Hydroformylation of mixture of isomeric octenes to C_9-aldehydes catalyzed by Rh–phosphine oxide complexes

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Abstract

The hydroformylation of mixture of isomeric octenes to C_9-aldehydes has been studied using rhodium complex catalysts in an autoclave (100 ml). Phosphine oxide ligands showed high activities in the hydroformylation. The yield of C_9-aldehydes was about 90% by using $[Rh(CH_3COO)_2]_2$–Ph_3PO as the catalyst at $140°C$ and $10.5\,MPa$. Triphenyl phosphine ligand was found to be inactive in the synthesis of C_9-aldehydes from mixture of isomeric octenes. Different rhodium precursors ($[Rh(CH_3COO)_2]_2$, $Rh_6(CO)_{16}$, and $Rh(CO)(PPh_3)(acac)$) showed similar performance in the Rh–Ph_3PO system. The yield of C_9-aldehydes was influenced by the reaction conditions. The suitable reaction temperatures were in the range of $120–140°C$ for the Rh–phosphine oxide systems. High pressures were favorable for the formation C_9-aldehydes. The yield of C_9-aldehydes increased with the increase of P/Rh ratio when the ratio of P/Rh was below 20, while no significant changes were found in the yield of C_9-aldehydes when P/Rh ratio was larger than 20. In situ IR spectroscopy demonstrated the presence of Rh–H bond in the intermediate species in Rh–Ph_3PO catalyzed hydroformylation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydroformylation; Mixture of isomeric octenes; C_9-aldehydes; Rhodium complex; Phosphine oxide

1. Introduction

Hydroformylation of olefins is an important process in petrochemical industries and fine chemicals industries. Rhodium complexes and cobalt complexes have been used as the catalysts in the hydroformylation [1,2]. Compared to Co-based catalysts, Rh-based catalysts have several advantages, such as high activities, mild reaction conditions, easy recovery of catalyst and high yield of *n/i* ratio of products [2]. In the rhodium-catalyzed hydroformylation, the traditional phosphine ligands, such as triphenyl and trialkyl phosphines have been widely used in the hydroformylation of lower olefins like ethylene and propene [3–5],

but other new phosphine ligands have also been applied [6–8]. Also, there are several researches on the hydroformylation of straight long-chain α-olefins like 1-octene by using phosphine ligands [9–11], but only a few researches have been reported on the hydroformylation of the mixture of long-chain and branched olefins [12].

Recently, the hydroformylation of the mixture of long-chain and branched olefins, such as the mixture of isomeric octenes to C_9-aldehydes has caused great attention because the high performance plasticizer, such as di-iso-nonyl phthalate (DINP) has been requested with the development of the plastic industries. For the hydroformylation of the mixture of long-chain and branched olefins (here, defined as higher olefins), the activities of catalysts and the recovery of used catalysts

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are the key factors in the Rh-catalyzed oxo synthesis. Traditional phosphine ligands have contributed greatly to the synthesis of aldehydes in the hydroformylation of lower olefins, but they showed much lower activities for the formation of aldehydes in the hydroformylation of the mixture of long-chain and branched olefins [13]. On the other hand, phosphine oxides like trialkyl or triphenyl phosphine oxides have been considered as inactive ligands in the hydroformylation of lower olefins. However, it has been reported recently that triphenyl phosphine oxide is an efficient ligand in the hydroformylation of higher olefins like octenes or nonenes catalyzed by rhodium catalysts, but at pressures up to 200 bar [12,14]. In our recent works, we have investigated the hydroformylation of mixture of isomeric octenes catalyzed by rhodium complex catalysts in order to develop a process for the oxo synthesis of C_9-aldehydes in high yield at mild reaction conditions and a recovery process of Rh in high efficiency. In this paper, we have examined the activities of the catalyst systems comprised of Rh and phosphine oxides and the effect of reaction conditions on the formation of C_9-aldehydes. The active species involved in the hydroformylation has also been studied by in situ IR.

