

Heterogenized Catalysts Containing Cobalt–Rhodium Heterobimetallic Nanoparticles for Olefin Hydroformylation

Jee Young Kim · Ji Hoon Park · Ok-Sang Jung ·
Young Keun Chung · Kang Hyun Park

Received: 1 October 2008 / Accepted: 9 November 2008 / Published online: 26 November 2008
© Springer Science+Business Media, LLC 2008

Abstract This paper focuses on the catalysis of the hydroformylation of aliphatic olefins and aromatic olefins using the multi-faceted cobalt–rhodium heterobimetallic nanoparticle (Co_2Rh_2). The Co_2Rh_2 nanocatalyst retained its catalytic activity, allowing for 5 cycles through the reaction.

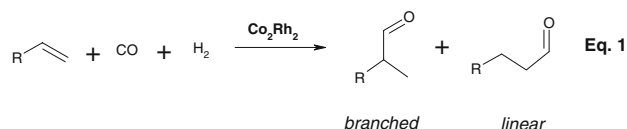
Keywords Hydroformylation · Nanoparticle · Catalyst · Heterobimetallic · Heterogeneous catalyst

1 Introduction

Metal nanoparticles have attracted a lot of attention due to their chemical and physical characteristics that differ from bulk metal [1–6]. For the last several years, almost all metals listed on the periodic table have opened various fields for applications ranging from photo and DNA assays to QDTs. Among the fields, transition metal nanoparticles have become a very important class of catalysts, particularly those used for hydrogenation, oxidation, coupling reactions, and some photocatalytic reactions [7–10].

Hydroformylation, developed by Otto Roelen in 1938, is one of the most versatile methods for the synthesis of fine

chemicals through the functionalization of $\text{C}=\text{C}$ bonds and as such has been positioned as a very important industrial process. It forms new carbon–carbon bonds and carbon–hydrogen bonds through the addition of CO and H_2 to alkenes, creating new stereocenters. In addition, through enantiomeric approaches, it can be applied to pharmaceutical and agrochemical industries. The strengths of the hydroformylation are that only catalytic amounts of a late transition metal catalyst (rhodium(I)) are necessary and it is an atom economic and environmentally friendly reaction whereby all the starting materials are made into products. Even so, the hydroformylation is still not used much for organic synthesis because of its difficulty to control selectivity and many developed catalysts are homogeneous [11].



Recently, cobalt, rhodium, and palladium nanoparticles have been used in the hydroformylation reaction [12–15]. The current literature employs one metal nanoparticle for hydroformylation. For example, Rh nanoparticle (5 nm) composed in ionic liquids, for hydroformylation of 1-alkenes with an linear/branch (*l/b*) ratio over 25% [12]; carbon nano-tube (CNT)-supported cobalt nanoparticles in the metal-organic chemical vapour deposition (MOCVD) method with 59 ~ 68% conversion and a 1.26 ~ 1.53 *l/b* ratio [13]; SiO_2 -supported Pd [14]; and CNT-supported Rhodium [15]. These examples show that reactivity in hydroformylation increases with the nanoparticles compared to commercial grade and bulk metals.

Recently, heterobimetallic nanoparticles as catalysts have attracted much attention because of their superior,

J. Y. Kim · O.-S. Jung · K. H. Park (✉)
Department of Chemistry, Pusan National University,
Pusan 609-735, South Korea
e-mail: chemistry@pusan.ac.kr

J. H. Park · Y. K. Chung
Intelligent Textile System Research Center, and Department
of Chemistry, College of Natural Sciences, Seoul National
University, Seoul 151-747, South Korea
e-mail: ykchung@snu.ac.kr

catalytic performance compared to that of single nanometals [16–23]. For example, Crooks reported [24] that the hydrogenation rate of allyl alcohol is enhanced in the presence of bimetallic nanoparticles compared to platinum or palladium nanoparticles. Thus, we synthesized Co/Rh hetero-bimetallic nanoparticles to study their catalytic activity in the Pauson–Khand-type reaction and other related reactions [16–20].

2 Experimental Section

2.1 General Remarks

THF was freshly distilled from sodium benzophenone ketyl prior to use. Reagents were purchased from Aldrich Chemical Co. and Strem Chemical Co. and were used as received. Reaction products were analyzed by ^1H NMR. ^1H NMR spectra were obtained on Bruker DPX-300 (300 MHz). Chemical shift values were recorded as parts per million relative to tetramethylsilane as an internal standard unless otherwise indicated, and coupling constants in Hertz. Co/Rh heterobimetallic nanoparticles immobilized on charcoal were investigated by transmission electron microscopy (TEM) on a JEM 100C transmission microscope. The samples were prepared by placing a drop of the solution on carboncoated Cu grids and allowing this to dry in air. Counting 200 particles from enlarged TEM images monitored the particle size and size distribution. Co and Rh contents were determined using inductive coupled plasma atomic emission spectroscopy (ICP-AES) with the Shimadzu ICPS-1000 IV device. The analysis showed that the cobalt- to-rhodium ratios were 1.09 for Co_2Rh_2 , respectively.

