Effects of ammonium salts as additives in Rh–Ph_3PO catalytic system on hydroformylation of mixed octenes

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The effects of ammonium salts as the additives in the $[Rh(CH_3COO)_2]_2$–Ph_3PO catalytic system on the hydroformylation of mixed octenes have been studied. The yield of isononyl aldehydes increased when an ammonium salt such as $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $(NH_4)_2Cr_2O_7$, $(NH_4)_2CrO_4$ or $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$ was added to $[Rh(CH_3COO)_2]_2$–Ph_3PO-catalyzed hydroformylation of mixed octenes. The loss of rhodium in the distillation process for separating the products and the catalyst was reduced and the concentration of Rh in the distillate decreased from 0.115 to 0.057 ppm, when an ammonium salt such as $(NH_4)_2CrO_4$ was added into $[Rh(CH_3COO)_2]_2$–Ph_3PO-catalyzed hydroformylation. The stretching vibration (2040 cm^{-1}) of the Rh–H bond of the active species was observed in the spectra of *in situ* IR. The investigation of *in situ* IR showed that the peak intensity of Rh–H vibration increased and the temperature range at which the Rh–H vibration peak could be observed in IR was widened when $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was used as additive in the system $[Rh(CH_3COO)_2]_2$–Ph_3PO.

KEY WORDS: ammonium salt; additive; hydroformylation; mixed octenes; *in situ* IR

1. Introduction

Hydroformylation of olefins is an important reaction in petrochemical industry and fine chemical industry. Rhodium complexes have been successfully used as the catalysts. For the hydroformylation of lower olefins, phosphines have been usually used as ligands [1]. However, Rh–phosphine catalytic systems have shown lower activity for the hydroformylation of higher olefins, especially for the branched and inner olefins [2]. The hydroformylation of mixed octenes from the dimerization of C_4 olefins can produce valuable isononyl aldehydes. However, it is most important to develop an effective catalytic system for the hydroformylation of mixed octenes. Of late years, a lot of research works about the hydroformylation of higher olefins have been done [3]. The Rh–Ph_3PO catalytic system showed better catalytic performances than the Rh–Ph_3P system for the hydroformylation of mixed octenes [4]. However, the stability of the Rh–Ph_3PO catalytic system was not quite ideal owing to the too weak electron donor properties of Ph_3PO. Therefore, the improvement of catalytic performances and the suitable stability for the catalytic system are still very urgent. Recently, we have been studying the hydroformylation of mixed octenes for developing an effective catalytic system. In this work, we have studied the effects of some inorganic ammonium salts such as $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $(NH_4)_2Cr_2O_7$, $(NH_4)_2CrO_4$ and $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$, etc. as additives in the $[Rh(CH_3COO)_2]_2$–Ph_3PO system on the catalytic performances and on the reduction of Rh loss in the distillation process for separating the products and the catalyst. Rh–Ph_3PO modified with the ammonium salts has been shown to be an effective system for the hydroformylation of mixed octenes and stable in the distillation process. An *in situ* IR study was also performed in order to clarify the role of the ammonium salts in the catalytic system.

2. Experimental

Mixed octenes containing 15–20% of n-octenes, 50–60% of methyl heptenes and 20–30% of dimethyl hexenes were obtained from the dimerization of C_4 raffinate-II. Rh precursors $[Rh(CH_3COO)_2]$ and Ph_3PO ligand were purchased from Acros Organics Company of Belgium. Other reagents were purchased from Beijing Chemical Reagent Company.

The hydroformylations of mixed octenes were carried out in a 100 ml (or 300 ml) high-temperature, high-pressure autoclave. The normal reaction conditions were as follows: mixed octenes 30 ml, Rh/octenes $=$ 128 ppm, P/Rh $=$ 46 (atom ratio), $CO/H_2 = 1$, $T = 140\,^\circ C$, $P = 8.0$ MPa, reaction time $=$ 150 min. The reaction mixture was analyzed by gas chromatography (HP 4890D, capillary column HP-5 30 m $\times$ 0.25 mm; 50–280 °C; 10 °C min^{-1}; FID detector). The separation of catalyst from the products was carried out in a vacuum distillation apparatus. The concentration of rhodium in the distillate (aldehydes) was measured using the ICP-mass method (IRIS Advantage model).

