of the valves being closed. Valve 3 is opened to reduce the pressure by 0.2 MPa and then closed. Valves 2 and 4 are then opened to enable liquid to be transferred to the cell (II) due to the negative pressure in the system, and then valve 4 is closed. After measurement, valves 4 and 5 are alternatively opened and closed to pulse liquid back into

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