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Hydroformylation of 1-hexene for oxygenate fuels on supported cobalt catalysts

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Abstract

The supported Co/SiO_2 and Co/active carbon (A.C.) catalysts were studied as heterogeneous catalysts in the liquid-phase hydroformylation of 1-hexene. The pore size of silica support significantly influenced the activity and selectivity of Co/SiO_2 catalysts in hydroformylation of 1-hexene. The silica supported cobalt catalyst exhibited the best hydroformylation reaction performance at 403 K, and catalytic activity for this kind of catalyst increased with the increasing initial reaction pressure. The addition of small amount of noble metal significantly improved the activity and selectivity for Co/SiO_2. The solvent effects for Co/SiO_2 and Co/A.C. catalysts in the hydroformylation reaction of 1-hexene were investigated and alcoholic solvents promoted the oxygenate formation significantly.

Keywords: Hydroformylation; 1-Hexene; Syngas; Noble metal; Silica; Active carbon

1. Introduction

Hydroformylation, the addition of synthesis gas (CO and H_2) to alkenes, is one of the most important syngas-related reactions [1]. The hydroformylation reaction was first discovered on a heterogeneous Fischer–Tropsch (F–T) catalyst [2]. All current commercial processes are based on homogeneous catalysts, mostly using rhodium. The successful development of a heterogeneous catalyst for hydroformylation is expected to avoid the drawbacks of homogeneous catalysis, such as, very high pressure, the catalyst separation and recovery of rhodium at ppm level to ensure economical operation, due to the high cost of rhodium. A great number of papers and patents concerning olefin hydroformylation catalyzed by rhodium complexes or other noble metals supported on silica or other oxide supports [3,4], zeolites [5] or polymers [6] have been published, and these catalysts are very effective for olefin hydroformylatoin. The advantages of noble metal catalysts include very mild conditions, high conversion rate of alkenes and high selectivity to *n*-aldehydes. On the supported catalysts, CO insertion and subsequent hydrogenation have been found to be much faster than competing reaction route consisting of CO dissociation and hydrogenation of the surface carbon species. Even if rhodium is the most active hydroformylation catalytic component, efforts have been made to study and exploit cheaper metals, thus replacing rhodium in catalysis for economic reasons.

Cobalt is extensively applied in homogeneous process of this reaction due to its high activity and low cost. Supported cobalt catalysts were known to be highly active for Fischer–Tropsch synthesis (FTS). Nevertheless, supported cobalt catalysts usually show low catalytic activity and selectivity for olefin hydroformylation because of high catalytic activity for olefin hydrogenation proceeding at the same time [7]. Thus far, only few papers concerning supported cobalt catalysts for hydroformylation are available. Kainulainen et al. [8] applied Co/SiO_2 catalyst in the liquid-phase hydroformylation of 1-hexene and studied the effect of precursor for cobalt on silica. The highly dispersed active cobalt favoring CO insertion benefits the hydroformylation of olefins. On the other hand, it was reported that the activity and selectivity of supported cobalt catalysts for hydroformylation could be promoted by various promoters. The promoting effect of Ru was found for the hydroformylation

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of 1-hexene over Co/A.C. catalyst by the present authors [9]. Active carbon has also been found to exhibit beneficial characteristics in carbonylation; it can suppress dissociative hydrogen adsorption and inhibit dissociative CO adsorption [10]. These special characteristics of active carbon are also important for hydroformylation, which is governed by reaction of molecular-state CO.

Oxygenates, such as alcohols and esters, can be used as clean engine and vehicle fuels due to their high efficiency and low emission. The olefins produced in the Fischer–Tropsch synthesis (FTS) can be hydroformylated to oxygenate fuels with syngas. It is of great practical importance to develop a solid catalyzed process to produce oxygenates from syngas at low pressure without any compression after FTS process. The main oxygenate from hydroformylation is aldehyde and it can easily be hydrogenated to form alcohol, the final target product. More importantly, since the high pressure in the industrial hydroformylation process using homogeneous catalyst is critical to keep high n/i (normal/isomer) ratio of the formed aldehydes, and since *iso*-aldehyde is acceptable if it is used as fuel after hydrogenation to branched alcohol, the reaction pressure in our experiments can be lowered significantly and high pressure is not necessary. Here 1-hexene was selected as a model compound of FTS derived olefins.

