



# Hydroformylation of 1-hexene over ultrafine cobalt nanoparticle catalysts

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## ABSTRACT

A new method was developed to fabricate ultrafine cobalt nanoparticles with an average diameter of 2.8 nm from large precursory cobalt nanoparticles (around 20 nm). The obtained ultrafine nanoparticles have a narrow size distribution and a much higher Co/B ratio than that of precursory cobalt nanoparticles (almost 100 times higher). The 2.8 nm cobalt nanoparticles were used to catalyze hydroformylation of 1-hexene and syngas (CO: H<sub>2</sub> = 1) at 100 °C and 2.4 MPa, resulting in an average TOF (turnover frequency) of 130 h<sup>-1</sup>. Through the mercury poisoning experiments, it was observed that the presence of Hg(0) can effectively suppress the catalytic activity of the 2.8 nm Co nanoparticle catalyst system, demonstrating that a heterogeneous catalysis mechanism was followed in the ultrafine catalyst system.

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## 1. Introduction

Co-based and Rh-based complex catalysts are widely used in homogeneous hydroformylation [1–3], which plays important roles in chemical industry. Homogeneous systems have the advantage of high catalytic activity and selectivity, but the catalysts are difficult to separate from the products. In order to improve the catalyst separation, many efforts have been devoted to perform the hydroformylation reaction in the heterogeneous mode [4–16], among which the employment of soluble or non-supported nanoparticles is receiving increasing attention [12–16].

It is well known that soluble or non-supported transition-metal nanoparticles with particle size of 1–10 nm can give rise to novel and unique catalytic behavior as high as that of homogeneous complex catalysts [17,18]. Non-supported Rh(0) nanoparticles have been used as catalysts in hydroformylation [12,13,15]. For example, 2 nm Rh colloids stabilized with poly(ethylene imine) amide were claimed to be an efficient catalyst in the hydroformylation of 1-hexene with 98% conversion and 96% selectivity toward aldehydes at 80 °C and 9 MPa (CO: H<sub>2</sub> = 1) [12]. Employing an aqueous Rh colloid stabilized by PVP, Liu et al. concluded that hydroformylation of propylene occurred in a heterogeneous fashion at a biphasic aqueous system [13]. Moreover, it is proposed by Dupont that although “soluble” Rh nanoparticles (5.0 nm, without protector) were used to catalyze the hydroformylation of 1-hexene, some Rh species etched from the Rh nanoparticles may be the active sites indeed [15]. In addition, there is only one report concerning cobalt catalyst

in which Co–B alloyed nanoparticles with a size of 41 nm catalyzed hydroformylation of 1-octene in butyl ether at 120 °C and 5 MPa, resulting in 71.1% conversion of 1-octene, 98.7% selectivity toward aldehydes and a TOF (turnover frequency) of 3 h<sup>-1</sup> with a reaction time of 2.5 h [16].

Preparation of ultrafine cobalt nanoparticles smaller than 5 nm in size has been a challenge [19]. Among a few reported successful examples [19–26], 2 nm Co nanoparticles were obtained from CoCl<sub>2</sub>·6H<sub>2</sub>O reduced by HCOONa in ethyl glycol at 180 °C [19], whereas 2.5–3 nm Co nanoparticles were prepared from Co(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>2</sub> that was reduced by H<sub>2</sub> in toluene at room temperature [26]. NaBH<sub>4</sub> as a good reductant is usually used to prepare noble metal nanoparticles. However, when NaBH<sub>4</sub> is used to reduce cobalt salts in aqueous phase, the formation of Co–B alloy is hardly avoided [27], which may significantly reduce the catalytic activity of the Co particles. It is, therefore, an interesting topic to decrease the amount of B in Co–B alloyed nanoparticles.

