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Article

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

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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 cm^{-1} are assigned to terminal CO adsorptions distributed over different Co sites. A band at 2054 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 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

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

110 h^{-1} at 10 MPa and 130°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°C , giving an average TOF of 130 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 N_2 atmosphere, while $\text{Co}_2(\text{CO})_8$ was

handled in a glove box under an 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 (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

Fig. 1. Schematic diagram of the in situ FTIR system (a) and in situ FTIR cell (b).

the autoclave (I) through E. When the pressure in the autoclave (I) needs to be reduced, G and F are opened to release the gas from the system. The whole operation is quick and convenient.

Details of the in situ FTIR cell (II) are shown in Figure 1b. Briefly, two customized CaF₂ windows are spaced by two lead sheets to make a 0.5 mm slot for the reaction mixture to flow through. The stainless steel shell of the cell (II) is coiled with heating wire to maintain the temperature close to that of the autoclave (I). The in situ FTIR cell (II) can work at the condition of at least 3 MPa pressure and 200 °C.

The in situ transmission FTIR spectra were recorded with a resolution of 2 cm⁻¹ and accumulation of 1 scan using a Bruker TENSOR 27 spectrometer.

2.3. Other characterizations

Inductive coupling plasma-atomic emission spectroscopy (ICP-AES, Perkin Elmer Optima 2000 DV), JEM-2010 HR-TEM with an energy dispersive X-ray spectroscopy (EDX) system, Agilent GC and GC-MS were used as described in detail in our previous report [15].

2.4. In situ IR reactions

The reactions were performed at 2 MPa and 100 °C. Taking 20-nm Co nanoparticle catalysts as an example: 20 ml of 20-nm Co catalysts (1.5 mmol) was decanted to a clean autoclave together with 2 ml of 1-hexene. The autoclave was flushed with syngas to guarantee no other components remained, and then pressurized with syngas to 2 MPa. The autoclave, operably connected to the in situ FTIR cell and a syngas cylinder, was

heated to the reaction temperature (100 °C), and then in situ FTIR measurements were initiated. The measurements were conducted every 10 min for the length of the reaction. After each measurement, the pressure was adjusted back to 2 MPa to maintain an even baseline of IR spectra.

2.5. Pressure drop reactions

The reactions were performed at 100 °C. Catalysts (20 ml) were decanted to a clean autoclave together with 3 ml of 1-hexene. For Co₂(CO)₈, operations were performed in a glove box under an N₂ atmosphere. During the reaction, the autoclave is maintained as a closed system with no gas flowing. After pressurized with 2 MPa syngas, the autoclave was heated to the reaction temperature. The pressure and time were then recorded.

2.6. Mercury poisoning test

Mercury poisoning tests have been widely used to study the nature of catalytic reactions [16]. In the present in situ IR study, when the peak (1727 cm⁻¹) corresponding to heptaldehyde appeared, Hg (0), with a Hg/Co ratio around 320, was added under pressure into the autoclave by a syngas pulse. FTIR spectra were then collected.

3. Results and discussion

3.1. The reaction evaluation

To compare the catalytic performance of 2.8 nm ultrafine Co nanoparticles with Co₂(CO)₈, hydroformylation reactions catalyzed by the two catalysts were performed with the same cobalt concentration and sufficient 1-hexene under the same reaction conditions (100 °C, 2 MPa syngas). The activities observed, as listed in Table 1, reveal that the activity of the 2.8-nm Co nanoparticles is nearly twice that of Co₂(CO)₈, strongly suggesting that the ultrafine Co nanoparticles are much more active than traditional complex catalysts at low reaction pressures. On the other hand, Table 1 also indicates that the 20-nm Co particles are far less active. Figure 2 shows the time-dependent pressure drop profile during the hydroformylation of 1-hexene at 100 °C with an initial reaction pressure of 2.3 MPa. Clearly, the pressure drop observed in the hydroformylation reaction with the 2.8-nm Co nanoparticles is much faster than that observed in the hydroformylation reaction with the cobalt carbonyl complex, while the same reaction involving the larger 20 nm particles showed only a marginal drop. It can also be seen from Fig. 2 that a fast pressure drop is observed during the first 60 min of the hydroformylation reaction for both the 2.8 nm particles and the carbonyl systems, showing the good catalytic activity of both catalysts at this stage. The pressure drops in both studies were observed to slow down after the first 60 min. However, considering the slowdown rate, the rate of the pressure drop for the cobalt carbonyl system is significantly faster than that of the ultrafine Co nanoparticles. It is known that cobalt carbonyl catalysts are

Table 1

Concentrations and activities of $\text{Co}_2(\text{CO})_8$ and 2.8-nm Co NPs with the same concentration ($\sim 8.0 \times 10^{-3}$ mol/L).