In the present work, the conventional supported Co/SiO_2 and Co/A.C. catalysts were applied as heterogeneous catalysts in the liquid-phase hydroformylation of 1-hexene, meanwhile, the reaction performance and characterization of various catalysts were discussed. As the dispersion of the supported cobalt was very important for this reaction, the influence of pore size of silica support was investigated. The hydroformylation of 1-hexene was carried out under different reaction conditions, such as different temperatures and initial pressures, to find the best reaction condition. As the activity and selectivity of supported cobalt catalysts for hydroformylation could be promoted by various promoters, the promotional effects of noble metal, such as Pd, Ru and Pt, were investigated for silica supported cobalt catalysts. The solvent effects for Co/SiO_2 and Co/A.C. catalysts in the hydroformylation reaction of 1-hexene were also studied.

2. Experimental

Co/SiO_2 catalysts were prepared by the incipient wetness impregnation of aqueous solution of cobalt nitrate onto various silica supports, such as Q-3, Q-6, Q-10, Q-15, Q-30 and Q-50, which were obtained from Fuji Silysia Chemical Co. The active carbon-supported cobalt catalysts were prepared by impregnation of cobalt nitrate aqueous solution onto active carbon (Kanto Chemical Co., specific surface: 1071.7 m^2/g, pore volume: 0.43 m^3/g, pellet size: 20–40 mesh). The cobalt loading of catalysts was 10 wt.%. The noble metal promoted Co/SiO_2 catalysts were prepared by co-impregnation of cobalt nitrate, cobalt acetate and noble metal nitrate salts aqueous solution onto silica ID gel (Fuji Davision, specific surface: 270 m^2/g, average pore diameter: 8.7 nm). The cobalt loading of all catalysts was 10 wt.%. After impregnation, the catalyst precursors were dried at 393 K for 12 h, and then calcined at 673 K for 6 h (calcination of Co/A.C. was under nitrogen flow). At last, the catalysts were reduced by hydrogen at 673 K for 6 h and passivated by 1% oxygen at room temperature.

Hydroformylation reaction was carried out in a magnetically stirred autoclave with inner volume of 75 ml. The catalyst and 1-hexene were loaded into the reactor with a stirrer. The hydroformylation reactions were carried out with different temperatures and pressures. The CO and H_2 ratio of syngas was 1/1. The weight of catalyst was 0.10 g, and 1-hexene or 2-hexene was 40 mmol. When the initial pressure of syngas was 5.0 MPa, the initial reaction gas contained 70 mmol CO and 70 mmol H_2. Some solvents were used in hydroformylation reactions of 1-hexene also, and the ratio of reactant to solvent is 1/2 (reactant: 40 mmol; solvent: 80 mmol). After the reaction, the reactor was cooled to 273 K and depressurized. After filtration to remove the solid catalyst, the liquid products were analyzed quantitatively by gas chromatograph (Shimadzu GC 14A) with a capillary column and a flame ionization detector (FID).

BET surface area and pore diameter were determined by adsorption method (Micomeritics Gemini 2360), where nitrogen was used as adsorbent. Supported metal crystalline size of the passivated catalysts was detected by XRD (Rigaku, RINT2000 X-ray diffractometer with Cu Kα radiation). The cobalt content of the fresh or used catalyst was determined by inductively coupled plasma (ICP) atomic emission spectrometer (Hitachi P-4010).

The reduction level was determined after reduction of the catalyst followed by O_2 titration at 673 K. The reduction percentage was calculated by assuming stoichiometric conversion of metallic Co to Co_3O_4.