In this report, we prepared ultrafine Co nanoparticles with an average diameter of 2.8 nm through a new method, i.e., through pretreating large precursory Co nanoparticles under hydroformylation reaction conditions, ultrafine 2.8 nm Co nanoparticles with very low B/Co ratio were produced. The ultrafine Co nanoparticles were used to catalyze the hydroformylation of 1-hexene with CO and H<sub>2</sub>, which was proven to act through a heterogeneous catalytic path.

## 2. Experimental

### 2.1. Chemicals

The substrates were obtained from commercial sources and used without further purification. All the solvents used for reactions

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were analytical reagent (A.R.). 1-Hexene (97%) and  $\text{RhCl}(\text{PPh}_3)_3$  (99%) were provided from Alfa Aesar, Sigma–Aldrich, respectively.

## 2.2. Preparation of ultrafine Co nanoparticles

The precursory Co nanoparticles were prepared by chemical reduction using  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NaBH}_4$  as starting materials. Typically, 0.4 g  $\text{NaBH}_4$  solid was added quickly into a well-stirred beaker of 20 ml aqueous solution of 0.1 M  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and 0.5 M polyvinyl pyrrolidone (PVP) and then stirred vigorously. The mixture turned from red to black instantly and stable colloids formed. The colloids were kept for 5 min until no gas escaped. Subsequently, the beaker was placed on a column magnet which separated the solution into two layers in 15 min. After the upper transparent liquid was removed, the precursory Co nanoparticles in the lower solid layer were washed three times with deionized water, and the separation was carried out by magnet. The precursory Co nanoparticles were further washed by methanol twice and toluene three times.

The ultrafine cobalt nanoparticles were obtained from the pretreatment of the precursory Co nanoparticles. The pretreatment was carried out in a stainless steel autoclave (120 ml) with a magnetic stirrer. After adding 2 mmol the precursory Co nanoparticles, 20 ml toluene and a certain amount of 1-hexene (0.5–3.0 ml) were transferred into the autoclave. The reactor was flushed three times with syngas ( $\text{CO}:\text{H}_2 = 1$ ) to guarantee no other component remained. Then the autoclave was pressurized up to 2 MPa with syngas, heated to 100 °C under vigorous stirring of 600 rpm and then kept at 100 °C for different periods of time (1–3 h). Subsequently, the autoclave was cooled down in a water-ice bath and depressurized. The mixture in the autoclave was transferred into a conical beaker placed on a magnet under the protection of  $\text{N}_2$ . After 30 min, the upper clear supernatant was removed and kept under the protection of  $\text{N}_2$ . The ultrafine Co nanoparticles dispersed in the clear supernatant could be separated by centrifugation. The clear supernatant containing the ultrafine Co nanoparticles was utilized entirely as the cobalt nano-catalyst system in hydroformylation reactions. The amounts of residual alkenes and aldehydes were determined by gas chromatography and were subtracted in the product analysis after subsequent hydroformylation reaction.

## 2.3. Characterization

The cobalt and boron contents of precursory Co nanoparticles and the ultrafine Co nanoparticles were measured by inductive coupling plasma-atomic emission spectroscopy (ICP-AES, Perkin Elmer Optima 2000 DV).  $\text{HClO}_4$  and  $\text{H}_2\text{O}_2$  were used to dissolve Co nanoparticles and the concomitant organic compounds into the aqueous phase. For the cobalt nano-catalyst systems, rotational evaporation in reduced pressure was used in preparation of samples for ICP detection.

**Table 1**

ICP results of precursory Co nanoparticles and the catalyst 1–5.

Catalyst	1-Hexene added in pretreatment (ml)	Pretreatment <sup>a</sup> time (h)	Co concentration (mg/ml)	B concentration (mg/ml)	Co/B (atoms/atoms)
Precursory Co <sup>b</sup>	–	–	5.89	9.72	0.111
1 <sup>c</sup>	0	1	0.490	0.00519	17.3
2 <sup>c</sup>	0.5	1	0.437	0.00684	11.7
3 <sup>c</sup>	1.0	1	0.596	0.00970	11.2
4 <sup>c</sup>	2.0	2	0.585	0.0110	9.73
5 <sup>c</sup>	3.0	3	0.319	0.00646	9.04

<sup>a</sup> Pretreatment condition: 20 ml toluene, 100 °C, 2.4 MPa syngas ( $\text{CO}:\text{H}_2 = 1$ ), 600 rpm, precursory cobalt nanoparticles of 2 mmol cobalt content.

