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# The beneficial effect of alkali metal salt on supported aqueous-phase catalysts for olefin hydroformylation

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Alkali metal salt modified SAP (supported aqueous-phase) rhodium catalysts prepared by coimpregnation method using alkali metal chloride were found to be active and selective for olefin hydroformylation. The salt addition promoted the formation of aldehydes with high selectivity, the aldehyde yield being increased more than 2.5 times at a proper salt/Rh ratio. Changes in stretching frequency of the carbonyl species were detected during ethene hydroformylation, which appeared at ca. 1625 $cm^{-1}$ on the non-modified SAP catalyst sample, while at ca. 1586 $cm^{-1}$ on the KCl-modified one, as shown by in situ IR spectroscopy. The results of a deuterium isotope effect experiment showed that the hydroformylation rate for aldehyde formation on SAP rhodium catalyst under atmospheric pressure of $CO/D_2$ was about 1.3 times faster than that under $CO/H_2$, implying that the rate-determining step involved in aldehyde formation is most probably a step related with hydrogen. The role of the alkali metal salt is discussed in relation with the reaction mechanism.

**Keywords:** hydroformylation; supported aqueous-phase catalyst; rhodium-complex; alkali metal salt; promoter; in situ IR

## 1. Introduction

The development of supported aqueous-phase catalysts (SAP catalysts) has been attracting increasing attention since 1989 [1–16], because of high activity and easy separation of product–reactant from the catalyst. The SAP catalysts proved to be effective in promoting the hydroformylation of water-insoluble olefins, as indicated by the results of a variety of liquid-phase olefin hydroformylation reactions with certain SAP catalysts, such as $HRh(CO)[P(m\text{-}C_6H_4SO_3Na)_3]_3$, $Co_2(CO)_6[P(m\text{-}C_6H_4SO_3Na)_3]_2$ or $Pt[P(m\text{-}C_6H_4SO_3Na)_3]_2Cl\text{–}SnCl_3$ supported on controlled pore glass [1–11]. An example of the method is the hydroformylation of oleyl alcohol

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with a SAP catalyst at 100°C and 51 bar of $CO/H_2$ (v/v = 1). The catalyst was a controlled pore glass impregnated with $HRh(CO)[P(m\text{-}C_6H_4SO_3Na)_3]_3$ and $P(m\text{-}C_6H_4SO_3Na)_3]_3$. Extensive experimentation demonstrated that the rhodium is not leached into the organic phase [1–9]. Since neither oleyl alcohol nor the hydroformylation products are soluble in water, the activity positively supports the hypothesis that the immobilization is completed due to strong interactions between the sulfonated group of the phosphine and the silanol groups on the surface of the support, such as silica or glass. The water-soluble complexes supported on a hydrophilic support may remain dissolved in the aqueous phase and works at the aqueous–organic interface during the catalytic reactions [1,3]. Horvath [4] has further proposed that the hydrophilic support holds the water soluble phosphines by hydrogen bonding of the hydrated sodium-sulfonated groups to the surface, although the exact nature of this interface is unknown.

The mechanism of olefin hydroformylation by homogeneous transition-metal complexes or heterogeneous catalysts has been studied extensively. Certain carbonyl complexes were identified as catalytically active reaction intermediates [17–19]. On the other hand, the distinct effect of alkali metal salts on catalytic activity has been demonstrated for hydroformylation over silica-supported group VIII metal catalysts [20,21] and for $CO–H_2$ reactions over Rh [22,23] and Pd [24,25] metal catalysts. However, so far investigations have never been reported about the promotion effect of alkali metal chloride on hydroformylation over SAP catalysts.

We have investigated the catalytic effects of alkali metal salt additives on SAP rhodium catalysts in liquid-phase olefin (e.g., 1-hexene, 1-heptene, 1-octene, and methyl 10-undecenoate) hydroformylation. In this article, the promoting effects of LiCl, NaCl, and KCl on the activity and selectivity of SAP rhodium catalysts for liquid-phase olefin hydroformylation are reported. The interactions of the alkali metal salt with CO and the reaction intermediates related to the catalytic mechanism are also discussed, together with the experimental results of the kinetic investigation, XRD and in situ IR studies.

## 2. Experimental

### 2.1. CATALYSTS

$P(m\text{-}C_6H_4SO_3Na)_3$ (trisodium salt of tri-(*m*-sulfonphenyl)-phosphine, TPPTS) was synthesized by known methods [26,27]. The results of characterization of the solid products by $^{31}P$ solution NMR indicated that the solid was a mixture of sodium salts of sulfonphenyl-phosphines (~ 91 wt%) with sulfonphenyl-phosphine oxides (~ 9 wt%). $Rh(acac)(CO)_2$ was prepared by the known method, with IR absorption peaks agreeing with the literature [28]: 2066(vs), 1599(vs), 1526(s), 1382(s), 1350(s) and 763(w) $cm^{-1}$.