3. Results and discussion

3.1. Hydroformylation reaction of 1-hexene over various silica supported cobalt catalysts

With the Co/SiO_2 catalysts, *iso*-heptanal and *n*-heptanal (C_7-al) were obtained as the main hydroformylation products with *n*/*iso* ratio of 0.9–1.2, while small amounts of heptanol (C_7-ol) and condensation products ($C_{13} + C_{14}$) were also produced. The selectivity for isomerization of 1-hexene was less than 10%. No *n*-hexane was formed, indicating that the hydrogenation of 1-hexene was completely suppressed on Co/SiO_2 catalyst under reaction conditions of 403 K and 5.0 MPa.

As shown in Table 1, the cobalt catalysts supported on various silica supports with different pore sizes had quite different reaction performance. Although the selectivity of oxygenates was very high for all catalysts, only 3.9% of

Table 1
Hydroformylation of 1-hexene over Co supported silica catalysts

Catalyst (10 wt.%)	1-Hexene conversion (%)	Selectivity (%)				C7-al + ol yield (%)	*n*/*iso*
		Isomers	C7-al	C7-ol	C13–C14		
Co/Q-3	3.9	7.2	77.5	9.2	5.9	3.4	1.2
Co/Q-6	37.1	8.9	87.5	1.2	2.2	32.9	0.9
Co/Q-10	35.5	8.4	87.4	0.8	3.2	31.4	0.9
Co/Q-15	24.9	8.2	86.3	3.5	1.8	22.4	0.9
Co/Q-30	17.1	8.1	78.5	12.5	0.7	15.6	0.9
Co/Q-50	14.7	7.6	78.2	12.9	1.2	13.4	1.0

Reaction conditions: catalyst, 20–40 mesh, 0.10 g; 1-hexene, 40.0 mmol CO/H_2(1:1), 5.0 MPa; reaction temperature, 403 K; reaction time, 2 h.

1-hexene was converted over Co/Q-3 catalyst while the cobalt supported on Q-15, Q-30 and Q-50 catalysts were moderately active for 1-hexene hydroformylation. High 1-hexene conversions of 37.1 and 35.5% were obtained over Co/Q-6 and Co/Q-10 catalysts respectively. Q-6 and Q-10 were most suitable with the average pore diameters of 6 and 10 nm.

Table 2 presents some properties of various Co/SiO_2 catalysts. With the increase of pore diameter from Q-3 to Q-50, the surface area of the support and the corresponding catalyst decreased. The pore size of support had also great influence on the properties of the Co/SiO_2 catalyst. As shown in Table 2, the reduction degree increased with the increasing pore diameter of the support. The reduction degree of Q-3 was as low as 29.3%, while over 90% of cobalt was reduced for cobalt catalysts derived from Q-10 to Q-50. On the other hand, with the increase of pore diameter and the decrease of surface area of the support, the dispersion of cobalt metal on the catalyst surface was descended while the cobalt particle size was enlarged, as shown in Table 2.

Based on above, the catalytic performance was directly related to the pore size of silica support. For support with very small pore size and high surface area, there existed strong interaction between the supported cobalt and silica surface, resulting in formation of small supported cobalt particle size on the surface of support. The well-dispersed cobalt with small particle size could provide more edge and corner sites, which were advantageous to adsorption of linear-adsorbed CO and the insertion of CO during the hydroformylation reaction [11]. On the other hand, the strong interactions as well as the introduction of cobalt into the small size pores also made the supported cobalt difficult to be reduced, leading to the low reduction degree of the catalyst. The catalysts Co/Q-6 and Co/Q-10 with very small cobalt particle size and relative high reduction degree showed the best performance for 1-hexene hydroformylation. Although with the smallest particle size, the activity of Co/Q-3 was the lowest due to its extremely low reduction degree.