2. Experimental

The rhodium precursors were purchased from Strem Chemicals Inc. and used as precursors directly. Ph_3PO, $(n\text{-}C_8H_{17})_3PO$, $(n\text{-}C_4H_9)_3PO$ and Ph_3PS were purchased from Acros Organics Co. Mixture of isomeric octenes were obtained from the dimerization of C_4 raffinate-II, which comprise 15–20% n-octenes, 50–60% methyl heptenes and 20–30% dimethylhexenes. Syngas ($CO/H_2 = 1/1$) of high pure grade was purchased from Beijing Analytic Instrument Co. Other reagents were purchased from Beijing Chemical Reagent Co.

The hydroformylations of mixture of isomeric octenes were carried out in an autoclave, which has an internal capacity of 100 ml, at 40–160°C and 4–10.5 MPa pressure ($CO/H_2 = 1$) for 1–10 h. A typical reaction procedure is as follows: 30 ml of mixture of isomeric octenes, 5.9 mg of $[Rh(CH_3COO)_2]_2$ (Rh concentration was 128 ppm), and 0.342 g of Ph_3PO (the molar ratio of P to Rh was 46:1) were placed into the autoclave. The autoclave was purged first with

nitrogen gas for three times at 3.0 MPa pressure, then with syngas for another three times at 1.0 MPa. The autoclave was heated to 140°C under the atmospheric pressure of syngas, then syngas was pressurized into the autoclave up to 8.0 MPa at 140°C. The mixture in the autoclave was stirred at 140°C for 2.5 h with the continuous supply of syngas at 8.0 MPa. After the hydroformylaion, the autoclave was removed from the electric furnace and then cooled in an ice bath. After depressurizing, the reaction mixture was analyzed by gas chromatography (HP 4890D, capillary column HP-5 30 m × 0.25 mm; 50–280°C; 10°C min^{-1}; FID detector). The yield of C_9-aldehydes is defined as the ratio of total moles of C_9-aldehydes and C_9 alcohols formed in the hydroformylation to the moles of mixture of isomeric octenes charged (even though the formation of C_9 alcohols was very little).

In situ IR spectra of Rh–Ph_3PO complexes were determined in a stainless steel high pressure and high temperature IR cell and recorded with a Perkin-Elmer Model PE-2000 FT–IR spectrometer with 20 time scans at 4 cm^{-1} resolution. Rhodium precursor, Ph_3PO and 1-octene were mixed as a paste state in a mortar. This paste was spread on the CaF_2 window of the in situ IR cell. The IR cell was connected with syngas cylinder by stainless tube and equipped with an electric heater for controlling temperature. The IR cell was first purged with N_2 gas at normal pressure, then pressurized by syngas ($CO/H_2 = 1/1$) up to 2.0 MPa at room temperature and heated to the desired temperature to start recording IR spectra.

3. Results and discussion

3.1. Activity and selectivity of Rh–phosphine oxide complex systems

The results of Rh-catalyzed hydroformylations of the mixture of isomeric octenes with and without ligands are shown in Table 1. $[Rh(CH_3COO)_2]_2$–Ph_3PO system showed comparatively high activity in the hydroformylation of mixture of isomeric octenes at 140°C and 8.0 MPa, and C_9-aldehydes was formed in the yield of 75% (Table 1, No. 2). However, the yield was only 45.9% in the case of 'without a ligand' (Table 1, No. 1). When using $(n\text{-}C_8H_{17})_3PO$ instead of Ph_3PO as a ligand, the yield of C_9-aldehydes was also high (Table 1, No. 3). Another phosphine oxide

Table 1
Hydroformylation of mixed octenes over Rh complex catalysts[a]