The *in situ* IR measurements of catalytic systems were performed with a PE 2000 IR spectrometer. The mixed paste of the rhodium precursor, Ph_3PO and 1-octene was spread on the CaF_2 window of the *in situ* IR cell. The cell was purged with N_2 gas at the normal pressure, then pressurized by syngas ($CO/H_2 = 1/1$) up to 2.0 MPa at room temperature and

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heated to the desired temperature to start recording the IR spectra.

3. Results and discussion

3.1. Effects of ammonium salts as additives on hydroformylation of mixed octenes

For the hydroformylation of mixed octenes catalyzed by the $[Rh(CH_3COO)_2]_2$–Ph_3PO system, we have investigated the influences of the reaction conditions on the activity and selectivity, and a suitable reaction temperature (140 °C) has been adopted [5]. Therefore, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $(NH_4)_2Cr_2O_7$, $(NH_4)_2CrO_4$ and $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$ were also examined as additives in the $[Rh(CH_3COO)_2]_2$–Ph_3PO catalytic system in the hydroformylation of mixed octenes at 140 °C. Table 1 lists the results about the catalytic activities of $[Rh(CH_3COO)_2]_2$–Ph_3PO modified by these ammonium salts. The results showed that these ammonium salts with large anions containing transition metals with high valence as the additives could improve the performances of the catalytic system. The $[Rh(CH_3COO)_2]_2$–Ph_3PO system modified with the ammonium salts was favorable for the formation of isononyl aldehydes. In order to evaluate the role of the NH_4^+ cation, ammonium acetate (CH_3COONH_4) was tested as an additive in the $[Rh(CH_3COO)_2]_2$–Ph_3PO system and it did not show a positive effect on the catalytic activity and the formation of isononyl aldehydes (table 1, No. 6). From this result and considering the high oxidation state of the transition metals (Cr, Mo and W) involved in the anions of the ammonium salts, it could be supposed that those anions containing transition metals with high oxidation state played the role of modifying the catalytic performance of the $[Rh(CH_3COO)_2]_2$–Ph_3PO system through affecting the status of electron surrounding rhodium. Experimental results showed that inorganic ammonium salts such as $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $(NH_4)_2Cr_2O_7$, $(NH_4)_2CrO_4$ and $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$ were better additives for the hydroformylation of mixed octenes.

The effect of added amount of the ammonium salt ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) on the hydroformylation of mixed octenes has also been examined. The results are shown in table 2. It can be seen that the effect of added amount of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ on the yield of isononyl aldehydes was not obvious at the examined range of N/Rh atom ratio from 1 to 28. Even when a small amount of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (N/Rh = 1/1) was added into the reaction system, a positive effect of the additive on the formation of isononyl aldehydes could be observed (table 2, No. 2).

3.2. Effect of ammonium salts on Rh loss in the distillation process

Rh concentration in the distillate is the measure for valuing the loss extent of Rh in the distillation process. Two steps are required for obtaining isononyl aldehydes from mixed octenes. The first step is the hydroformylation of mixed octenes and the second one is the separation of the target product (isononyl aldehydes) from the reaction mix-

Table 1
Effect of ammonium salts as additives on hydroformylation of mixed octenes.[a]

No.	Additive	Amount of ammonium salt (N/Rh, atom ratio)	Yield of isononyl aldehydes (%)	TOF[b] (min^{-1})
1	None	0	55.5	27.2
2	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	7	63.0	31.9
3	$(NH_4)_2Cr_2O_7$	7	62.3	31.6
4	$(NH_4)_2CrO_4$	7	59.3	30.2
5	$[(NH_4)_5H_5(H_2(WO_4)_6)\cdot H_2O$	7	60.2	30.1
6	CH_3COONH_4	7	49.4	25.3

[a] Catalyst $[Rh(CH_3COO)_2]$–Ph_3PO, P/Rh = 46 (atom ratio), Rh/octenes = 128 ppm, mixed octenes = 30 ml, $T = 140$ °C, $CO/H_2 = 1/1$, $P = 8.0$ MPa, reaction time = 150 min.