Fig. 1 exhibited the reaction performance of Co/Q-10 under different reaction temperatures. As shown in Fig. 1A, the 1-hexene conversion increased with increased reaction temperature until 423 K to 47%, and then, decreased to 43% at 453 K. The yield of oxygenates, including heptanal and heptanol, increased with the increasing reaction temperature until 403 K, reaching the highest oxygenates yield as 34% at 403 K, and then, the yield of oxygenates decreased with the increasing reaction temperature to 8% at 453 K. The ratio of *n*-heptanal to *iso*-heptanal (*n*/*iso*) decreased with the increasing reaction temperature, indicating that the low reaction temperature was advantageous to forming *n*-heptanal. At high reaction temperature, such as from 423 to 453 K, the hexane was formed and the selectivity of hexane increased from 1.2 to 3.5% with increased reaction temperature as shown in Fig. 1B, indicating that high reaction temperature contributed to hydrogenation of 1-hexene. Generally, high reaction temperature was favorable to form isomer, inner olefins which were formed from isomerization of 1-hexene. The selectivity of oxygenates decreased with the increasing reaction temperature, due to the increased selectivity of isomer. Based on these, at reaction temperature of 403 K, the Co/Q-10 exhibited the

Table 2
Properties of Co/SiO_2 catalysts

Catalyst (10 wt.%)	Pore diameter (nm)[a]	Surface area (m^2/g)		Reduction degree (%)[b]	Co particle size (nm)[c]
		Support	Catalyst		
Co/Q-3	3	514.4	369.7	29.3	6.6
Co/Q-6	6	396.1	328.2	79.9	7.6
Co/Q-10	10	324.6	284.5	90.3	9.0
Co/Q-15	14.1	169.2	161.1	95.6	13.3
Co/Q-30	29.1	110.3	105.3	95.7	18.3
Co/Q-50	52.4	64.6	61.5	93.9	16.1

[a] Average pore diameter of support.

[b] O_2 titration: after 673 K reduction, assuming the following reaction occurred during the oxidation at 673 K: $3Co + 2O_2 \rightarrow Co_3O_4$.

[c] Determined by XRD.

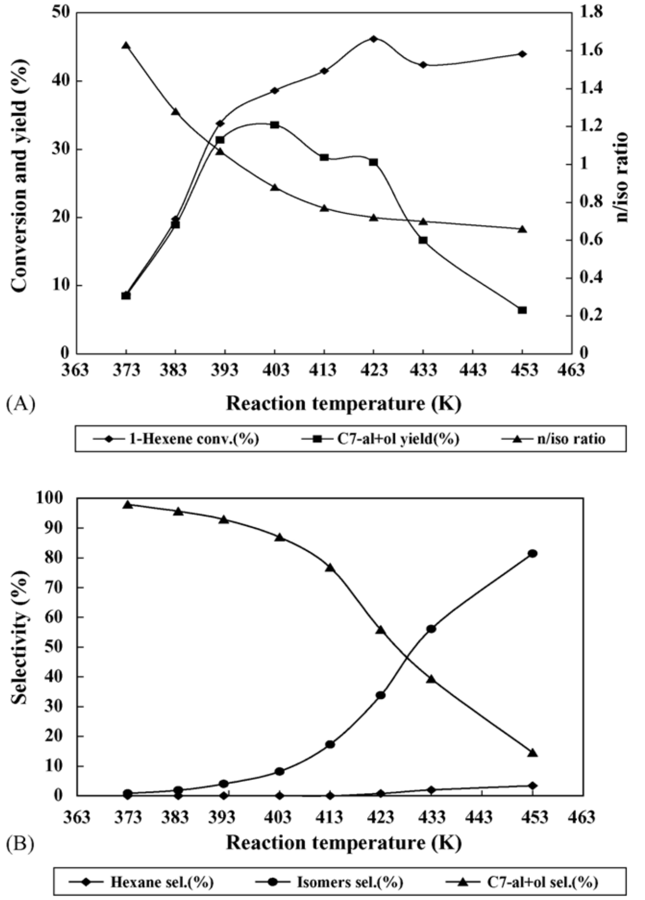

Fig. 1. The influence of reaction temperature on hydroformylation of 1-hexene over 10 wt.% Co/Q-10 catalyst. Reaction conditions: catalyst, 0.10 g; 1-hexene, 40.0 mmol; CO/H_2 (1:1), 5.0 MPa; reaction time, 2 h.

best hydroformylation reaction performance, as relatively high 1-hexene conversion and selectivity of oxygenates, resulting in the highest yield of oxygenates. The 403 K was the most favorite reaction temperature for hydroformylation of 1-hexene over Co/Q-10 catalyst.