No.	Rh precursor	Ligand	Ratio of P/Rh	Pressure (MPa)	Conversion of octenes (%)	Yield of iso-NA (%)
1	$[Rh(CH_3COO)_2]_2$		46/1	8.0	49.0	45.9
2	$[Rh(CH_3COO)_2]_2$	Ph_3PO	46/1	8.0	79.1	74.8
3	$[Rh(CH_3COO)_2]_2$	$(n\text{-}C_8H_{17})_3PO$	23/1	9.0	72.8	70.2
4	$[Rh(CH_3COO)_2]_2$	$(n\text{-}C_4H_9)_3PO$	23/1	9.0	54.6	54.2
5	$[Rh(CH_3COO)_2]_2$	$(PhO)_3PO$	46/1	8.0	52.9	52.0
6	$[Rh(CH_3COO)_2]_2$	Ph_3P	46/1	8.0	20.7	19.0
7	$[Rh(CH_3COO)_2]_2$	$(PhO)_3P$	46/1	8.0	31.9	31.8
8	$[Rh(CH_3COO)_2]_2$	$(n\text{-}C_4H_9O)_3P$	46/1	8.0	31.9	28.4
9	$[Rh(CH_3COO)_2]_2$	Ph_3PS	46/1	8.0	33.3	32.7
10	$Rh_6(CO)_{16}$[b]	Ph_3PO	46/1	10.5	86.5	84.8
11	$Rh(CO)(PPh_3)(acac)$[b]	Ph_3PO	46/1	10.5	85.0	79.8
12	$[Rh(CH_3COO)_2]_2$[b]	Ph_3PO	46/1	10.5	87.1	83.7

[a] Reaction conditions: Rh = 128 ppm, mixed octenes = 30 ml, $CO/H_2 = 1/1$, reaction temperature: 140°C, reaction time: 150 min.
[b] At 120°C.

ligand, $(n\text{-}C_4H_9)_3PO$ also showed a plus effect on the formation of C_9-aldehydes compared to the case of only using $[Rh(CH_3COO)_2]_2$ without a ligand, but the activities of $[Rh(CH_3COO)_2]_2$–$(n\text{-}C_4H_9)_3PO$ was lower than that of $[Rh(CH_3COO)_2]_2$–Ph_3PO or $[Rh(CH_3COO)_2]_2$–$(n\text{-}C_8H_{17})_3PO$ system. Phosphate ligand, $(PhO)_3PO$ showed near same activity and selectivity as $(n\text{-}C_4H_9)_3PO$ (Table 1, No. 5). When using phosphine ligand Ph_3P instead of Ph_3PO, the activity of $[Rh(CH_3COO)_2]_2$–Ph_3P was very low (Table 1, No. 6). Phosphite ligands ($(PhO)_3P$ and $(n\text{-}C_4H_9O)_3P$), and phosphine sulfite ligand (Ph_3PS) (Table 1, Nos. 7–9) also showed negative effect on the formation of C_9-aldehydes. Upon these results, it is clearly evident that the catalyst systems comprised of Rh and phosphine oxides are active for the formation of oxo aldehydes in the hydroformylation of mixture of isomeric octenes, although phosphine oxides have been considered as been inactive in the hydroformylation of lower olefins.

Although Ph_3P has been an excellent ligand in the hydroformylation of lower olefins (C3, C4 olefins), it shows negative effect in Rh-catalyzed hydroformylation of the mixture of isomeric octenes. The different behaviors between Rh–phosphine oxide systems (abbreviated as Rh–P=O) and Rh–phosphine systems (abbreviated as Rh–P) in the hydroformylations of higher olefins (mixture of long-chain and branched olefins) and lower olefins (ethylene, propene) could be considered to be related to the factors, such as dynamic

stability of the catalytic species and reactivity of the substrates (olefins). That is to say, in the Rh–P catalyzed hydroformylation of ethylene and propylene, because of their relatively high reactivity, they are easily activated by the active species and coordinate with Rh to form transition state species, although the active species of the catalysts in the Rh–P system is stable. However, in the case of the hydroformylation of higher olefins, such as mixture of isomeric octenes, in the Rh–P systems, because of the relatively low reactivity of mixture of isomeric octenes and the relatively high stability of Rh–P active species, it is hard to coordinate with Rh for these olefins; while in the Rh–P=O systems, it is relatively easy to coordinate with Rh for mixture of isomeric octenes because of the relatively low stability of Rh–P=O active species.

Besides using $[Rh(CH_3COO)_2]_2$, $Rh_6(CO)_{16}$ and $Rh(CO)(PPh_3)(acac)$ were also examined as precursors of rhodium (Table 1, Nos. 10, 11). The results in $Rh_6(CO)_{16}$–Ph_3PO system and $Rh(CO)(PPh_3)(acac)$–Ph_3PO system were nearly same as that in $[Rh(CH_3COO)_2]_2$–Ph_3PO system (Table 1, No. 12). This suggests that the active species involved in the hydroformylation is same even in the cases of different Rh precursors.