Catalyst	<i>n</i> / <i>iso</i> ratio	Activity (h^{-1})
$\text{Co}_2(\text{CO})_8$	1.6	42.3
2.8-nm Co NPs	1.9	77.2
20-nm Co NPs	1.6	3.71

Activity = mmol of aldehydes product/mmol of Co catalysts/hour of reaction time, aldehydes determined by GC. Reaction was conducted at 100 °C, 2 MPa.

Fig. 2. Pressure-time profile for the hydroformylation of 1-hexene catalyzed by $\text{Co}_2(\text{CO})_8$ and 2.8-nm Co NPs. The first point was recorded when the temperature of the system reached 100 °C.

normally very active at relatively high pressure, for example, higher than 5 MPa. However, due to the low CO pressure in the present study, this may make the precursor, $\text{Co}_2(\text{CO})_8$, especially the reaction intermediates such as $\text{HCo}(\text{CO})_4$ unstable, resulting in a fast deactivation under the mild conditions [18,19].

Importantly, when the nanoparticle catalyst system is used in liquid phase reactions, there is always a debate about whether the homogeneous species leaching out of the solid catalyst is the real active species for catalyzing the reaction or not. However, the current reaction data clearly indicates that the cobalt carbonyl catalyst has a much lower hydroformylation activity than that of the nanoparticles under the present reaction conditions. Instead, it is the nanoparticle catalyst itself that provides excellent activity under low syngas pressure and low reaction temperature conditions.

3.2. $\text{Co}_2(\text{CO})_8$ as catalyst precursor

To determine how the hydroformylation reaction occurs in the presence of the 2.8-nm Co nanoparticles, *in situ* IR experiments were conducted and were compared with those of the homogeneous system. Figure 3 shows that at 0 min, the FTIR spectrum is dominated by the adsorptions of the $\text{Co}_2(\text{CO})_8$ molecules (2071 s, 2042 vs, 2021 s, and 1849 m cm^{-1}). However, as the hydroformylation of 1-hexene starts to occur, evidence of the real catalyst, $\text{HCo}(\text{CO})_4$ [7,8,20] appears at 2031 vs (10 min), with a rise between 2042 and 2021 cm^{-1} , accompanied by the formation of a weak band at 2106 cm^{-1} (30 min),

which is representative of molecular $\text{RCH}_2\text{CH}_2\text{CoCo}(\text{CO})_4$. The band at 1727 cm^{-1} , which is representative of the formation of an aldehyde species, appears after 10 min, and reaches a maximum at 60 min, and then remains almost unchanged until 90 min, which is in good agreement with the pressure drop observations (Fig. 2). This, in another way, indicates the loss of activity. One of the reasons for the observed deactivation could be due to the formation of cobalt particles, as demonstrated by the appearance of a broad band centered at 1892 cm^{-1} . This band appears within 10 min of the reaction starting and increases with reaction time. Until 60 min, when the reaction stops, the band at 1892 cm^{-1} becomes clear, with all formerly observed characteristic peaks merging together to form a very broad band centered at 2027 cm^{-1} , which represents different CO adsorptions on the surface of Co particles mixed with those of residual $\text{Co}_2(\text{CO})_8$. This clearly indicates the decomposition of the carbonyl molecules into carbonyl clusters. It should be noted that a significant amount of precipitates were visibly observed after the reaction, which agrees well with the appearance of the Co nanoparticle-related CO absorption bands in the corresponding IR study [21].

