

SYNTHESIS AND CATALYSIS OF A SILICA-SUPPORTED COBALT CARBONYL CLUSTER

YUN-PU WANG, SHU-MEI ZHANG, AI-MIN ZHANG, NAN WU,
Department of Chemistry, Northwestern Teachers' College, Lanzhou (China)

YU-ZHONG LUO and HONG-XIANG FU
Lanzhou Institute of Chemical Physics, Academia Sinica, Lanzhou (China)
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Summary

The supported metal cluster, $\text{Co}_4(\text{CO})_8(\mu_2\text{-CO})_2(\mu_4\text{-PC}_6\text{H}_4)/(\text{SiO}_2)$ (**2**), which decomposed at 290°C, was synthesized. The cobalt and phosphorus contents were 10.51 and 2.64%, respectively. The IR spectrum of **2** exhibits absorptions at 2010 and 1840 cm^{-1} assigned to the terminal carbonyl and bridged carbonyl, respectively. The effects of the reaction conditions and the structure of olefins on the hydroformylation using **2** have been investigated. Nearly 100% conversion and selectivity could be reached by hydroformylation of 1-hexene under conditions of 130°C, 40 kg/cm^2 , $\text{H}_2/\text{CO} = 1$, for 6 h. The rate order of hydroformylation of olefins was as follows: 1-hexene > cyclohexene > diisobutene > styrene. The catalytic activity was kept almost constant after ten-time repeated use (240 h).

Introduction

The chemistry and catalysis of metal clusters have become an important new research area. This importance derives not only from the promise of future commercial success, but also from an academic interest. These clusters have a bridge between heterogeneous and homogeneous catalysis and provide insight into reactions occurring at the surface of metals.

Pittman reported hydroformylation of olefins by homogeneous $\text{Co}_4(\text{CO})_8(\mu_2\text{-CO})_2(\mu_4\text{-PC}_6\text{H}_5)_2$ (**1**) [1]. We have reported on the cobalt clusters $\text{YCCO}_3(\text{CO})_9$ and $\text{Co}_4(\text{CO})_8(\mu_2\text{-CO})_2(\mu_4\text{-PC}_6\text{H}_5)_2$ linking to silica gel and polystyrene [2–5]. These are more active and selective for olefins hydroformylation. Moreover, they are associated with the convenience for ready separation and recovery of catalysts, but, they still have some shortcomings. The use of silica as a support gives high mechanical strength, but it is difficult to functionalize. When polystyrene is used as

support, it is easy to functionalise at the benzene rings, but it swells after much use.

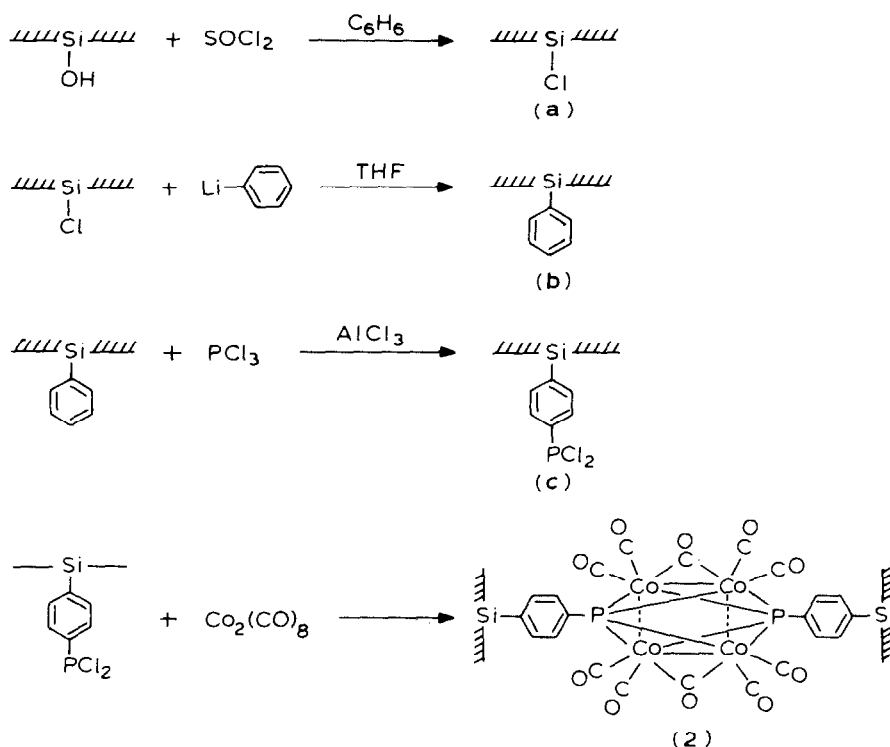
To overcome these shortcomings, the high strength of silica and the easy functionalization of polystyrene were combined into one. In this work phenyl groups were first linked to SiO_2 , then they were phosphonated by PCl_3 , and finally the $\text{Co}_4(\text{CO})_8(\mu_2\text{-CO})_2(\mu_4\text{-PC}_6\text{H}_4)_2/(\text{SiO}_2)$ (**2**) was synthesized.