Impregnated SAP rhodium catalysts were prepared according to the literature [9,10]. The rhodium loading was controlled to be 0.02 mmol per gram of $SiO_2$ in the case of the kinetic experiment, and 0.04 mmol per gram of $SiO_2$ in the case of the isotope effect experiment as well as in situ IR study, respectively. The solution of $Rh(acac)(CO)_2$–hexane was preimpregnated into $SiO_2$ (80–100 meshes, 203 $m^2/g$) by incipient wetness technique and the organic solvent (hexane) evaporated off under vacuum. Incipient wetness was then used to add an aqueous solution with TPPTS amount in the ratio TPPTS/Rh = 10 (mol/mol) to the above sample. Water was removed from the solid under vacuum at room temperature. The impregnated solid was exposed to a $CO/H_2$ mixture at atmospheric pressure and room temperature for at least 12 h to complete the formation of rhodium-phosphine complexes. The analysis by means of constant weight at 383 K showed about 15% weight loss, which is contributed to water of solvation. An aqueous solution of LiCl, or NaCl, or KCl was coimpregnated with TPPTS in aqueous solution respectively, followed by evaporation under vacuum at room temperature. The catalysts thus obtained are denoted as modified SAP catalysts.

### 2.2. HYDROFORMYLATION OF OLEFINS

Hydroformylation was carried out in a fixed bed reactor at 373 K under $CO/H_2$ (v/v = 1) 4.0 MPa pressure. The homogeneous mixture of solvent (*n*-decane) and liquid olefin was added into the reaction system by means of a SY-02A type microfeed-high-pressure pump and the flow-rate of the reactant was readjusted by selecting different output positions on the pump micrometer. The products were analyzed by an FID-GC with the following columns: 5% XE-60 (1 m) and 10% polyethyleneglycolsebacate (3 m) for hydroformylation of methyl 10-undecenoate and $C_6$–$C_8$ olefins respectively.

### 2.3. SPECTROSCOPIC CHARACTERIZATION OF CATALYST

$^{31}P$ solution NMR of water-soluble ligand TPPTS was taken with a Jeol JNM-FX100 spectrometer; X-ray powder diffraction measurements were performed using a Rigaku Diffractometer Ru-200A with Cu $K_\alpha$ radiation.

Infrared spectra were taken with a Nicolet 740 FTIR spectrometer with a resolution of 4 $cm^{-1}$. The catalyst disk in the infrared (IR) cell was subjected to further treatments by flowing nitrogen at room temperature or up to 373 K prior to the adsorption and reaction studies. Each spectrum was produced by accumulating 160 scans at 4 $cm^{-1}$ resolution. CO adsorption, the reaction of preadsorbed CO with $C_2H_4/H_2$ (v/v = 1) and ethene hydroformylation on SAP rhodium catalysts were studied in an IR cell that served as a batch reactor at several temperature points up to 393 K with pressure of 0.1–1.0 MPa of ($C_2H_4/CO/H_2$ = 0.5/1/1, v/v). The spectra for the adsorbed species were recorded by subtracting the $SiO_2$ and ligands (TPPTS) backgrounds.

## 3. Results and discussion

### 3.1. HYDROFORMYLATION OF $C_6$–$C_{11}$ STRAIGHT CHAIN TERMINAL OLEFINS

The immobilization of the SAP rhodium catalysts offers advantages in product isolation and catalyst recycling. Indeed, the hydroformylation of 1-hexene, 1-heptene, 1-octene and methyl 10-undecenoate over SAP rhodium catalysts can be easily carried out in a fixed bed reactor under pressure of $CO/H_2$, as shown in fig. 1. The results of hydroformylation of these $C_6$–$C_{11}$ straight-chained terminal olefins over SAP rhodium catalysts demonstrated that the turnover frequency (TOF) decreased, whereas the ratios of normal/branched ($n/b$) aldehydes increased with increasing carbon number of the substrate. The selectivity towards aldehydes for a given olefin was over 99% on the present catalyst.

Table 1 shows the TOF and STY (space-time yield) for heptanal formation of 1-hexene hydroformylation on alkali metal salt modified SAP catalysts. The TOF and STY for heptanal formation in 1-hexene hydroformylation were remarkably increased over SAP rhodium catalysts modified with LiCl or NaCl or KCl respectively; analogous results were also observed in the case of other olefins such as 1-heptene, 1-octene, and methyl 10-undecenoate. As a result, the TOF and STY for aldehyde formation on the present catalyst system modified with alkali metal salt were higher than on the catalyst without alkali metal salt.