3.3. 2.8-nm ultrafine cobalt particles as the catalyst

To our surprise, the 2.8-nm Co nanoparticles present a picture very similar to that of the $\text{Co}_2(\text{CO})_8$ system, though the positions and relative strengths of the observed peaks in the FTIR spectrum are somewhat different from each other, implying that it is highly possible that the absorption bands of CO bound to the Co nanoparticles may overlap with those of the cobalt carbonyls, while there is a balance between the soluble cobalt carbonyls species and the Co nanoparticles. However, different from the case of the homogeneous $\text{Co}_2(\text{CO})_8$ system (Fig. 3), it can be seen from Fig. 4 that these bands are very stable under the present reaction conditions. The intensity of the aldehyde peak at 1727 cm^{-1} increases very quickly, while the peak attributed to 1-hexene at 1641 cm^{-1} disappears very quickly, exhibiting a very high catalytic activity for those ultrafine Co nanoparticles. After 60 min, most of the 1-hexene was consumed, while the production of aldehydes reached a maximum. At that time, and in the absence of 1-hexene, the surface of the Co nanoparticles may be partly exposed to the syngas and the broad band centered at 1885–1886 cm^{-1} is a strong indication of the CO adsorptions on the surfaces. Different to the carbonyl catalyst (Fig. 3), even after 60 min, the peaks at 2041 and 2021 cm^{-1} remained almost unchanged. Meanwhile, it is interesting to note that a new terminal carbonyl species was observed at 2054 cm^{-1} with the depletion of 1-hexene. This peak is considered to represent molecular $\text{HCo}(\text{CO})_4$, as it is accompanied by another stronger peak at 2031 cm^{-1} , as observed in Fig. 3. We therefore believe that, for the Co nanoparticle system, a similar mechanism with that shown in Scheme 1 occurs though the various adsorption/reaction processes on the surface of the nanoparticles. However, as an important intermediate for the carbonyl system, $\text{RCH}_2\text{CH}_2\text{CoCo}(\text{CO})_4$ (2106 cm^{-1}) should not be considered a qualified intermediate for the Co nanoparticle because the

Fig. 3. In situ FTIR spectra of 1-hexene hydroformylation catalyzed by $\text{Co}_2(\text{CO})_8$. 0.28 mmol of $\text{Co}_2(\text{CO})_8$ dissolved in a mixture of 20 ml of toluene and 2 ml of 1-hexene in the stainless steel autoclave was pressurized with 2 MPa syngas ($\text{CO}:\text{H}_2 = 1$). The system was heated to 100 °C rapidly, then the reaction mixture was forced into the FTIR cell for measurement under pressure.

five-coordination geometry cannot be arranged on the surface of the Co nanoparticle, even at its edge. It is for this reason that the peak at 2106 cm^{-1} does not appear in Fig. 4. With the consumption of 1-hexene, $\text{RCH}_2\text{CH}_2\text{COCo}$ would be an attainable intermediate which then transforms into an aldehyde, while

Fig. 4. In situ FTIR spectra of the hydroformylation of 1-hexene catalyzed by 2.8-nm Co NPs. 20 ml of solution containing 2.8 nm ultrafine Co NPs (0.16 mmol) and 2 ml of 1-hexene in the stainless steel autoclave were pressurized with syngas ($\text{CO}:\text{H}_2 = 1$) at 2 MPa. The system was heated rapidly to 100 °C and FTIR measurements taken. The negative peak at 1727 cm^{-1} at 0 min is due to the spectra subtraction of aldehyde produced during the pretreatment with pure aldehyde.

leaving the surface vacancies on the Co nanoparticle available for reoccupation by CO. Therefore, we have tentatively assigned the 2054 cm^{-1} peak to $\text{RCH}_2\text{CH}_2\text{COCo}$, i.e., 1-hexene combines with the cobalt surface to form surface alkyl group, and the adjacent CO species then inserts into the alkyl-Co bond, leading to the formation of $\text{RCH}_2\text{CH}_2\text{COCo}$. With further hydrogen elimination, it then fulfills the reaction cycle.

3.4. 20-nm cobalt particles as the catalyst precursors

The reaction catalyzed by the 20-nm Co nanoparticles was performed to study the formation of 2.8-nm Co nanoparticles. As shown in Fig. 5, two weak peaks representing $\text{RCH}_2\text{CH}_2\text{COCo}(\text{CO})_4$ clearly exist at 2104 and 2001 cm^{-1} , indicating the involvement of a homogeneous species. These peaks are observed to disappear when 1-hexene is mostly consumed after 90 min. Meanwhile, similar to the spectra of $\text{Co}_2(\text{CO})_8$, the peaks at 2041 and 2021 cm^{-1} combine together at 2027 cm^{-1} , indicating the simultaneous formation of the homogeneous carbonyl species and the heterogeneous nanoparticles, which implies a particle refining process. In the reaction, the 20-nm Co nanoparticles adsorb 1-hexene, CO, and H_2 to complete the catalytic cycle. The adsorbed species reduce the Co-Co bonds and split the Co nanoparticles into much smaller particles, which have significant catalytic activities. On the other hand, the dissolving of the cobalt atoms into solvent, combined with their splitting into smaller particles, leads to the formation of molecular complexes. In the case of ultrafine nanoparticles, due to their small size, the ultrafine particles will not split any more, instead they may undergo another process. Without splitting, the dissolving of the Co atoms becomes too difficult to release sufficient $\text{HCo}(\text{CO})_4$ during the reaction catalyzed by the 2.8-nm Co nanoparticles.