3.2. Effect of reaction temperatures

The reaction temperature has a considerable influence on the formation of C_9-aldehydes [15]. The
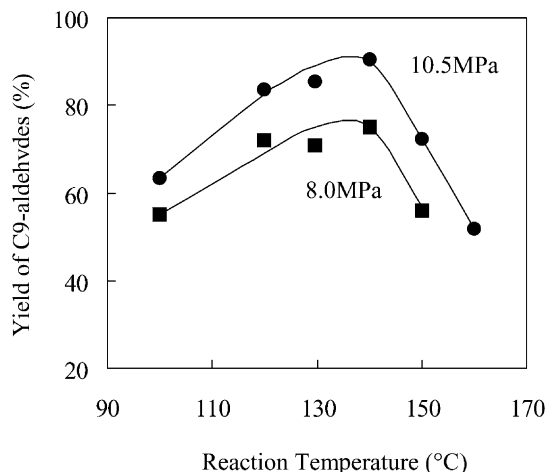
Fig. 1. Effect of reaction temperatures on C_9-aldehydes yield in $[Rh(CH_3COO)_2]_2$–Ph_3PO catalyzed hydroformylation of mixture of isomeric octenes at 10.5 and 8.0 MPa. Reaction conditions: Rh = 128 ppm, P/Rh = 46/1, mixture of isomeric octenes = 30 ml, CO/H_2 (1/1) pressure: 8.0 MPa, reaction time: 150 min.
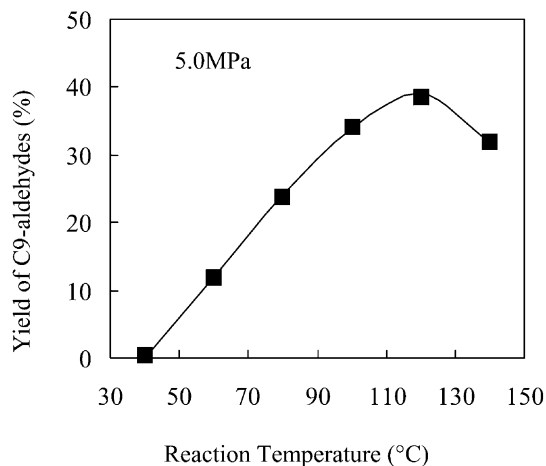

Fig. 2. Effect of reaction temperatures on C_9-aldehydes yield in $[Rh(CH_3COO)_2]_2$–Ph_3PO catalyzed hydroformylation of mixture of isomeric octenes at 5.0 MPa. Reaction conditions: Rh = 128 ppm, P/Rh = 46/1, mixture of isomeric octenes = 30 ml, CO/H_2 (1/1) pressure: 5.0 MPa, reaction time: 150 min.

effect of reaction temperatures was examined in $[Rh(CH_3COO)_2]_2$–Ph_3PO system in the range of 60–160°C at the pressures of 8.0, 10.5 and 5.0 MPa, respectively. Fig. 1 shows the effect of the reaction temperatures on the hydroformylation of mixture of isomeric octenes at the pressures of 10.5 and 8.0 MPa. The yield of C_9-aldehydes was low at low reaction temperatures (<100°C). This was because the rate of reaction was low at low temperatures. In both cases of 10.5 and 8.0 MPa, the yield of C_9-aldehydes increased as increase of reaction temperature firstly, but at 140°C the yield passed through maximum and decreased with further increase in reaction temperature. In case of 8.0 MPa, the yield of C_9-aldehydes was only 56.0% at 150°C. While in case of 10.5 MPa, relatively high activity of the catalyst could be kept at high temperature (150°C) and this was perhaps due to higher stability of the catalytic species at high pressures than at low pressures. The decrease of the formation of C_9-aldehydes at high temperatures (150–160°C) was due to the decomposition of the catalytic species at high temperatures and also due to the condensation of C_9-aldehydes (the formation of the dimmer of C_9-aldehydes was confirmed at the high temperatures) It has been reported that

the condensation products formed from aldehyde in hydroformylation would increase rapidly when the reactions were carried out at high temperatures [16].