[b] Turnover frequency, defined as moles octenes converted per mole Rh per minute.

Table 2
Effect of additive amount of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ on performances of $[Rh(CH_3COO)_2]$–Ph_3PO.[a]

No.	Additive	Amount of ammonium salt (N/Rh, atom ratio)	Yield of isononyl aldehydes (%)	TOF[b] (min^{-1})
1	None	0	55.5	27.2
2	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	1	62.8	31.8
3	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	7	63.0	31.9
4	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	14	63.7	32.2
5	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	20	63.0	32.3
6	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	28	62.2	31.6

[a] Catalyst $[Rh(CH_3COO)_2]$–Ph_3PO, P/Rh = 46 (atom ratio), Rh/octenes = 128 ppm, mixed octenes = 30 ml, $T = 140$ °C, $CO/H_2 = 1/1$, $P = 8.0$ MPa, reaction time = 150 min.

[b] Turnover frequency, defined as moles octenes converted per mole Rh per minute.

Table 3
Effect of ammonium salts on Rh loss in distillation process.[a]

Additive	Yield of isononyl aldehydes (%)	Rh concentration in distillate (ppm)
$(NH_4)_2CrO_4$	81.8	0.057
$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	84.2	0.061
None	78.6	0.115

[a] Catalyst $[Rh(CH_3COO)_2]$–Ph_3PO, P/Rh = 47 (atom ratio), amount of ammonium salt N/Rh = 7/1, Rh/octenes = 13.8 ppm, mixed octenes = 100 ml, T = 140 °C, CO/H_2 = 1/1, P = 17.0 MPa. Distillation conditions: vacuum = 2–3 mm Hg, bottom temperature = 120 °C.

ture which contains isononyl aldehydes, unreacted olefins, a few other by-products and the catalyst. Rh loss in the distillate comes from the distillation process. It is clear that the Rh concentration in the distillate is closely connected with the loss of the Rh and could be decided by the stability of Rh complex in the system. Therefore, the Rh concentration in the distillate under the constant distillation conditions is one of the important target parameters like yield of isononyl aldehydes for the development of an effective catalytic system.

The experiments have proved that ammonium salt additives influenced not only the yield of isononyl aldehydes but also the Rh concentration in the distillate [6]. The effect of the additives ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $(NH_4)_2CrO_4$) on Rh concentration in the distillate is shown in table 3. It can be seen from table 3 that in the case with ammonium salts as additives, the Rh concentration in the distillate decreased obviously, i.e., the addition of ammonium salts could reduce the loss of Rh in the distillation process. Therefore, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $(NH_4)_2CrO_4$, etc., are considered to be good additives for the modification of the Rh–Ph_3PO system.

3.3. Role of ammonium salts as additives

As mentioned above, the addition of ammonium salts to the $[Rh(CH_3COO)_2]_2$–Ph_3PO catalytic system could increase the yield of isononyl aldehydes in the hydroformylation of mixed octenes and also decrease Rh loss in the distillation process of the products. In order to reveal the role of the ammonium salts as additives in the hydroformylation, *in situ* IR measurements of the $[Rh(CH_3COO)_2]_2$–Ph_3PO and $[Rh(CH_3COO)_2]_2$–Ph_3PO–$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ systems in the hydroformylation of 1-octene have been carried out. Figures 1 and 2 show the *in situ* IR spectra for these two catalytic systems.