The influence of initial reaction pressure for hydroformylation of 1-hexene over Co/Q-10 catalyst was investigated also. As shown in Fig. 2, the conversion of 1-hexene and selectivity of oxygenates increased with the increased initial reaction pressure. The isomer selectivity, however, decreased with the increased initial reaction pressure. At high reaction pressure, the CO molecular was easy to be adsorbed on the active sites, benefiting CO insert reaction, contributing to forming oxygenates products. Generally, high initial pressure was suitable for hydroformylation over Co/Q-10 catalyst.

3.2. Hydroformylation reaction of 1-hexene over noble metal promoted Co/SiO_2 catalysts

The present authors reported that catalysts prepared by mixed impregnation of cobalt nitrate and cobalt acetate onto silica ID support displayed higher activity than the catalysts prepared from either mono-precursor, due to the highly dispersion and reducibility of supported cobalt [12]. Because the highly dispersed and reduced supported cobalt was advantageous to hydorformylation, this kind of catalysts were applied in hydorformylation reaction of 1-hexene and the promotional effects of noble metals for this kind of catalysts were investigated in this study.

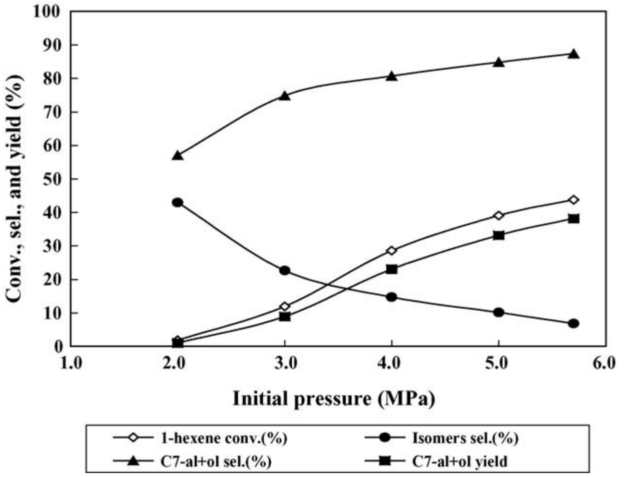

Fig. 2. Effect of syngas initial pressure on hydroformylation of 1-hexene over 10 wt.% Co/Q-10 catalyst. Reaction conditions: catalyst, 0.10 g; 1-hexene, 3.35 g; CO/H_2 (1:1), 2.0–6.0 MPa; reaction temperature, 403 K; reaction time, 2 h.

Table 3 presented catalytic performance of various catalysts, including the reaction result of silica supported 0.5 wt.% Pt, Pd and Ru catalysts for reference. At the reaction conditions of 403 K and 5.0 MPa initial syngas pressure, hydrogenation of 1-hexene was completely suppressed. Without cobalt, the catalysts of 0.5 wt.% Pt/SiO_2, 0.5 wt.% Pd/SiO_2 and 0.5 wt.% Ru/SiO_2 showed very high selectivity, more than 80%, for isomerization reaction with 1-hexene conversion of about 20% and oxygenates yield of about 5%, indicating that the noble metal/silica catalysts had a negligible activity for 1-hexene hydroformylation, as 1-hexene was mainly converted to isomers.

For supported cobalt catalysts, isomerization of 1-hexene gave about 10% selectivity, and oxygenates, including aldehydes (C_7-al) and alcohols (C_7-ol), predominated the product. Small amount of condensation products (C_{13}/C_{14}) was also detected. Without noble metal promoting, the catalyst 10N, which was prepared from cobalt nitrate only, showed higher activity than catalyst 5N + 5A, where the later was a 10 wt.% Co/SiO_2 catalyst prepared by co-impregnation of cobalt nitrate and cobalt acetate. The additions of only 0.5 wt.% of Pt, Pd and Ru promoters improved the catalyst performance significantly, while palladium exhibited the best promoting effect. 89.7% 1-hexene conversion and 88.9% selectivity to oxygenate products were realized on catalyst 5N + 5A + 0.5Pd. The promoting effect for 5N + 5A was more remarkable than that for 10N, as shown in the two Ru-added catalysts.