The effect of the reaction temperatures at lower pressure (5.0 MPa) is shown in Fig. 2. The tendency of the effect of the reaction temperatures on the yield of C_9-aldehydes was same as the cases of at 10.5 and 8.0 MPa. Below 60°C, C_9-aldehydes yield was very low and almost no reaction occurred at 40°C, 5.0 MPa. Only about 12% C_9-aldehydes yield was obtained at 60°C. In the examined temperature range of 40–140°C, effect of the reaction temperature on the yield of C_9-aldehydes was dramatic. The most suitable reaction temperature for getting the maximum yield was 120°C at 5.0 MPa. The yield was lower at 140°C than that at 120°C. This was due to less stability of the catalytic species at lower pressure (5.0 MPa) and higher temperature (140°C).

As mentioned above, when the reaction temperatures increased to a certain extent, the yield of C_9-aldehydes decreased with the further increase of the temperature. This is related to the stability of the catalytic species in the reaction. The temperatures of stable existence of the catalytic active species varied with the syngas pressures. When the pressures were

high, the catalytic active species could exist stably at relatively high temperatures. We also examined the hydroformylation of the mixture of isomeric octenes at syngas pressure of 16 MPa and found that the conversion of octenes could reach to about 95% even at the reaction temperature of 160°C. However, when the temperature increased to 180°C, the conversion of octenes decreased to about 64% even at 16 MPa syngas pressure. This clearly showed that the catalytic active species decomposed partially at high temperature (180°C).

3.3. Effect of syngas pressures and reaction time

On the other hand, the syngas pressure also affects the formation of C_9-aldehydes greatly. The effect of pressures of syngas was examined at 140°C in $[Rh(CH_3COO)_2]_2$–Ph_3PO system. The result is shown in Fig. 3. The yield of C_9-aldehydes increased almost linearly as the syngas pressures increased in the pressure range 4–8 MPa. Above the pressure of 10 MPa, the increase of C_9-aldehydes yield was not so rapid. The stability of the catalytic species has a relationship with pressure [17]. Too low pressure would result in less stability of the catalytic species. About 90% yield of C_9-aldehydes was obtained when reaction was carried out at 140°C and 10.5 MPa.
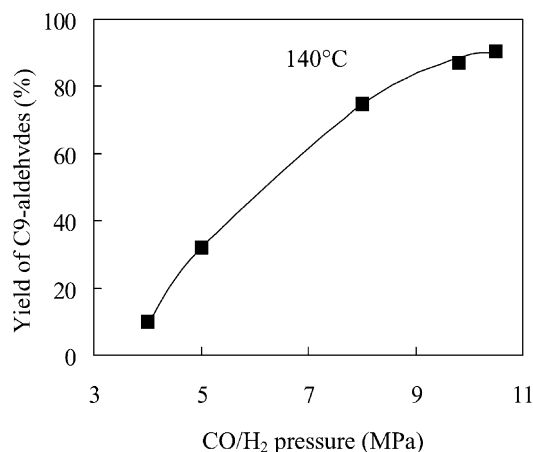
Fig. 3. Effect of CO/H_2 pressures on C_9-aldehydes yield in $[Rh(CH_3COO)_2]_2$–Ph_3PO catalyzed hydroformylation of mixture of isomeric octenes at 140°C. Reaction conditions: Rh = 128 ppm, P/Rh = 46/1, mixture of isomeric octenes = 30 ml, reaction temperature: 140°C, reaction time: 150 min.
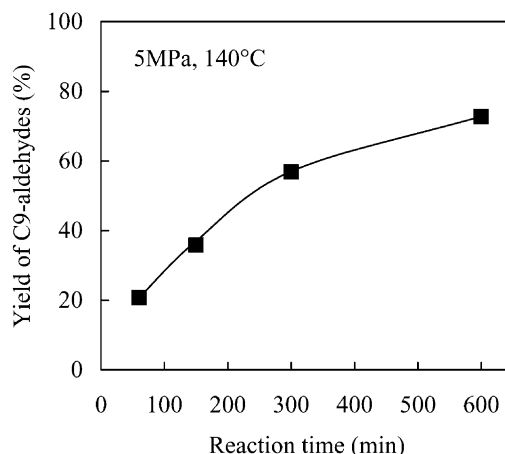
Fig. 4. Effect of reaction times on C_9-aldehydes yield in $[Rh(CH_3COO)_2]_2$–Ph_3PO catalyzed hydroformylation of mixture of isomeric octenes at 5.0 MPa and 140°C. Reaction conditions: Rh = 128 ppm, P/Rh = 46/1, mixture of isomeric octenes = 30 ml, reaction temperature: 140°C, CO/H_2 pressure: 5.0 MPa.