For the hydroformylation of olefins catalyzed by Rh-based complex catalytic systems, it has been considered that the catalytic active species should be $HRh(CO)_x(L)_y$ ($x + y = 3$ or 4, L = phosphine ligands) in the reaction system in the presence of phosphine ligands [7–9]. In IR spectra of Rh–P complexes, the peak at about 2040 cm^{-1} attributed to the Rh–H stretching vibration is one of the signs of catalytic active species [9,10]. From the IR spectra of figures 1 and 2, the vibration frequency (2040 cm^{-1}) of the Rh–H bond of the active species was observed. The broad peaks at about 2120 and 2175 cm^{-1} in the spectra of figures 1 and 2 were the contribution of gas phase CO absorption due to the high pressure of syngas in the IR cell.

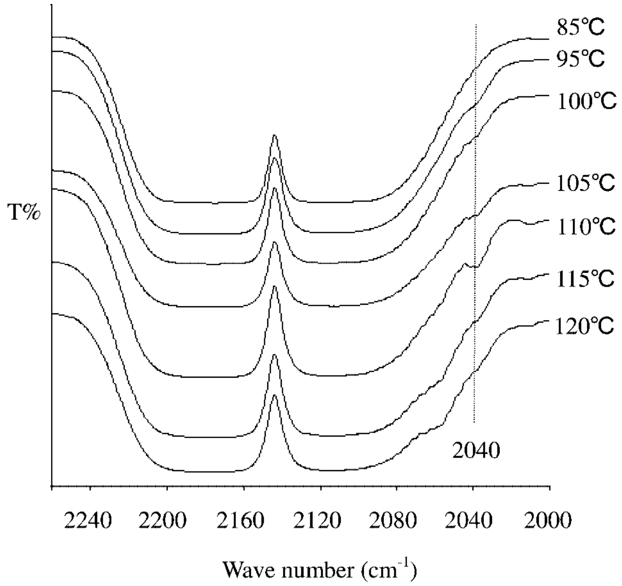

Figure 1. *In situ* infrared spectra of $[Rh(CH_3COO)_2]_2$–Ph_3PO in hydroformylation of 1-octene. P/Rh = 5, pressure = 2.0 MPa.

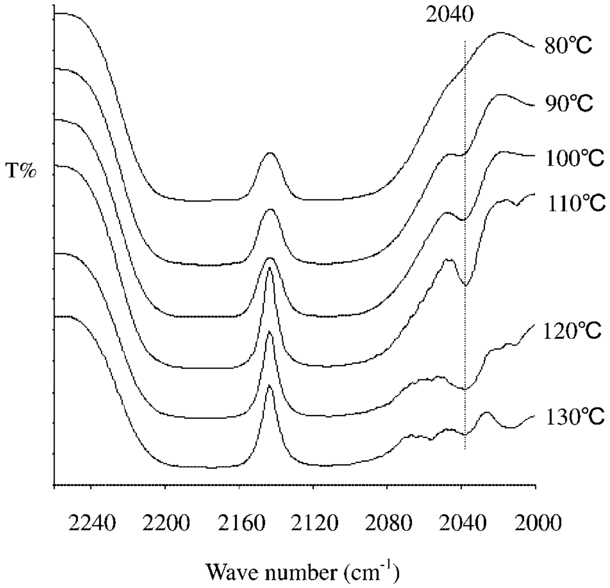

Figure 2. *In situ* infrared spectra of $[Rh(CH_3COO)_2]_2$–Ph_3PO–$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in hydroformylation of 1-octene. N/P/Rh = 2.5/2.5/1, pressure = 2.0 MPa.