As the present authors reported else where [13], the addition of Ru significantly improved the Co reducibility but

Table 3
Promoting effect of noble metal on hydroformylation of 1-hexene over cobalt supported on silica catalysts

Catalyst	1-Hexene conversion (%)	Selectivity (%)				C_7-al + ol yield (%)	*n*/*iso*
		Isomers	C_7-al	C_7-ol	C_{13}/C_{14}		
10N	38.8	7.6	76.2	10.0	6.2	33.51	0.9
5N + 5A	20.8	8.1	85.7	1.9	4.2	18.23	0.9
10N + 0.5Ru	46.3	7.3	7.3	1.6	3.8	41.2	1.0
5N + 5A + 0.5Pt	42.4	12.1	78.2	1.5	8.2	33.82	0.7
5N + 5A + 0.5Pd	89.7	11.2	77.9	5.3	5.6	74.69	0.8
5N + 5A + 0.5Ru	72.4	27.5	66.4	2.3	3.9	49.73	0.8
0.5 wt.% Pd/SiO_2	24.5	78.7	21.3	0.0	0.0	5.2	2.7
0.5 wt.% Ru/SiO_2	17.6	85.7	14.3	0.0	0.0	2.5	2.8
0.5 wt.% Pt/SiO_2	18.7	83.0	17.1	0.0	0.0	3.2	2.4

Reaction conditions: catalyst, 20–40 mesh, 0.10 g; 1-hexene, 40.0 mmol; reaction temperature, 403 K; initial pressure of CO + H_2 (1:1), 5.0 MPa; reaction time, 2 h.

had only a slight effect for Co dispersion, and addition of Pt or Pd significantly increased the Co dispersion but slightly increased Co reducibility, while the Pd promoted 5N + 5A catalyst had higher reduction degree than the Pt promoted one. It was considered that the addition of Ru formed the large cobalt particle, which was disadvantageous to hydroformylation reaction, resulting in relatively low activity for hydroformylation. On the other hand, with the small particle size and relatively high reduction degree, the 5N + 5A + 0.5Pd catalyst showed the best reaction performance in hydorformylation reaction of 1-hexene.

3.3. The solvent effects for hydroformylation of 1-hexene via Co/SiO$_2$ and Co/A.C. catalysts

Some alcohols, paraffins, benzene, toluene, THF and distilled water were applied as solvent in the hydroformylation of 1-hexene over 10 wt.% Co/Q-6 catalyst. The reaction results were presented in Table 4. At reaction temperature 403 K, hydrogenation of 1-hexene to hexane did not occur.

As shown in Table 4, the application of methanol and ethanol as solvent greatly accelerated the hydroformylation of 1-hexene. Nearly 100% 1-hexene conversion was obtained after 2 h reaction. The activities were significantly higher than that without solvent. THF and *n*-propanol were also good solvents for the reaction with 1-hexene conversion of 66.9 and 46.4% respectively. Although benzene seems to be benefit for the formation of C_7 alcohol and condensation products, C_{13} and C_{14}, the existences of benzene, toluene, *n*-octane and water in the reaction system suppressed 1-hexene hydroformylation reaction.