The effect of reaction time on the hydroformylation of mixture of isomeric octenes was examined at 60, 150, 300 and 600 min, respectively, under the conditions of 5.0 MPa and 140°C, firstly. The results are shown in Fig. 4. In the examined reaction time range, the yield of C_9-aldehydes increased with increase of the reaction time at 5.0 MPa and 140°C. For the reactions carried out at higher pressure (8.0 MPa, 140°C), the effect of the reaction time was also dramatic in the range of 0–120 min (Fig. 5), but above 120 min, the saturation of the increase in the yield was observed.

3.4. Effect of P/Rh ratios

It has been reported that the ratio of phosphine to rhodium has a significant influence on the catalytic performance of Rh catalysts [18,19]. The effect of P/Rh ratios was tested in the range of P/Rh ratio from 0 to 46 using $[Rh(CH_3COO)_2]_2$–Ph_3PO system at 140°C and 8.0 MPa syngas pressure. The result is shown in Fig. 6. At low P/Rh ratio stage (lower than 10/1), almost no change in the yield of C_9-aldehydes could be found, while it increased with the increase of P/Rh ratio in the range 10–20 of P/Rh ratio. When P/Rh ratio was larger than 20, the C_9-aldehydes yield was nearly constant. From these results, it can be
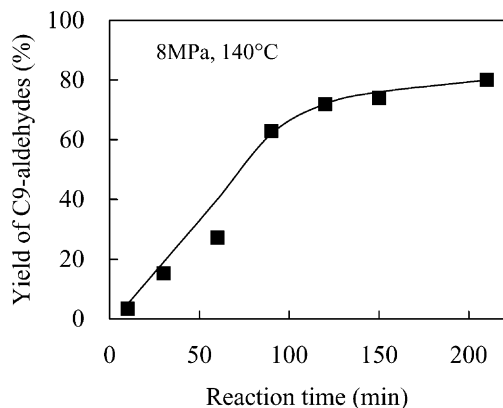
Fig. 5. Effect of reaction times on C_9-aldehydes yield in $[Rh(CH_3COO)_2]_2$–Ph_3PO catalyzed hydroformylation of mixture of isomeric octenes at 8.0 MPa and 140°C. Reaction conditions: Rh = 128 ppm, P/Rh = 46/1, mixture of isomeric octenes = 30 ml, reaction temperature: 140°C, CO/H_2 pressure: 8.0 MPa.

concluded that the P/Rh ratio should be larger than 20 in order to obtain higher C_9-aldehydes yield in the hydroformylation of mixture of isomeric octenes. The change of the yield of C_9-aldehydes with the P/Rh ratio can be explained as follows. When the ratio of P/Rh was low (P/Rh < 10/1), the additional amount of Ph_3PO was not enough to create the stable intermediates which were resultant from $[Rh(CH_3COO)_2]_2$,
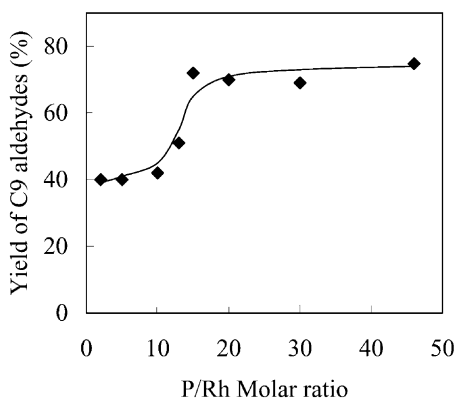

