Oxygenates Synthesis by Hydroformylation of 1-hexene over Co Nanoparticle Catalyst

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(Received January 5, 2017)

Non-supported nanoparticles exhibited novel and unique catalytic performances in some reactions. The non-supported cobalt nanoparticles (Co NPs) colloidal suspension was directly used as catalyst for hydroformylation reaction of 1-hexene, to investigate the difference of catalytic performance between non-supported Co NPs and supported Co catalyst (Co/SiO2) for aldehyde synthesis. The Co NPs exhibited higher activity on the hydroformylation and selectivity of heptanal than supported Co/SiO2. The higher hydroformylation performance could be contributed to the higher metal surface and larger amount of active sites of non-supported Co NPs, without the coverage of support.

Key Words
Oxygenate fuels, Non-supported nanoparticles, Hydroformylation, Cobalt, Aldehyde

1. Introduction

Hydroformylation of alkenes, as one of the most important syngas-related reactions, has been widely applied in the synthesis of aldehyde by addition of syngas (CO and H2) to alkenes (Scheme 1) [1]. Nowadays, more than 10 million tons each year of aldehydes are produced by industrial hydroformylation. These aldehydes are not only versatile feedstock for the synthesis of various chemicals (such as surfactants, and plasticizers) but also excellent oxygenated fuel candidates as aldehydes can be simply hydrogenated to higher alcohols [2].

Almost all of current commercial hydroformylations are using homogeneous catalysts, especially rhodium-ligand complexes [3]. Although the homogeneous catalyzed hydroformylation is effective, the homogenous process still has some drawbacks such as the high reaction pressure, the low separation efficiency of products and catalyst from the solvent, the recovery and loss of Rh catalyst [3]. The successful implementation of a heterogeneous catalyst for hydroformylation is expected to avoid these drawbacks of homogeneous catalysts.

Until now, a wide range of researches has been performed on the heterogeneous hydroformylation catalyzed by solid-supported transition metals catalysts, such as Rh, Co, Ir and Ru [4]. Although Rh is the most active catalytic component on hydroformylation, its low reserve and high

![Scheme 1 Hydroformylation of 1-alkene](image-url)
cost promote studies on cheaper metal catalyst. Many efforts have been made to develop Co-based heterogeneous catalysts due to its low cost and high activity, whose catalytic activity on hydroformylation is only lower than Rh in all of the metal elements. Nevertheless, solid-supported Co catalysts usually exhibited unsatisfactory catalytic activity on hydroformylation of alkenes and always need much harsher reaction conditions. Recently, non-supported nanoparticles were found some novel and unique catalytic performance in some cases. Until now, the difference of catalytic performance between non-supported Co and supported cobalt catalyst is rarely investigated for hydroformylation of alkenes. In the present work, non-supported cobalt nanoparticles colloidal suspension (Co NPs) was used as catalyst for hydroformylation of 1-hexene. The catalytic performance over Co NPs was investigated at different temperatures and compared with Co supported on SiO₂.

2. Experiment

2.1 Catalysts preparation

The non-supported Co NPs colloidal suspension (2 wt% Co NPs in n-hexane) was provided by Tateyama Kagaku Co. Ltd (Patent: JP W02005/099941).

The cobalt supported on SiO₂ (Co/SiO₂) catalyst was prepared by an incipient wetness impregnation method. After impregnation, the catalyst precursor was vacuumed at room temperature for 1 h and dried at 120 °C for 12 h. After calcined at 400 °C for 2 h, the catalyst was reduced by H₂ at 400 °C for 10 h and passivated by 1% O₂/N₂ at room temperature. The loading of Co was 10 wt%.

2.2 Catalytic activity test

The reaction of the 1-hexene hydroformylation was carried out in an autoclave with an inner volume of 85 mL. 1.6 mL n-hexane containing 2 wt% Co NPs and 10 mL 1-hexene were loaded into the autoclave in the glovebox under N₂. For Co/SiO₂, 0.21 g catalyst and 10 mL 1-hexene were loaded into the autoclave in the glovebox under N₂ to keep the same mass of Co with Co NPs. After flux with 1.0 MPa syngas (CO:H₂ = 1:1) thrice to purge the residual air, 5.0 MPa syngas was sealed in the reactor at the room temperature. The hydroformylation reaction was conducted at 90-130 °C for 1 h with a temperature ramp of 3 °C/min under continuous stirring. After the reaction, the reactor was cooled down in an ice water mixture for 20 min, and was then depressurized to the atmospheric pressure. After the solid catalyst was filtered from the solution, the liquid products (n-hexadecane as the solvent and n-dodecane as the internal standard substance) were analyzed quantitatively with a gas chromatograph (Shimadzu GC 2014) equipped with a capillary column and a flame ionization detector (FID).