Fig. 5. In situ FTIR spectra of the hydroformylation of 1-hexene catalyzed by 20-nm Co NPs. 20 ml of solution containing 20 nm precursor Co NPs (2.0 mmol) and 2 ml of 1-hexene in the stainless steel autoclave were pressurized with syngas ($\text{CO}:\text{H}_2 = 1$) at 2 MPa. The system was heated to 100 °C rapidly and measured.

Fig. 6. In situ FTIR spectra of a mercury poisoning experiment of 2.8-nm Co nanoparticles. After the reaction (some 1-hexene remained in the autoclave), excessive Hg (0) was loaded into the autoclave under pressure, and the FTIR spectra were then recorded. The gases remained the same.

3.5. Mercury poisoning experiment

Mercury poisoning experiments are expected to provide useful information to understand the mechanism for the Co nanoparticle catalyzed hydroformylation reaction. The poisoning of the 2.8-nm Co nanoparticles with mercury, as shown in Fig. 6, leads to the sudden decrease in the intensity of the peaks at 2041 and 2021 cm^{-1} , followed by their gradual disappearance. However, the band at 2070 cm^{-1} and the bridging adsorption band at 1886 cm^{-1} remain almost unchanged. This result clearly indicates that the three peaks at 2041, 2021, and 2070 cm^{-1} are not associated with just one molecule of $\text{Co}_2(\text{CO})_8$. The peaks observed at 2041 and 2021 cm^{-1} , which also exist in Fig. 4, belong to different surface species, possibly CO adsorption on step and kink sites of Co. Meanwhile, it can be seen from Fig. 6 that, as soon as the band at 2054 cm^{-1} disappeared (from around 5 to 20 min), the band at 2031 cm^{-1} , which represents $\text{HCo}(\text{CO})_4$, gradually recovered, demonstrating that the band at 2054 cm^{-1} belongs to the surface species. Meanwhile, the bands observed at 2070 and 2002 cm^{-1} , may be attributed to the occurrence of terminal CO adsorptions taking place on the Co-Hg alloy. It is noted that the intensity of the 2070 cm^{-1} peak increased with increasing reaction time, providing strong support for the adsorption of terminal CO on the Co-Hg alloy. In addition, the peak observed at 2070 cm^{-1} in Fig. 4 is also likely to represent a surface bound CO species. From the mercury poisoning experiments, we can see that, **1.** Molecular $\text{Co}_2(\text{CO})_8$ dissolved in toluene has three terminal carbonyl vibrations at 2071, 2042, and 2021 cm^{-1} , and the CO adsorbed on the Co nanoparticle has the same adsorptions. **2.** The terminal adsorption band at 2070 cm^{-1} and the bridging adsorption band at 1885 cm^{-1} should represent the CO adsorbed over the strong-

est adsorption sites as they are both observed in the mercury poisoned particles. **3.** This again suggests that there is an equilibrium between the $\text{Co}_2(\text{CO})_8$ molecules and the 2.8-nm Co nanoparticles, i.e., the system, indeed, is a co-existence system of nanoparticle-stabilized carbonyl molecules, and molecular carbonyl stabilized ultrafine nanoparticles.

Unlike the mercury-poisoning experiment involving Co NPs, homogeneous catalysts (if stable in the reaction conditions), are not sensitive to mercury. Since $\text{Co}_2(\text{CO})_8$ is unstable under mild conditions with 2–3 MPa syngas, there will be a considerable amount of precipitates due to the decomposition of $\text{Co}_2(\text{CO})_8$ to Co particles, as explained in section 2.2. Moreover, the $\text{Co}_2(\text{CO})_8$ system is heterogeneous in nature and as such, is not suitable for conducting mercury-poisoning experiments under the same conditions with Co NPs. Instead, we tried another typical homogeneous catalyst: $\text{RhCl}(\text{PPh}_3)_3$ for alternative under syngas, 100 °C at a pressure of 2 MPa, which was also tested for verification in our previous work [15]. As shown in Fig. 7, hydroformylation was conducted with $\text{RhCl}(\text{PPh}_3)_3$ as a catalyst. The observed peak at 1978 cm^{-1} is assigned to the Rh-CO bond. After 60 min, when all of the 1-hexene was consumed, excessive Hg (0) and 2 ml of 1-hexene were purged into the autoclave. According to the spectra, none of the peaks showed an obvious change and the catalytic activity remained, showing that homogeneous catalysts are quite different from Co nanoparticle catalysts.