Fig. 6. Effect of P/Rh ratios on C_9-aldehydes yield in $[Rh(CH_3COO)_2]_2$–Ph_3PO catalyzed hydroformylation of mixture of isomeric octenes at 140°C and 8.0 MPa. Reaction conditions: Rh = 128 ppm, mixture of isomeric octenes = 30 ml, $CO/H_2(1/1)$ pressure: 8.0 MPa, reaction temperature: 140°C, reaction time: 150 min.

Ph_3PO and CO/H_2, that is, the formation of the stable intermediates need enough Ph_3PO ligand. With the increase of P/Rh ratio (in the range 10–20 of P/Rh), the intermediates formed in the reaction became stable and finally the activity of catalyst improved. The intermediates keep being stable when the additional amount of Ph_3PO was enough (P/Rh ratio >20). Therefore, the further increase of Ph_3PO did not affect the C_9-aldehydes yield much.

3.5. In situ IR characterization

It has been reported that the active species was $HRh(CO)_2(Ph_3P)_2$ in the hydroformylation of lower olefins (C2, C3, etc.) catalyzed by Rh–Ph_3P system [3]. We suppose that an active species related to Rh–H bond would be involved in the hydroformylation of mixture of isomeric octenes catalyzed by Rh–phosphine oxide systems. In order to confirm the Rh–H bond, in situ IR examinations of $[Rh(CH_3COO)_2]_2$–Ph_3PO system and $[Rh(CH_3COO)_2]_2$–Ph_3P system were performed at 2.0 MPa of CO/H_2 pressure and 85–130°C. Figs. 7 and 8 show the in situ IR spectra of these two catalytic systems. The IR absorptions of gas phase of CO are
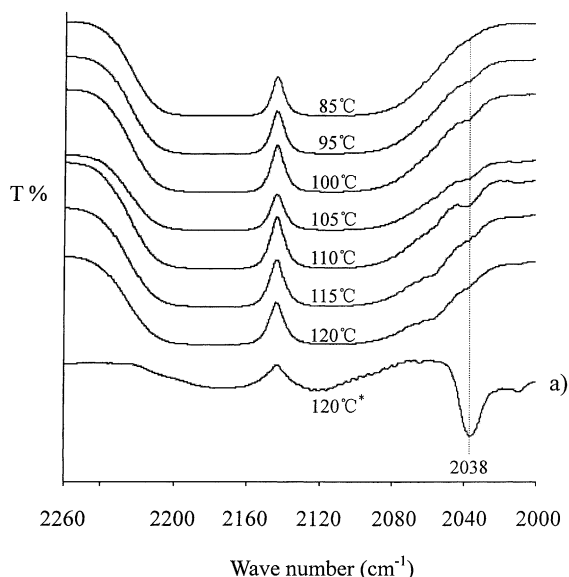

Fig. 7. In situ IR spectra of $[Rh(CH_3COO)_2]_2$–Ph_3PO in hydroformylation of 1-octene (a) measured at 120°C after depressurizing.
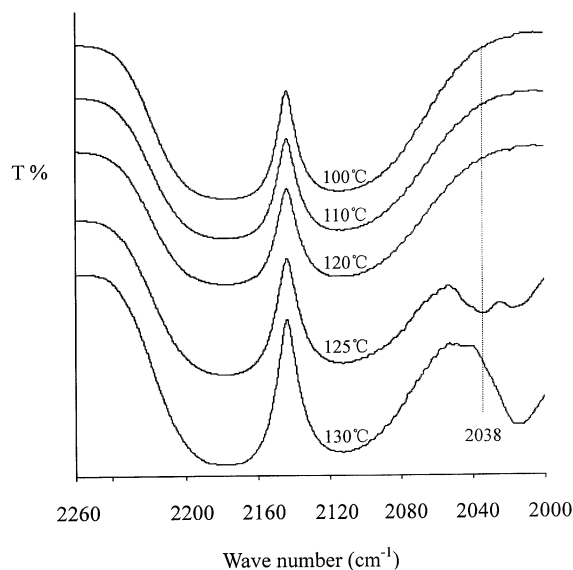
Fig. 8. In situ IR spectra of $[Rh(CH_3COO)_2]_2$–Ph_3P in hydroformylation of 1-octene.