<sup>b</sup> Precursory Co nanoparticles.

<sup>c</sup> The cobalt nano-catalyst system (20 ml) as the supernatant of the mixture in the autoclave after separation by the attraction of magnet.

The surface morphologies and the particle size distribution of Co nanoparticles were detected by a JEOL, JEM-2010 equipped with an energy dispersive X-ray spectroscopy (EDS) system. The accelerating voltage of the HR-TEM (high-resolution transmission electron microscope) was 300 kV. The samples for high-resolution TEM were prepared by dispersion in the ethanol or toluene on a carbon-coated copper grid at room temperature. The histogram of the nanoparticles size distribution was obtained from measurements of about 300 particles (600 counts), and was reproduced in different regions of the Cu grid, assuming spherical shape, found in an arbitrary chosen area of enlarged micrographs.

## 2.4. Hydroformylation with ultrafine Co nanoparticles

20 ml ultrafine cobalt catalyst (0.1–0.2 mmol) was decanted to a clean autoclave together with 3 ml 1-hexene. The autoclave was sealed and cleaned by the flush of syngas to guarantee no other component remained, and then pressurized with syngas to 2 MPa. The autoclave was placed in a pre-heated electric furnace, heated to the reaction temperature at 100 °C in 5 min (the pressure was 2.4 MPa at 100 °C), and then transferred into an oil bath which kept stable temperature at 100 °C. It was recorded as the starting of hydroformylation reaction. At the end of the reaction, the autoclave was transferred from the oil bath to a water-ice bath to quench the reaction. After the internal standard of n-dodecane was injected into the autoclave, the mixture in the autoclave was stirred for 20 min at room temperature. The liquid mixture was analyzed quantitatively by GC (gas chromatograph, Agilent 6820) equipped with an OV-101 capillary column and a FID (flame ionization detector). The organic compounds were characterized by GC-MS (gas chromatograph–mass spectrometer, Agilent 7890A-5975C) and by comparison of their GC retention times with those of standard samples.

## 2.5. Mercury poisoning test

The mercury poisoning test was performed in the hydroformylation reaction. At a point with quick pressure drop in the proceeding of reaction, ~320 equivalent mole (vs Co or Rh catalyst) of Hg (0) was pressurized into the autoclave by a syngas pulse through a tube linked to the autoclave during the reaction. The pressures vs time data in the reaction were collected. A controlled experiment with  $\text{RhCl}(\text{PPh}_3)_3$  catalyst was also preformed.