In the reaction products with methanol and ethanol as solvents, large amount of ester (heptanoic acid methyl ester and heptanoic acid ethyl ester, respectively) and ether (1,1-dimethoxy-heptane and 1,1-diethoxy-heptane), and trace amount of heptanoic acid were also detected. The formation of ester and ether are as follows:

$$RCH = CH_2 + CO + R'OH \rightarrow RCH_2CH_2COOR' \quad (1)$$

$$RCHO + 2R'OH \rightarrow RCH(OR')_2 + H_2O \quad (2)$$

where RCHO stands for the aldehyde produced in the hydroformylation process. As shown in Table 4, with methanol or ethanol as solvent, the selectivity of olefins isomers was very low. It seems that the solvents inhibited isomerization of 1-hexene. The formation of ester and ether revealed that methanol and ethanol played not only as solvents but also as reactants. The conversion of heptanal

Table 4
Effects of solvent on hydroformylation of 1-hexene over 10 wt.% Co/Q-6 catalysts

Solvent	1-Hexene conversion (%)	Selectivity (%)				C_7-al + ol yield (%)	*n*/*iso*
		Isomers	C_7-al	C_7-ol	C_{13}–C_{14}		
None	37.1	8.9	87.5	1.3	2.2	32.9	0.9
Methanol	99.5	4.8	49.2	45.1[a]	0.8	93.9	0.5
Ethanol	99.7	4.3	61.5	33.4[a]	0.6	94.6	0.6
n-Propanol	46.4	12.3	74.8	6.5	6.1	37.8	0.7
n-Pentane	30.5	13.3	82.2	0.9	3.4	25.4	1.2
n-Heptane	37.5	10.5	85.7	3.6	0.0	33.5	1.3
n-Octane	3.5	18.7	81.3	0.0	0.0	2.8	1.8
Benzene	5.9	3.8	59.9	6.9	29.2	3.9	1.6
Toluene	3.6	0.0	100.0	0.0	0.0	3.6	2.0
THF	66.9	9.69	90.31	0	0	60.4	1.3
H_2O	1.08	11.57	88.43	0	0	0.96	1.1

Reaction conditions: catalyst, 20–40 mesh, 0.10 g; 1-hexene, 40.0 mmol; CO/H_2 (1:1), 5.0 MPa; solvent/1-hexene = 2:1 (mol); reaction temperature, 403 K; reaction time, 2 h.

[a] The data include the selectivity of ester and ether.

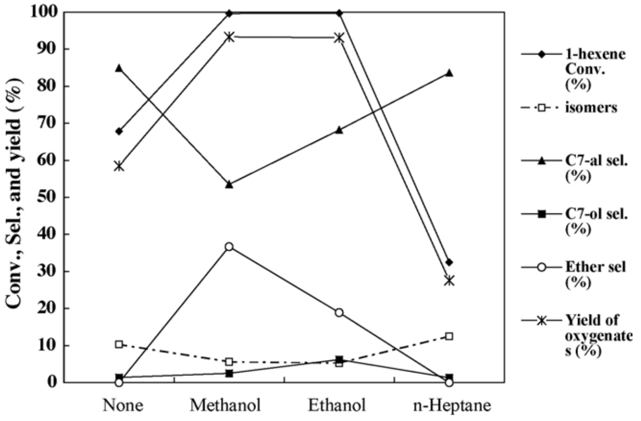

Fig. 3. The solvent effects for hydroformylation of 1-hexene via Co/A.C. catalysts. Reaction conditions: catalyst, 0.10 g; 1-hexene, 40.0 mmol; CO/H_2 (1:1), 5.0 MPa; solvent/1-hexene = 2:1(mol); reaction temperature, 403 K; reaction time, 2 h.

to ester and ether leaded to the decrease of heptanal concentration, and enhanced the hydroformylation of 1-hexene greatly. The low *n*/*iso* ratio of aldehydes could also be attributed to the conversion of 1-heptanal to ester and ether.

Concerning on the various solvents, it was considered that polarity of the solvent might be an important factor influencing the reaction. No ester and ether, however, were detected in the products with *n*-propanol as solvent. Relatively high activity could be obtained from *n*-pentane and *n*-heptane but not *n*-octane as solvent. It was indicated that the molecular size of solvent was also important for the reaction. In general, the solvent with higher polarity and smaller molecular size was advantageous to hydroformylation of 1-hexene over Co/Q-6 silica catalyst.