The effects of reaction conditions and structure of olefins on the hydroformylation, using the supported cluster **2**, have been investigated. The recirculation of the catalyst was also studied.

Results and discussion

I. Preparation of the catalyst $\text{Co}_4(\text{CO})_8(\mu_2\text{-CO})_2(\mu_4\text{-PC}_6\text{H}_4)_2/(\text{SiO}_2)$ (**2**)

This catalyst was synthesized via the following route:



The cobalt and phosphorus contents of the supported cluster were 10.51 and 2.64%, respectively. The ratio $\text{Co}/\text{P} = 2.09$ in the supported cluster **2** is in good agreement with the $\text{Co}/\text{P} = 2.0$ in the cluster $\text{Co}_4(\text{CO})_8(\mu_2\text{-CO})_2(\mu_4\text{-PC}_6\text{H}_5)_2$ (**1**).

Differential thermal analysis showed that the cluster **1** was decomposed at 154°C in air, whereas the supported cluster **2** was decomposed at 290°C .

The IR spectrum of the supported cluster **2** showed absorption bands at 2010 and 1840 cm^{-1} assigned to the terminal and bridged carbonyl of the cluster and they are comparable with those (2040vs , 2032s , 2016s and 1866w cm^{-1}) of cluster **1** [6], which was also synthesized by us.

TABLE 1
THE SPECIFIC ACTIVITY OF DIFFERENT CATALYSTS ^a

Catalyst	Reaction time (h)	Conversion (mol%)	Selectivity (mol%)	Specific activity olefinic conversion		n/i ^b
				1 g	Co × min	
1	24	40.3	100	1.75 ×	10 ⁻¹	0.4
2	6	100	100	5.25 ×	10 ⁻¹	1.1
3	6	80.3	100	4.85 ×	10 ⁻¹	0.7

^a Conditions: 130°C, 40 kg/cm²; H₂/CO = 1; 1-hexene 25 ml; toluene 150 ml. ^b Ratio of normal to iso-product.

TABLE 2
EFFECT OF STRUCTURE OF OLEFIN ^a

Olefin	Conversion (mol%)	Hydrogenation (mol%)	Yield of aldehyde and alcohol (mol%)	Selectivity (mol%)	n/i
1-Hexene	100	–	100	100.	1.1
Cyclohexene	92.3	15.8	76.5	82.9	–
Diisobutene	48.1	–	48.1	100	n
Styrene	13.8	–	13.8	100	n

^a Catalyst 5 g; 130°C; 40 kg/cm²; H₂/CO = 1; toluene 150 ml; time 6 h.

TABLE 3
EFFECT OF TEMPERATURE ^a

Temp. (°C)	Conversion (mol%)	Yield of aldehyde and alcohol (mol%)	Selectivity (mol%)	n/i
110	80.6	80.6	100	2.0
120	84.7	84.7	100	1.3
130	100	100	100	1.1
140	91.4	91.4	100	0.8
150	78.7	78.7	100	0.6

^a Reaction conditions: Catalyst 5 g; toluene 150 ml; 1-hexene 25 ml; 40 kg/cm²; H₂/CO = 1; 6 h.

TABLE 4
EFFECT OF PRESSURE ^a

Pressure (kg/cm ²)	Conversion (mol%)	Yield of aldehyde and alcohol (mol%)	Selectivity (mol%)	n/i
20	60.8	60.8	100	1.3
30	86.0	86.0	100	1.1
40	89.3	89.3	100	1.1
50	92.3	92.3	100	1.0
60	92.6	92.6	100	1.0

^a Catalyst 0.5 g; 1-hexene 1 ml; toluene 4 ml; 130°C; H₂/CO = 1; 24 h.