It can be seen from the figures that the appearance and disappearance of the Rh–H bond (at about 2040 cm^{-1} in the spectra) were related with the temperatures. In the case of the $[Rh(CH_3COO)_2]_2$–Ph_3PO system, no signal was detected up to 85 °C in the range of 2000–2100 cm^{-1}. A weak absorption at 2040 cm^{-1} was observed when the temperature reached 95 °C (figure 1). This absorption reached its maximum intensity at 110 °C and then decreased with the temperature, and finally, disappeared in the spectra when

Table 4
Temperature range of Rh–H vibration peak appearance and disappearance in *in situ* IR.

Catalytic system	T_a [a] (°C)	T_d [b] (°C)	T_R [c] (°C)
$[Rh(CH_3COO)_2]_2$–Ph_3PO [d]	∼ 95	∼ 115	95–115
$[Rh(CH_3COO)_2]_2$–Ph_3PO–$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ [e]	∼ 85	above 130	85–130

[a] T_a appearance temperature of Rh–H vibration peak.
[b] T_d disappearance temperature of Rh–H vibration peak.
[c] T_R existent temperature range of Rh–H vibration.
[d] P/Rh = 5 (atom ratio), $P = 2.0$ MPa.
[e] N/P/Rh = 2.5/2.5/1, $P = 2.0$ MPa.

the temperature was over 120 °C. In contrast, in the case of the $[Rh(CH_3COO)_2]_2$–Ph_3PO–$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ system, the absorption at 2040 cm^{-1} was observed clearly at 90 °C, reached maximum in intensity at 110 °C and still could be detected even at 130 °C (figure 2). Table 4 lists the difference in the temperature of Rh–H vibration peak appearance and disappearance in the *in situ* IR for these two catalytic systems. It is clear that the temperature range at which the Rh–H vibration peak could be observed in IR for the catalytic system with the ammonium salt was wider than that for the system without the ammonium salt. The peak intensity of Rh–H vibration for the catalytic system with the ammonium salt was stronger than that for the system without the ammonium salt. It is usually considered that the stability of the Rh active species is related with the temperature and syngas pressure. Lower temperatures are required in order to stabilize the catalytic species at relatively lower pressures. It should be noticed that the pressure of syngas was relatively low (2.0 MPa) in the present measurement of *in situ* IR.

The results from IR indicate that the catalytic active species formed *in situ* in the hydroformylation for the $[Rh$–$(CH_3COO)_2]_2$–Ph_3PO–$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ system existed in a wider temperature range than for the $[Rh(CH_3COO)_2]_2$–Ph_3PO system. In other words, the addition of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ to the Rh–Ph_3PO catalytic system increased the stability of catalytic active species. We think that the transition metals (Cr, Mo and W) with high oxidation state contained in the anions of the ammonium salts play the role of modifying the catalytic performance of the $[Rh(CH_3COO)_2]_2$–Ph_3PO system through affecting the status of electron surrounding rhodium. The interaction between the transition metals with high oxidation state with the center metal (rhodium) of the complex may cause the change of the electron properties of Rh, and finally, lead to the favorable coordination between Rh and Ph_3PO ligand which is a weak electron donor.

4. Conclusions

Inorganic ammonium salts such as $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $(NH_4)_2Cr_2O_7$, $(NH_4)_2CrO_4$ and $(NH_4)_5H_5[H_2\ WO_4]_6\cdot H_2O$ as the additives in $[Rh(CH_3COO)_2]_2$–Ph_3PO catalytic system can increase the yield of isononyl aldehydes in the hydroformylation of mixed octenes and also can decrease the loss of Rh in the distillation process of the products. The concentration of Rh in the distillate decreased from 0.115 to 0.057 ppm. The catalytic system $(Rh(CH_3COO)_2)_2$–Ph_3PO modified with ammonium salt $(NH_4)_2Mo_7O_{24}\cdot 4H_2O$ is favorable for the formation and stable existence of catalytic active species. The ammonium salts, mentioned above, are good additives for improvement of the properties of the $(Rh(CH_3COO)_2)_2$–Ph_3PO system used in the hydroformylation of mixed octenes.

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