Fig. 3 exhibited the reaction performance of hydroformylation of 1-hexene over Co/A.C. catalyst under various solvents, including none solvent. The catalytic activity of 1-hexene hydorformylation was greatly promoted by the solvent of methanol and ethanol. The selectivity of isomers was decreased to less than 5%. The ethers, 1,1-dimethyoxy-heptane and 1,1-diethoxy-heptane, were produced respectively as one of the main products besides heptanal. The solvent of *n*-heptane did not exhibit any promotional effects for hydroformylation of 1-hexene over Co/A.C. catalyst.

It was obvious that the addition of alcoholic solvents to the reaction system improved substantially the hydroformylation of 1-hexene and promoted the formation of oxygenates on both Co/SiO_2 and Co/A.C. catalysts. It was considered that the alcoholic solvents might have several kinds of effects at the same time during reaction process. Firstly, they could take part in the catalytic cycle by coordination to the supported cobalt metal. Through electronic effect, the coordinated solvents might inhibit the dissociation of the adsorbed CO over the cobalt center and make it more active for the insertion to Co–olefin bond. Secondly, the methanol and ethanol acted also as reactants and reacted with the produced heptanal to form ethers or esters. The consumption of produced aldehydes benefited the conversion of 1-hexene to heptanal. Thirdly, proton and hydrogen binding of the solvents might also have effect on the reaction process.

Table 5
Cobalt elution of various Co/SiO_2 catalysts after reaction

Catalyst	Co content (wt.%)	
	Fresh	Used
Co/Q-3	9.4	8.7
Co/Q-6	9.5	8.5
Co/Q-10	10.1	8.8
Co/Q-15	10.5	9.1
Co/Q-30	9.7	8.5
Co/Q-50	9.6	8.5

3.4. Cobalt elution

Even for the supported catalyst, under typical hydroformylation conditions, the active metal has been reported to leach from the supports [14]. For the supported cobalt catalyst, some soluble cobalt species, such as cobalt carbonyls, could be formed and led to the elution of cobalt [8]. The cobalt contents of the fresh and used Co/SiO_2 catalysts were detected to estimate the amount of cobalt elution. As shown in Table 5, it was found that about 1 wt.% cobalt was dissolved from various Co/SiO_2 catalysts after 2 h hydroformylation reaction. Even if these catalysts had different reduction degree and cobalt particle size, there was no direct relationship between the 1-hexene conversion and the amount of dissolved cobalt.

The homogeneous hydroformylation reactions of 1-hexene, which used the filtered-off liquid as catalysts after hydroformylation reaction of respective Co/SiO_2 catalyst, were carried out under the same reaction conditions with heterogeneous reactions. For all this kind of reaction, the 1-hexene conversion was lower than 5% and selectivity of isomers was higher than 40%, with far lower yield of hydroformylated products than those of corresponding heterogeneous catalysts. It was considered that although there existed homogeneous reaction via the dissolved cobalt, most of the hydroformylation products originated from heterogeneous catalyst.

4. Conclusions

The hydroformylation of 1-hexene over various silica supported cobalt catalysts was investigated. The hydroformylation catalytic performance was directly related to the pore size of silica support. The catalysts Co/Q-6 and Co/Q-10 with smaller cobalt particle size and higher reduction degree showed the best performance for 1-hexene hydroformylation. The addition of only 0.5 wt.% of Pt, Pd and Ru promoters to Co/SiO_2, which prepared from mixture cobalt salts, improved the catalyst performance significantly. With the small particle size and higher reduction degree, 5N + 5A + 0.5Pd catalyst showed the best reaction performance in hydorformylation reaction of 1-hexene.

The solvent effects for hydroformylation of 1-hexene via Co/SiO_2 and Co/A.C. catalysts were also investigated in this study. The addition of alcoholic solvents to the reaction system improved substantially the hydroformylation of 1-hexene and promoted the formation of oxygenates. In this study, it was considered that although there existed homogeneous reaction over the dissolved cobalt, most of the hydroformylation originated from heterogeneous catalyst.

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