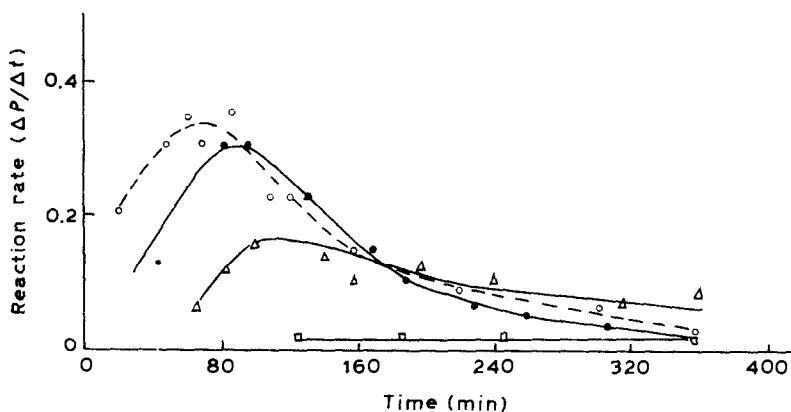


Fig. 1. Effect of various olefins on the reaction rate. \circ - - - - \circ cyclohexene; \circ — \circ 1-hexene; Δ — Δ diisobutene; \square — \square .

II. The hydroformylation activity of supported cluster 2

1. *Specific activity of different catalysts.* The hydroformylation of 1-hexene with the supported cluster **2**, as well as with **1** and $\text{Co}_4(\text{CO})_8(\mu_2\text{-CO})_2(\mu_4\text{-PC}_6\text{H}_5)_2/(\text{P})$ (**3**) [4] was investigated. The results are shown in Table 1. It can be seen that the supported tetranuclear cobalt cluster catalyst **2** has higher activity than the other two.

2. *Effect of the olefin structure.* The results of hydroformylation of 1-hexene, diisobutene, cyclohexene and styrene are given in Table 2 and Fig. 1. From Table 2 and Fig. 1 it can be seen that the rate order is 1-hexene > cyclohexene > diisobutene > styrene.

3. *Effect of parameters on reaction.* The results of hydroformylation of 1-hexene by using the supported cluster **2** over the range of 110–150°C are given in Table 3

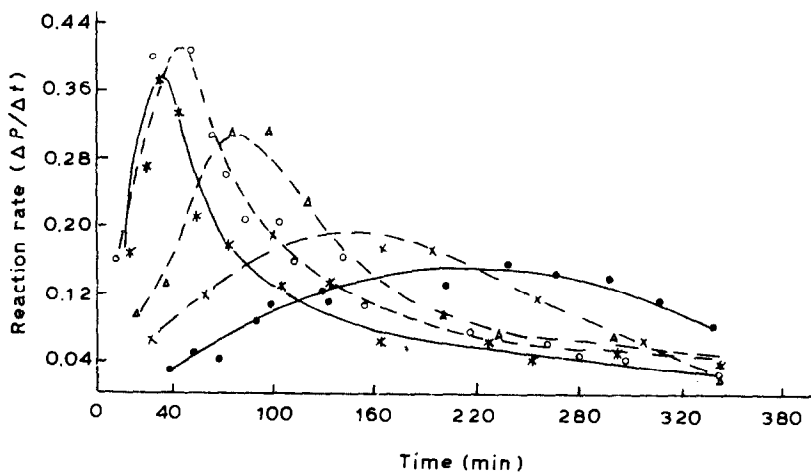


Fig. 2. Effect of temperature on the reaction rate. \bullet — \bullet 110°C; \times — \times 120°C; Δ - - - - Δ 130°C; $*$ — $*$ 140°C; \circ - - - - \circ 150°C.