3.6. Desorption of 2.8-nm cobalt nanoparticles

The desorption of CO from the surface of the 2.8-nm Co nanoparticles supports the nanoparticle-molecular carbonyl interaction. Figure 8 shows the spectra of the CO desorption from the surface of the 2.8-nm Co nanoparticles under N_2 at a pres-

Fig. 7. In situ FTIR spectra of the hydroformylation reaction conducted in the presence of the $\text{RhCl}(\text{PPh}_3)_3$ catalyst, followed by mercury poisoning. After the reaction, excessive Hg (0) and 2 ml of 1-hexene were introduced into the autoclave under pressure, the spectra were then recorded. The gases remained the same.

Fig. 8. In situ FTIR spectra of the desorption of CO from the surface of the 2.8-nm ultrafine Co nanoparticles in the absence of syngas at 100 °C. The system was purged with 2 MPa N₂.

sure of 2 MPa at 100 °C. The FTIR spectrum taken at 0 min repeats the original observation at 0 min as illustrated in Figure 4, however, after 10 min, all of the representative peaks assigned to the CO adsorption on the 2.8-nm nanoparticles have disappeared. Instead, a group of new peaks appear at 2066 vs, 2056 vs, and 1859 s cm⁻¹, which belong to Co₄(CO)₁₂ [22]. After a while, these peaks were found to weaken and disappear, indicating the dissociation of the tetranuclear clusters. In fact, Co₂(CO)₈ shows a similar desorption process in the absence of CO and O₂.

4. Conclusions

Co nanoparticles of 2.8 nm diameter were found to have a much higher activity than cobalt carbonyl complex catalysts in

the hydroformylation of 1-hexene under relatively low reaction pressure. In situ IR observation of the reaction under syngas (CO: H₂ = 1) at 2 MPa reveals for the first time that the linearly adsorbed CO molecules present a group of bands at 2071, 2041, and 2022 cm⁻¹, which appear at similar wavelengths to those of molecular Co₂(CO)₈. This group of bands is attributed to the terminal CO adsorptions over different sites of Co facets while the band at 1886 cm⁻¹ is a bridged CO. There is a balance between the soluble carbonyl complex and the heterogeneous nanoparticles in the ultrafine Co nanoparticle catalyst system, but it is the nanoparticles that are responsible for the much higher activity during the hydroformylation reaction. The peak at 2054 cm⁻¹, which has been observed for the first time, is believed to be attributed to an important intermediate, RCH₂CH₂COCO, which is bound to the 2.8-nm Co nanoparticle. Through this intermediate, the catalytic reaction is considered to proceed via the elimination of RCH₂CH₂COCO to leave a single H atom on the surface of the 2.8-nm Co nanoparticle.

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Graphical Abstract

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

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An in situ FTIR observation of the hydroformylation reaction conducted using a Co nanoparticle-based system suggests that some of the observed bands in the FTIR spectrum are similar to those of the original Co complex. The unique absorption band at 2054 cm⁻¹ corresponds to terminal CO adsorptions bound to different cobalt sites.

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超细钴纳米粒子催化 1-己烯低压氢甲酰化反应的原位红外光谱研究

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摘要: 利用原位透射红外光谱研究了 2.8 nm 超细钴纳米粒子在 2~3 MPa 合成气($\text{CO}:\text{H}_2 = 1:1$)和 100 °C 条件下催化的 1-己烯氢甲酰化反应. 结果表明, 在反应中出现与 $\text{Co}_2(\text{CO})_8$ 类似的红外吸收峰(2071, 2041 和 2022 cm^{-1}), 被证明是不同 Co 位点端式吸附 CO. 首次观测到了位于 2054 cm^{-1} 处吸收峰处的物种, 可能归属为 $\text{RCH}_2\text{CH}_2\text{COCO}$. 通过此中间物种, 产物醛可以在钴催化剂表面经由结合一个氢原子脱除反应而获得.

关键词: 钴纳米粒子; 氢甲酰化反应; 原位红外光谱; 汞中毒实验; 1-己烯

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