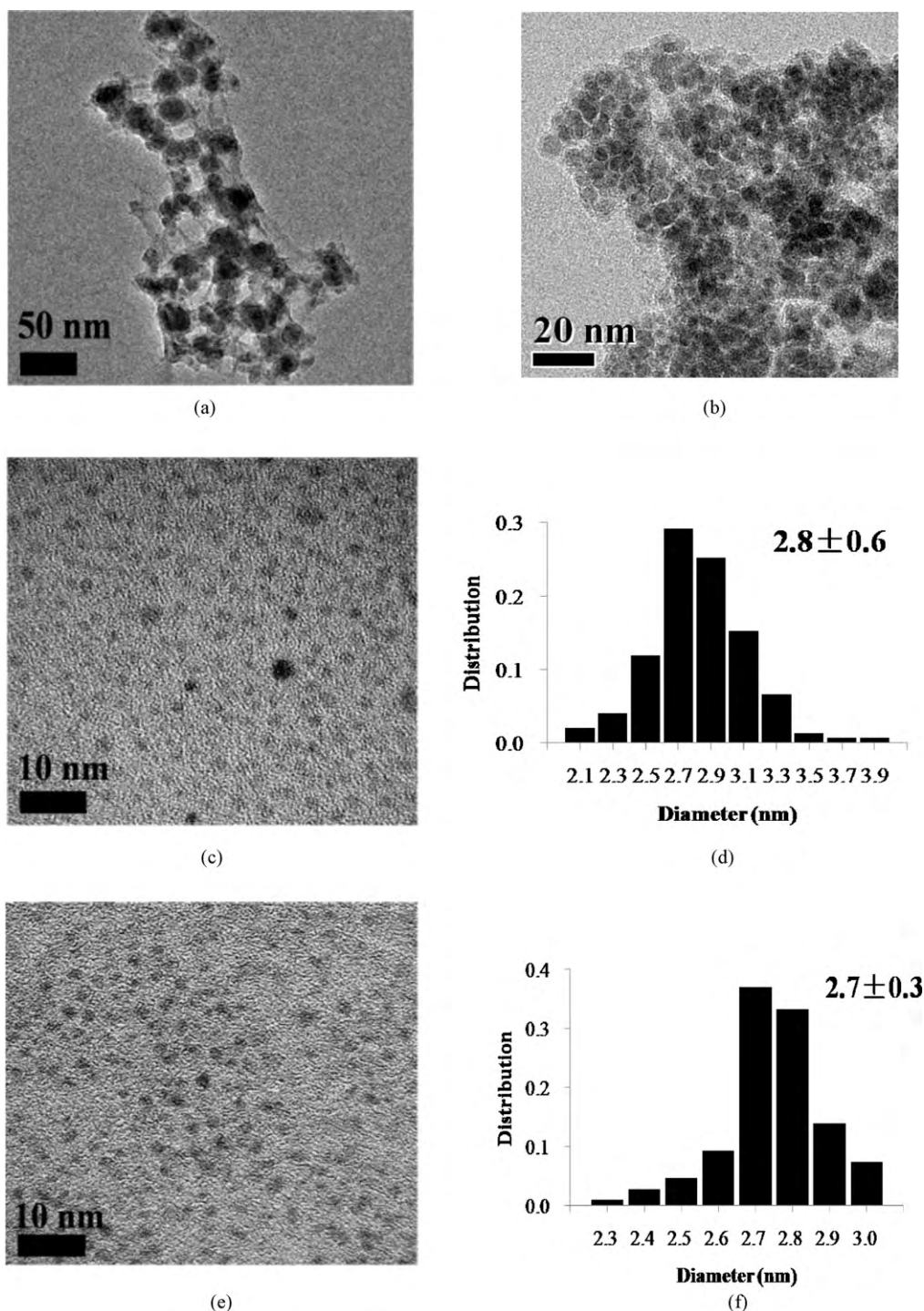
## 3. Results and discussion

### 3.1. Characterization of ultrafine Co nanoparticles

Five catalysts were obtained on different amounts of used 1-hexene, and their preparation details and compositions, determined by ICP, are listed in Table 1. It is concluded that the concentration of cobalt in the cobalt nano-catalyst systems did

not change remarkably, which was almost 1/10 of that of the precursory Co nanoparticles, although different amount of 1-hexene was used in the pretreatment. The ICP data also confirm the efficiency of the preparation. Taking catalyst **4** as an example, after separation/removal of large Co nanoparticles (with an average size of 8 nm) from reaction mixture by magnetic attraction, the upper clear supernatant containing ultrafine Co nanoparticles was collected. The ultrafine Co nanoparticles could be separated from the supernatant by centrifuging the supernatant at 18,000 rpm for 30 min, resulting in black solid at the bottom of the centrifuge tube. The Co concentration of the upper clear supernatant of the