2.2 Synthesis and Immobilization of Metal Nanoparticles on Charcoal

To a two-neck flask were added *o*-dichlorobenzene (24 mL), oleic acid (0.2 mL), and trioctylphosphine oxide (0.4 g). While the solution was heated at 180 °C, a solution of metal carbonyl, $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ (1.0 g), in 6 mL *o*-dichlorobenzene was injected into the flask. The resulting solution was heated to 180 °C for 2 h and then concentrated to a volume of 5 mL. The concentrated solution was cooled to room temperature. To the cooled solution was added 25 mL of THF. After the solution was well stirred for 10 min, flame-dried charcoal (2.0 g) was added to the solution. After the resulting solution was refluxed for 12 h, the precipitates were filtered and washed with diethyl ether (20 mL), dichloromethane (20 mL), acetone (20 mL), and methanol (20 mL). Vacuum drying gave a black solid.

2.3 Representative Procedure of the Catalytic Hydroformylation using Co_2Rh_2 Nanoparticles

1-Dodecene (5.94 mmol), 5 mol% Co_2Rh_2 (45 mg of the immobilized Co_2Rh_2), and THF (5 mL) were placed in a 100 mL stainless steel autoclave equipped with a stirring bar. The reactor was charged with 5 atm of CO and 5 atm H_2 and heated at 130 °C for 18 h. After the reactor was cooled to room temperature, the solution was filtered. In order to recycle the catalyst, it was filtered from the reaction mixture and dried in vacuum. It could then be reused for further catalytic reactions.

3 Results and Discussion

According to ICP-AES data of the immobilized Co/Rh heterobimetallic nanoparticles, the ratios of Co: Rh was 1.09:1, respectively. Thus, the method used in this study gave fixed stoichiometric Co/Rh bimetallic nanoparticles. HR-TEM photographs of the immobilized Co/Rh heterobimetallic nanoparticles and the corresponding particle size distribution histogram are shown in Fig. 1, respectively. HR-TEM shows that the diameter of the resulting well-dispersed, isolated, and anchored bimetallic nanoparticles is approximately 2 nm.

Cobalt–rhodium heterobimetallic nanoparticles (Co_2Rh_2) on charcoal were used for hydroformylation of different substrates. Using 1-dodecene as a model substrate, we first screened the reaction conditions (Table 1). The ratio of linear/branch was slightly dependent upon the reaction conditions, and ranged from 6:4 to 7:3 with the linear form slightly dominant. When the pressures of carbon monoxide

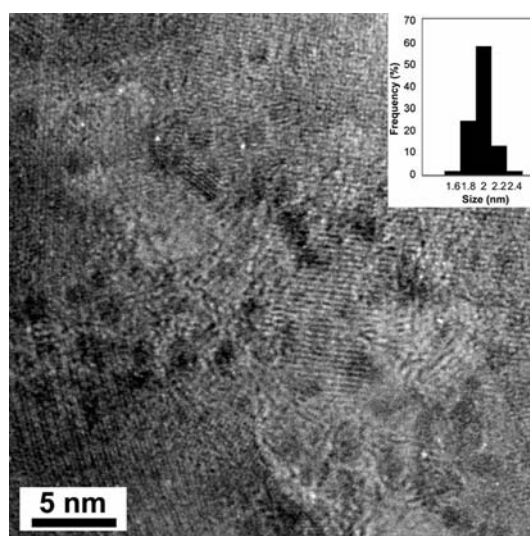


Fig. 1 HR-TEM images of Co_2Rh_2 nanoparticle, inset: histograms illustrating the particle size distribution

Table 1 Hydroformylation of 1-Dodecene catalyzed by Co_2Rh_2 ^a

Entry	<i>l/b</i> ^b	Time (h)	Temp (°C)	Convsn (%)	Select ^c (%)	<i>P</i> (atm)
1	72/28	12	60	46	28	5/5
2	71/29	18	60	57	30	5/5
3	58/42	6	150	100	26	5/5
4	60/40	12	40	20	16	10/10
5	66/34	12	50	25	20	10/10
6	62/38	12	60	100	67	10/10
7	61/39	2	80	100	66	15/15
8	60/40	2	100	100	76	30/30