in the range of 2100–2200 cm^{-1}. It has been reported in literature that IR absorption at 2038 cm^{-1} was assigned to the Rh–H vibration of $HRh(CO)_2(Ph_3P)_2$ in the hydroformylation catalyzed by Rh–Ph_3P system [20]. In order to confirm the absorption of the Rh–H bond in IR, we have also measured the IR spectra of pure reagent of $HRh(CO)(Ph_3P)_3$ by KBr method and the absorption at 2038 cm^{-1} was observed.

In case of in situ IR measurement of $[Rh(CH_3COO)_2]_2$–Ph_3PO system at 2.0 MPa, no signal at 2038 cm^{-1} was detected when the temperatures were lower than 85°C (Fig. 7). When the temperature of IR cell reached 100°C, the absorptions at 2038 cm^{-1} were observed. This means that the catalyst had been activated and the active species had been formed at 100°C. Further increasing temperature to 110°C, the intensity of the absorption peak of Rh–H bond (at 2038 cm^{-1}) became stronger. When the temperatures were higher than 115°C, the peak at 2038 cm^{-1} could not almost be observed. Comparing the spectra at 110 and 115°C, the results indicated that the active species was less stable and easily decomposed at higher temperature (above 115°C). In order to eliminate the influence of the absorption of gas phase CO at 2100–2200 cm^{-1} on Rh–H bond absorption and observe the absorption at 2038 cm^{-1} more clearly, the

IR cell was depressurized from 2.0 to 0.1 MPa after recording the spectrum of 120°C and measurement of spectrum at 120°C was performed once again. The peak at 2038 cm^{-1} was clearly observed at 120°C after depressurizing. (Fig. 7(a)).

In case of in situ IR measurement of $[Rh(CH_3COO)_2]_2$–Ph_3P system at 2.0 MPa (Fig. 8), the situation of the activation of the catalyst system was similar to the case of $[Rh(CH_3COO)_2]_2$–Ph_3PO system. The absorption of Rh–H bond (at 2038 cm^{-1}) was observed clearly at 125°C.

It is worth to note that 1-octene was used in the in situ IR measurement of catalytic systems and the reactivity of 1-octene is much higher than the mixture of isomeric octenes in the Rh catalyzed hydroformylation. We also confirmed the hydroformylation of 1-octene in the autoclave and found that about 15% yield of C_9-aldehydes was obtained by using $[Rh(CH_3COO)_2]_2$–Ph_3PO system at 2.0 MPa and 140°C. From the above in situ IR results, it was clearly that the active species containing Rh–H bond was involved in the hydroformylation of octenes catalyzed by Rh–phosphine oxide catalyst systems.

4. Conclusions

Phosphine oxides have been very active ligands in the Rh catalyzed hydroformylation of mixture of isomeric octenes to C_9-aldehydes. About 90% yield of C_9-aldehydes can be obtained at mild reaction conditions (140°C, 10.5 MPa) using $[Rh(CH_3COO)_2]_2$–Ph_3PO as the catalyst. Triphenyl phosphine has exhibited as an inactive ligand in the synthesis of C_9-aldehydes from mixture of isomeric octenes. Different rhodium precursors, such as $[Rh(CH_3COO)_2]_2$, $Rh(CO)(PPh_3)(acac)$ and $Rh_6(CO)_{16}$ have shown near same activities in the Rh–Ph_3PO system. The suitable reaction temperatures were in the range of 120–140°C for the Rh–P=O systems. High pressures were favorable for the formation C_9-aldehydes. The yield of C_9-aldehydes increased with the increase of P/Rh ratio when the ratio of P/Rh is below 20, while no significant changes were found in the yield of C_9-aldehydes when P/Rh ratio was larger than 20. The intermediate species containing Rh–H bond was involved in the Rh–Ph_3PO catalyzed hydroformylation.

Acknowledgements

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