centrifuge tube was  $7.61 \times 10^{-5}$  mg/ml, indicating that the ultrafine Co nanoparticles were separated almost thoroughly with high speed centrifugation. Moreover, it is interesting to note that the Co/B atom ratio is as high as 10, which is almost 100 times higher than the Co/B atom ratio of the precursory Co nanoparticles. As discussed in the literature, preparation of relatively pure cobalt nanoparticles with diameter smaller than 5 nm remains to be a challenging problem [19]. The reduction of cobalt salts by the use of  $\text{NaBH}_4$  as reductant always introduced a large amount of B atoms into the particles, which may inhibit the catalytic activity of cobalt nanoparticles. Our finding therefore offers an excellent solution not



**Fig. 1.** TEM images of (a) precursory Co nanoparticles, (b) cobalt nanoparticles in the lower solid layer separated by the attraction of magnet after pretreatment, (c) cobalt nanoparticles of the catalyst **4** with (d) diameter distribution, and (e) cobalt nanoparticles of the catalyst **4** after reaction of 18 h with (f) diameter distribution.



**Table 2**  
Hydroformylation of 1-hexene with the cobalt nano-catalyst systems<sup>a</sup>.

Catalyst	1-Hexene added in pretreatment (ml)	Cobalt atoms in catalyst <sup>b</sup> (mmol)	Conv. <sup>c</sup> (%)	Selectivity		Aldehyde yield (%)	n/iso <sup>d</sup>	TOF <sup>e</sup> (h <sup>-1</sup> )
				Ald.%	Iso-olefin%			
<b>1</b>	0	0.166	95	38	62	36	1.1	121
<b>2</b>	0.5	0.148	90	41	58	37	1.2	136
<b>3</b>	1.0	0.202	88	49	50	43	1.2	126
<b>4</b>	2.0	0.198	76	53	46	40	1.3	117
<b>5</b>	3.0	0.108	44	66	33	29	1.2	149

<sup>a</sup> Reaction condition: 3 ml 1-hexene, 20 ml the cobalt nano-catalyst system, 100 °C, 2.4 MPa syngas (CO: H<sub>2</sub> = 1), 600 rpm, 1 h.

<sup>b</sup> The amounts of cobalt in the cobalt nano-catalyst systems were determined by ICP detection.

<sup>c</sup> Conversion of 1-hexene.

<sup>d</sup> Mole ratio of n-heptaldehyde to iso-heptaldehyde.

<sup>e</sup> TOF = mmol of aldehydes product/mmol of surface Co atoms/h of reaction time, the mole amount of the surface Co atoms was based on magic number nucleus model of 2.8 nm Co nanoparticles, i.e., 45 percent of the amount of the total Co atoms.

only for the easy preparation of ultrafine cobalt nanoparticles, but also the remarkably decreased the B content in Co–B particles. The same strategy could be applicable in the preparation of other ultrafine metal nanoparticles, such as Fe and Ni nanoparticles, based on metal salt reduction by NaBH<sub>4</sub>.

The ultrafine cobalt nanoparticles of the cobalt nano-catalyst systems and the precursory nanoparticles were characterized by HR-TEM. The sizes and the distributions of those cobalt catalysts **1–5** were very similar. The representative image of the catalyst **4** is shown in Fig. 1(c). It is estimated that the average size of the particles is 2.8 nm in diameter. Compared with the precursory cobalt nanoparticles as shown in Fig. 1(a), the catalyst **4** is much smaller, finer and more uniform. After the supernatant liquid layer containing the ultrafine cobalt nanoparticles was separated, the cobalt nanoparticles (with an average size of 8 nm) left in the lower solid layer, as shown in Fig. 1(b), were smaller than the precursory nanoparticles (with an average size of 20 nm), indicating the precursory nanoparticles may act as a source for the production of ultrafine nanoparticles.