3. Result and discussion

Fig. 1 represents the TEM images and particle size distribution of the non-supported cobalt NPs colloidal suspension and Co/SiO₂ catalyst. The TEM image demonstrates that non-supported Co NPs is uniform and ultrafine. The mean size of Co NPs is about 4.4 nm.
analyzed by Dynamic Light Scattering (DLS) method. The mean size of Co particles on Co/SiO₂ catalyst is about 4.0-4.6 nm (Fig. 1 d), similar with that of unsupported Co NPs.

Hydroformylation of 1-hexene over non-supported Co NPs colloidal suspension or SiO₂-supported Co catalyst was conducted at the same reaction conditions. Fig. 2 compares the catalytic performances of 1-hexene hydroformylation over Co NPs and Co/SiO₂ at different temperatures for 1 h, respectively. The 1-hexene conversions of both Co NPs and Co/SiO₂ increase with the elevated reaction temperature. It is obvious that 1-hexene conversions over Co NPs are much higher than those of Co/SiO₂ at all temperatures as in Fig. 2. It is demonstrated that the non-supported Co NPs exhibits higher reaction activity than Co/SiO₂. The higher activity of Co NPs can be attributed to higher metal surface area and more exposed active sites of non-supported Co NPs, without cover from the support, than Co/SiO₂ catalyst. The Co surface area of 0.21 g Co/SiO₂ catalyst decided by H₂ chemisorption was 2.24 m², lower than 3.06 m² (theoretical average value based on 4.4 nm mean size of Co NPs) of 0.02 g Co NPs.

The catalytic performance of non-supported Co NPs and Co/SiO₂ catalysts can be compared more obviously from the yield of aldehydes, as in Fig. 3. For Co NPs, both higher 1-hexene conversion and higher aldehydes yield are realized. The yield of aldehydes over Co NPs is twice higher than that of Co/SiO₂. Except the aldehyde, the other product is mainly internal hexenes (2-hexene and 3-hexene), produced by the isomerization of 1-hexene.

The catalytic activity and n/i ratio of Co NPs are compared with those of Co/SiO₂ and homogeneous Co₂(CO)₈ as listed in Table 1. Due to the absence of ligand, the n/i ratios of all catalysts are about 1.3. Among three catalysts, unsupported Co NPs exhibits the highest yield of aldehyde and TOF. The activity and TOF of homogeneous Co₂(CO)₈ catalyst are lower than those of Co NPs, which may be attributed to the mild reaction conditions. The higher performance can also benefit from the higher metal surface area and more expose active sites of non-supported Co NPs than those of supported Co/SiO₂. Because these non-supported Co NPs are not covered by support, they can provide larger number of active sites than the supported Co NPs as illustrated in Fig. 4. These exposed active sites can adsorb and form much more linear-adsorbed CO molecules during reaction, which are beneficial for the catalytic activity and aldehydes yield in 1-hexene hydroformylation.

Otherwise the Co NPs after reaction (110 °C for 1h) were also characterized by TEM as shown in Fig. 5. After

![Graph](image1.png)

**Fig. 2** The conversion of 1-hexene at different temperature for 1 h over Co NPs and Co/SiO₂

![Graph](image2.png)

**Fig. 3** The selectivity and yield of aldehydes at different temperature for 1 h over Co NPs and Co/SiO₂

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield (%)</th>
<th>n/i ratio</th>
<th>TOF (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co NPs</td>
<td>52.3</td>
<td>1.27</td>
<td>123.3</td>
</tr>
<tr>
<td>Co/SiO₂</td>
<td>10.3</td>
<td>1.33</td>
<td>24.3</td>
</tr>
<tr>
<td>Co₂(CO)₈</td>
<td>43.4</td>
<td>1.31</td>
<td>95.3</td>
</tr>
</tbody>
</table>

a. Reaction condition: 110 °C for 1 h. b. Yield of aldehyde; c. n/i ratio of aldehyde; d. mmol of aldehydes /mmol of Co /hour; e. 0.17 mmol Co₂(CO)₈ was loaded in the reactor using the same method with Co NPs.
reaction, the particles size only changed slightly indicating the stability of Co NPs.

More reactions were carried out to investigate the hydroformylation performance of Co NPs under varied reaction pressures at 100 °C for 1 h (Fig. 6). Higher pressure favors forming more adsorbed CO on Co, which improves the conversion of 1-hexene and the selectivity of n-heptanal. When the pressure increases from 4 to 6 MPa, the n/i ratio of aldehydes increases from 1.27 to 1.79.

4. Conclusion
Non-supported Co NPs was employed as catalyst for hydroformylation of 1-hexene. The catalytic performance of non-supported Co NPs, being compared with that of SiO2 supported Co catalyt, was investigated at different temperature and pressure. The Co NPs exhibited higher activity and selectivity on the hydroformylation than supported Co/SiO2. The higher hydroformylation performance could be contributed to the higher metal surface and enhanced number of active sites of non-supported Co NPs, without the existence of coverage from support.

References