^a Reaction conditions: substrate (5.94 mmol) and catalyst (0.29 mmol)

^b Molar ratio of linear (*l*) to branched aldehyde (*b*) as determined by ¹H NMR

^c Selectivity for aldehydes

and hydrogen were at 5 atm and the reaction temperature 150 °C, the conversion was quantitative, but selectivity of the aldehyde was only 26%. Increasing the pressure of carbon monoxide and hydrogen to 30 atm at 100 °C led to an increase in the selectivity of aldehyde to 76% with a 100% conversion within a 2 h of the reaction time. However, the ratio of linear/branch decreased to 6:4. The reason why selectivity was not high is that the cobalt–rhodium heterobimetallic nanoparticle used is active towards hydrogenation, thus dodecane is formed [25, 26].

For a comparison, cobalt nanoparticles on charcoal (CNC) [27] were used for hydroformylation of 1-dodecene. In order to meet with the similar result with that of Co_2Rh_2 (Table 1, entry 2), the pressure for the reaction was increased by 6 times from CO/H_2 (5/5 atm) to CO/H_2 (30/30 atm). It was found when the pressure went down to CO/H_2 (20/20) atm, the *l/b* ratio was 6:4 and selectivity went down to 18%. When Co_2Rh_2 was used under the conditions of CO/H_2 (30/30) atm and 2 h of the reaction time, the conversion was 100% with a 76% of selectivity. When CNC was used, the conversion was 22% with 48% of selectivity.

In order to explain the synergistic effects of Co_2Rh_2 catalyst, the following concrete comparative experiment was carried out. The reaction condition was made same— CO/H_2 (5/5) atm, 60 °C, and 18 h. In the case of using CNC, hydroformylation reaction was hardly made. In the case of using Rh nanoparticle, low selectivity of 1.9% was found. *l/b* ratio was 1:1, which was very low. In addition, in the case of testing with the mixture of Co nanoparticle and Rh nanoparticle, low selectivity of 5.4% was found. Thus, compared to Co_2Rh_2 , the CNC had low reactivity, which implies that there might be certain synergistic effects in the case of Co_2Rh_2 . This observation is consistent with that Co_2Rh_2 was a much better catalyst than CNC for the

Pauson–Khnand reaction [19]. Now we keep striving to demonstrate the synergistic effects shown in Co_2Rh_2 .

Next, other aliphatic olefins were examined. The conditions for the reaction were as follows: fixed pressures of CO and H_2 at 5 atm; at 60 °C; and 18 h of a reaction time. In the case of aliphatic olefins, the *l/b* ratio was found at 7:3 ~ 8:2. In the case of 1-hexene, the *l/b* ratio was 74:26 and the conversion was 100% with a 66% of selectivity. When 1-octene was used, the *l/b* ratio was 78:22 and the conversion was 100% with a 98% of selectivity. Various vinyl arenes were also examined. The *l/b* ratio was 5:5 ~ 2:8. Styrene showed 100% conversion with a ratio of 38:64, while *p*-fluorostyrene showed almost a ratio of 5:5. Strangely, *p*-bromostyrene showed only 12% conversion with a 25:75 ratio (Table 2). In the case of arene compounds, hydrogenation did not occur under the conditions described, thus a selectivity >99% was found.

It was also found that the activity of catalyst maintained after 5 cycles (Table 3).

We also investigated the effects of other metals addition to this catalyst system. Commercially available metals (Pd,

Table 2 Hydroformylation of Vinyl arenes using Co_2Rh_2 as the catalyst^a

Entry	Olefin	Co_2Rh_2		
		<i>b/l</i> ^b	Convsn (%)	Selectivity ^c (%)
1	Styrene	38/62	100	>99
2	<i>p</i> -Methoxystyrene	33/67		>99
3	<i>p</i> -Bromostyrene	25/75	12	>99
4	<i>p</i> -Fluorostyrene	47/53	100	>99
5	Norbornene	–		

^a Reaction conditions: substrate (5.94 mmol), catalyst (0.29 mmol), CO/H_2 (5/5) atm, 60 °C, and 18 h

^b Molar ratio of linear (*l*) to branched aldehyde (*b*) as determined by ¹H NMR

^c Selectivity for aldehydes

Table 3 Reusability test for the Hydroformylation of 1-Dodecene catalyzed by Co_2Rh_2 ^a

Entry	Catalyst	<i>l/b</i> ^b	Convsn (%)	Selectivity ^c (%)
1	Co_2Rh_2	71/29	57	30
2	Recovered form entry 1	71/29	59	30
3	Recovered form entry 2	73/27	57	33
4	Recovered form entry 3	71/29	57	31
5	Recovered form entry 4	72/28	56	30