According to the magic number nucleus model [28,29], the cobalt particle consisted of five layers surrounding the center atom may have a diameter of 2.8 nm, which is near to our sample of cobalt catalyst observed in the 2.8 nm. In this case, the surface atoms should be 45 percent of the total atoms.

### 3.2. Hydroformylation of 1-hexene with the cobalt nano-catalyst systems

The hydroformylation reaction results over the prepared ultrafine cobalt nano-catalyst system are listed in Table 2. The TOFs of catalyst **1–5** all are around 130 h<sup>-1</sup>, which are much higher than the TOF (3 h<sup>-1</sup>) in the hydroformylation of 1-octene over Co–B nanoparticles [16]. Additionally, for catalysts **1–5**, the n/iso ratios and the yields of aldehydes are similar to each other, demonstrating that our preparation of small-size cobalt nanoparticles without the protection of any stabilizer is successful.

On the other hand, it is interesting to note that too much 1-hexene (3 ml) added in the pretreatment (catalyst **5**) caused the conversion of 1-hexene and the selectivity to iso-olefin decreased significantly, implying that the aldehydes formed *in situ* may take part in the control of balance between the activity and the stability for those particles.

It is surprising to find that the selectivity of iso-hexene (50%) is comparable with the selectivity of aldehydes. Namely, the activity of 1-hexene isomerisation is competitive to the activity of hydroformylation in this reaction system. Isomerisation of 1-olefin is the subsidiary reaction in hydroformylation catalyzed by Co<sub>2</sub>(CO)<sub>8</sub> complex system, but it is impossible for the degree of isomerisation to be comparable with the degree of hydroformylation which has a quite high TOF, close to the TOF in our hydroformylation reaction.

When Co<sub>2</sub>(CO)<sub>8</sub> complex system is used for hydroformylation, the general selectivity of iso-olefins is less than 20% and the reaction is accompanied with the hydrogenation of olefin. However, there is no hexane detected in the hydroformylation over 2.8 nm Co nanoparticles. These results imply the catalysis in hydroformylation over 2.8 nm Co nanoparticles was different from the homogeneous catalysis corresponding with Co<sub>2</sub>(CO)<sub>8</sub> complex system.

Reaction time as long as 18 h was performed to test the stability of the ultrafine cobalt nano-catalyst system. At the end of the reaction, a TTO (total turnover number) of 2340 was obtained, and the catalytic activity remained nearly unchanged. No visible precipitate can be observed in the autoclave. HR-TEM image of the mixture in the autoclave, as shown in Fig. 1(e), indicates that the size of cobalt nanoparticles after reaction is about 2.7 nm and the particles become more uniform and well-dispersed compared with those before the hydroformylation reaction. Because no stabilizer had been added, the good stability and the excellent dispersion might be attributed to the potential protection effect of the aldehydes formed *in situ*, such as 2-pentylnon-2-enal from dehydration of heptaldehyde condensation. The traditional stabilizer such as PVP is an oxygen-containing compound, which protects a metal core via weak oxygen–metallic atom interaction. The aldehydes formed, in principle, may play the same role as that of PVP. In fact, some interaction of a 14-carbon α,β-unsaturated aldehyde from dehydration of heptaldehyde with the Rh center in a complex catalysis has been reported in literature [30–33].

The ultrafine Co nano-catalyst system has a TOF similar with that of Co<sub>2</sub>(CO)<sub>8</sub> complex system, which was claimed to be one of the most efficient catalysts thus far [34,35]. It is noteworthy that Co<sub>2</sub>(CO)<sub>8</sub> complex system, of which the real catalyst is HCo(CO)<sub>4</sub>, is very unstable under current reaction conditions. For example, after modified by phosphine ligand, it is reported that a calculated TOF of 78 h<sup>-1</sup> was obtained from the hydroformylation of propene catalyzed by Co<sub>2</sub>(CO)<sub>6</sub>[P(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>3</sub>]<sub>2</sub> at 150 °C and 8 MPa syngas pressure [34]. Our catalysts, therefore, showed much better stability.