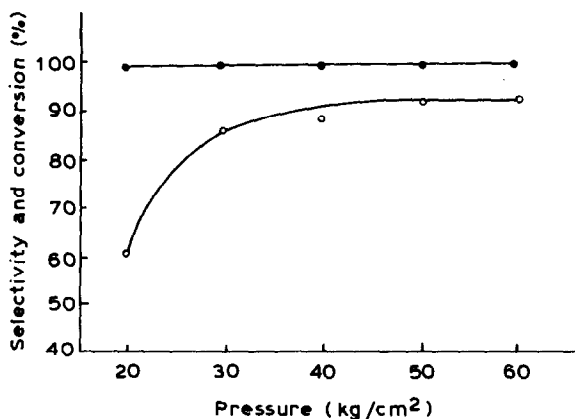


Fig. 3. Pressure effect upon hydroformylation. —●— Selectivity; —○— conversion.

and Fig. 2. It is apparent from Table 3 and Fig. 2 that the rate of hydroformylation increases with increasing temperature within the range 110–130°C, but the ratio of normal to branched chain aldehyde decreases with temperature. When the temperature is higher than 140°C, the conversion and yield are decreased perhaps owing to partial catalyst decomposition.

The effects of pressure upon the hydroformylation of 1-hexene are shown in Table 4 and Fig. 3.

Table 4 and Fig. 3 show that the conversion of 1-hexene and the aldehyde yield increase with an increase of total pressure within the range 20–50 kg/cm². The selectivity is independent of pressure.

The results of hydroformylation of 1-hexene by using the supported cluster **2** with $P(C_6H_5)_3$, added in different quantities, are given in Table 5.

Table 5 indicates that both conversion of 1-hexene along with the yield of aldehyde and alcohol decrease greatly with an increase in added $P(C_6H_5)_3$, but the ratio of *n*- to *iso*-products changed slightly. These results are different from those observed in the hydroformylation of 1-hexene with cluster **3** [4].

4. *Experiment of catalyst recirculation.* The supported cluster **2** was used 10 times. The activity of hydroformylation was not decreased at the end of 240 h. It was easy to separate and recover the catalyst. No swelling of catalyst was found.

TABLE 5
THE EFFECT OF $P(C_6H_5)_3$ ^a

$P(C_6H_5)_3$ added (mg)	Conversion (mol%)	Yield of aldehyde and alcohol (mol%)	Selectivity (mol%)	<i>n</i> / <i>i</i>
0	89.3	89.3	100	1.1
200	68.1	68.1	100	1.2
500	10.8	10.8	100	1.3
700	7.1	7.1	100	1.4

^a Catalyst 0.5 g; 1-hexene 1 ml; toluene 4 ml; 130°C; 40 kg/cm²; $H_2/CO = 1$; 24 h.

Experimental

Hydroformylation procedure

Hydroformylation was carried out in a 0.5 l autoclave with a magnetic stirrer or 0.1 l bomb. The hydroformylation products were analyzed by GLC, using a model 2305 gas chromatograph with TCD and H_2 as carrier gas; a $3\text{ m} \times 3\text{ mm}$ squalane column for hydrocarbons, and a $5\text{ m} \times 3\text{ mm}$ polyethylene glycol adipate column for alcohols and aldehydes.

Preparation of 2

Pre-treated SiO_2 (60 g) was placed in a three-necked flask, which was then degassed by a vacuum pump for 30 min at room temperature. 375 ml of dry benzene and 275 ml of $SOCl_2$ were added to the flask and the mixture was refluxed with stirring for 10 h. The mother liquid was poured out and the residue was washed with benzene and THF, and dried in vacuum. The intermediate **a** was obtained. Under nitrogen an excess of phenyllithium in THF was allowed to react with 30 g of intermediate **a** at room temperature for 10 h. The intermediate **b** to be obtained was washed successively with CH_2Cl_2 , C_2H_5OH and THF, and dried in vacuum. PCl_3 (5 ml) was added dropwise to a flask containing 30 g of the intermediate **b**, 23 g of $AlCl_3$ and 150 ml of nitrobenzene. The mixture was refluxed with stirring for 6 h. $POCl_3$ was then added to remove $AlCl_3$. The residue was washed with THF, CH_2Cl_2 and petroleum ether, and dried in vacuum to give the intermediate **c**. In the presence of CO, 15 g of $Co_2(CO)_8$ in 100 l of toluene was treated with 10 g of zinc dust for 2 h. Then **C** was added, and the mixture was heated at $120^\circ C$ with stirring for 10 h. Solid residue was washed with THF, CH_2Cl_2 and petroleum ether. The supported cluster **2** was obtained.

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