^a Reaction conditions: substrate (5.94 mmol), catalyst (0.29 mmol), CO/H_2 (5/5) atm, 60 °C, and 18 h

^b Molar ratio of linear (*l*) to branched aldehyde (*b*) as determined by ¹H NMR

^c Selectivity for aldehydes

Ni, and Ru) on charcoal of 0.1 wt% were used under the optimized reaction conditions for Co_2Rh_2 . The addition of Pd/C led to the 8:2 *l/b* ratio with a 100% conversion. In the case of Ni/C, the conversion increased, but the *l/b* ratio decreased to 6:4. In the case of Ru/C, no remarkable effect was found.

Our preliminary results showed that aromatic olefins have a better selectivity than aliphatic olefins. When the reusability of the catalyst was tested, there was no loss in conversion and selectivity after the 5th reaction cycle. Thus, if reaction conditions are examined in more detail, we expect that a very useful synthetic method can be developed. The advantages of Co_2Rh_2 -used hydroformylation are as follows: (1) the reaction can be carried out under solventless conditions, (2) the reusability of the catalyst, and (3) the easy separation of the products from the reaction mixtures. Furthermore, we recently found that the Reppe hydroformylation [28], a type of water gas shift reaction, could be improved by using TEA and H_2O (4:1) in the presence of the Co_2Rh_2 nanoparticles giving an *l/b* ratio of 91:1. Application to this particular hydroformylation will be researched further.

Acknowledgments This work was supported for 2 years by Pusan National University Research Grant. J.Y.K. thanks BK21 fellowship.

References

1. Rao CNR, Kulkarni GU, Thomas PJ, Edwards PP (2002) *Chem Eur J* 8:28
2. Schmidt H (2001) *Appl Organometal Chem* 15:331
3. Bönemann H, Richards RM (2001) *Eur J Inorg Chem* 2455
4. Rao CNR, Cheetham AK (2001) *J Mater Chem* 11:2887
5. Rao CNR, Kulkarni GU, Thomas PJ, Edwards PP (2000) *Chem Soc Rev* 29:27
6. Cie-hien JF, Clay RT, Sihn BH, Cohen RE (1998) *New J Chem* 7:685
7. Kakkar AK (2002) *Chem Rev* 102:3579
8. Roucoux A, Schulz J, Patin H (2002) *Chem Rev* 102:3757
9. Thomas JM, Raja R (2001) *Chem Rec* 1:448
10. Johnson BFG (1999) *Coord Chem Rev* 190–192:1269
11. Breit B, Seiche W (2001) Recent advances on chemo-regio- and stereoselective hydroformylation. *Synthesis* 1:1
12. Bruss AJ, Gelesky MA, Machado G, Dupont J (2006) *J Mol Catal A: Chem* 252:212
13. Zhang H, Qiu J, Liang C, Li Z, Wang X, Wang Y, Feng Z, Li C (2005) *Catal Lett* 101:211
14. Sakauchi J, Sakagami H, Takahashi N, Matsuda T, Imizu Y (2005) *Catal Lett* 99:257
15. Giordano R, Serp P, Kalck P, Kihn Y, Schreiber J, Marhic C, Duvail J-L (2003) *Eur J Inorg Chem* 4:610
16. Park KH, Son SU, Chung YK (2003) *Chem Commun* 15:1898
17. Park KH, Jung IG, Kim SY, Chung YK (2003) *Org Lett* 5:4967
18. Park KH, Jung IG, Chung YK (2004) *Org Lett* 6:1183
19. Park KH, Kim SY, Chung YK (2005) *Org Biomol Chem* 3:395
20. Park KH, Chung YK (2005) *Adv Synth Catal* 347:854
21. Thomas JM, Johnson BFG, Raja R, Sankar G, Midgley PA (2003) *Acc Chem Res* 36:20
22. Raja R, Khimyak T, Thomas JM, Hermans S, Johnson BFG (2001) *Angew Chem Int Ed* 40:4638
23. Hermans S, Raja R, Thomas JM, Johnson BFG (2001) *Angew Chem Int Ed* 40:1211
24. Scott RWJ, Wilson OM, Oh SK, Kenik EA, Crooks RM (2004) *J Am Chem Soc* 126:15583
25. Son SU, Park KH, Chung YK (2002) *Org Lett* 4:3983
26. Kang H, Heo E, Park KH (manuscript in preparation)
27. Park KH, Chung YK (2005) *Synlett* 4:545
28. Massoudi R, Kim JH, King RB, King AD Jr (1987) *J Am Chem Soc* 109:7428