### 3.3. Mercury poisoning test

Possibly, some soluble cobalt complex may act as the true catalyst in the hydroformylation reaction, as reported by Dupont [15], therefore, it is desirable to conduct the mercury poisoning tests to determine the reaction path in our catalyst system. Mercury poisoning tests have been widely used as one of the most decisive tests for distinguishing heterogeneous catalysis from homogeneous one [36–40]. In the test, mercury is added to poison the zerovalent metal core, causing either the formation of an amalgam or chemical adsorption on the metal surface. Therefore, suppression of the catalytic activity by the presence of Hg (0) is generally regarded as a strong evidence for heterogeneous catalysis on transition metals.

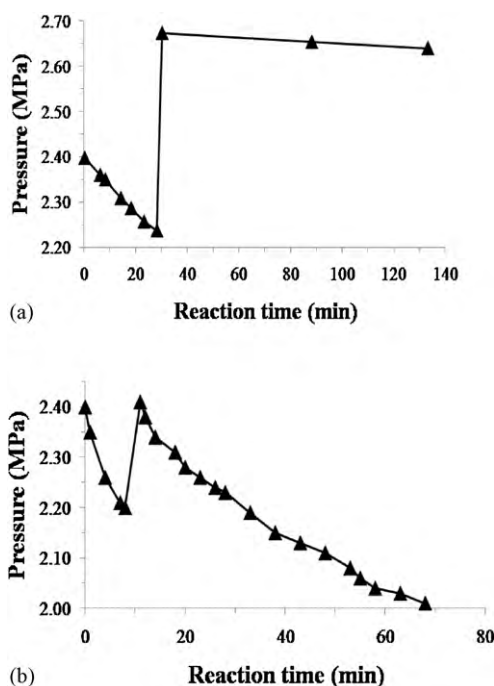


Fig. 2. Pressure–time plots and curve for mercury poisoning tests of hydroformylation of 1-hexene catalyzed by (a) the catalyst **4** and (b)  $\text{RhCl}(\text{PPh}_3)_3$ .

For our prepared cobalt catalyst, after 30 min reaction,  $\text{Hg}(0)$  was injected into the autoclave by an external syngas pulse, and a sudden pressure jump was observed since some syngas was injected into the autoclave inevitably (Fig. 2(a)). Clearly, the reaction was suppressed immediately because no pressure drop can be observed after the injection of  $\text{Hg}(0)$ . Comparatively, mercury poisoning test was also performed on a real homogeneous catalytic reaction with  $\text{RhCl}(\text{PPh}_3)_3$  as the catalyst, as shown in Fig. 2(b). A completely different picture was obtained, i.e., a gradual drop of the pressure in the reaction was observed even with the injection of  $\text{Hg}(0)$ , indicating that mercury poisoning cannot inhibit a typical homogeneous hydroformylation reaction. The comparison suggests that catalytic hydroformylation can be achieved in a completely heterogeneous mode by using soluble nanoparticles as the catalyst. To our knowledge, the carefully prepared 2.8 nm cobalt catalyst is the first successful example.

#### 4. Conclusions

The cobalt nano-catalyst system containing ultrafine and uniform nanoparticles (2.8 nm) has been fabricated through the pretreatment of precursor Co nanoparticles under hydroformylation reaction conditions. The preparation route not only controls particle size, but also decreases boron content in cobalt nanoparticles. The cobalt nano-catalyst systems exhibit very promising catalytic activities in the hydroformylation of 1-hexene under  $100^\circ\text{C}$  with 2.4 MPa syngas ( $\text{CO}:\text{H}_2 = 1$ ), a relatively mild condition, leading to an average TOF of  $130\text{ h}^{-1}$  and a TTO of 2340. The

presence of  $\text{Hg}(0)$  can inhibit the catalytic activity immediately, providing evidence for heterogeneous catalytic hydroformylation path over these cobalt nano-catalysts.

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