The results of 1-hexene hydroformylation on the KCl-modified SAP rhodium catalyst as a function of KCl content are shown in fig. 2. With the KCl/SAP rhodium catalyst system with KCl/Rh mole ratio in the range of 2–10, the maximum increments of TOF for heptanal formation and $n/b$ ratio were obtained when KCl/

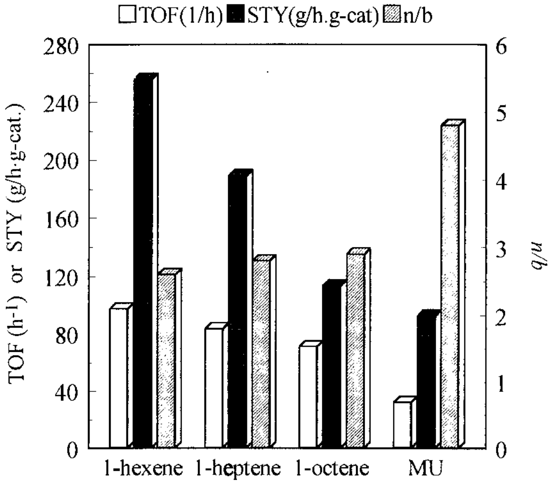

Fig. 1. Hydroformylation of several olefins over SAP rhodium catalysts; MU for methyl 10-undecenoate; reaction temperature 373 K; total pressure 4.0 MPa, $CO/H_2 = 1/1$; Rh loading 0.02 mmol/g-$SiO_2$.

Table 1
Hydroformylation of 1-hexene over SAP catalyst modified with alkali metal salt [a]

| Catalyst | Selectivity ($n/b$) | TOF ($h^{-1}$) |
|---|---|---|
| SAP | 2.7 | 97.4 |
| LiCl–SAP | 3.2 | 254.0 |
| NaCl–SAP | 3.3 | 243.3 |
| KCl–SAP | 3.3 | 260.1 |

[a] The reaction condition was the same as in fig. 1.

Rh mole ratio 2 was employed, and they were larger by a factor of 2.5 and 1.2 respectively than those on the catalyst without KCl addition. However, the TOF and $n/b$ were decreased, especially the TOF may be dramatically declined, as the KCl/Rh ratio in the catalyst was higher than 50.

### 3.2. XRD CHARACTERIZATION OF CATALYST

The powder X-ray diffraction (XRD) pattern of a series of SAP rhodium catalysts (KCl-modified and non-modified ones) revealed that the rhodium complexes or/and KCl was evenly dispersed on the surface of $SiO_2$ when lower KCl/Rh mole ratio (e.g., 10 or lower than 10) was employed. However, the diffraction features for KCl crystal at 28.4°, 40.5° and 66.3° ($2\theta$) appeared in the KCl-modified SAP rhodium catalyst with excessive KCl addition (e.g., KCl/Rh = 50), indicating that KCl was salted out on the surface of the catalyst in this case. As a result, the catalyst particle may become a highly hydrophilic electrolyte which inhibits the water-insoluble olefin to contact with the active center due to excessive KCl con-

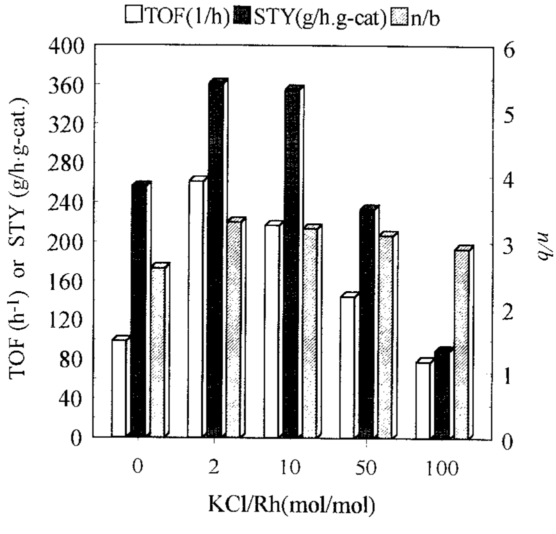

Fig. 2. Catalytic activities of the KCl-modified SAP rhodium catalysts for 1-hexene hydroformylation as a function of KCl content; the other reaction conditions were the same as fig. 1.

tent, i.e., excessive alkali metal salt addition in SAP rhodium catalysts may result in a decrease in catalytic activity.

### 3.3. IN SITU FTIR STUDY OF SAP RHODIUM CATALYSTS

We have conducted the ethene hydroformylation as a probing reaction to investigate the surface species on the functioning SAP catalysts by means of in situ IR spectroscopy. The in situ IR spectra of surface species on the functioning SAP catalysts without KCl and with KCl (KCl/Rh = 2) under the reaction condition for ethene hydroformylation are shown in figs. 3 and 4 respectively. In addition to the CO peaks at 1980–2040 $cm^{-1}$, peaks around 1700 $cm^{-1}$ and in the region of 1400–1600 $cm^{-1}$ were observed as shown both in figs. 3 and 4.

When CO was admitted to the catalysts surface at 373–393 K, several IR bands at 1985, 2012, 2017 and 2049 $cm^{-1}$ have been observed. The $\nu(CO) \approx 1985$ $cm^{-1}$ band is a stable peak under flowing $N_2$ and may be assigned to CO adsorption of complex $HRh(CO)(TPPTS)_3$, whereas the other $\nu(CO)$ bands may be gradually purged away by flowing $N_2$ and become reversible when CO is introduced into the system again, being assignable to weak and reversible CO adsorptions due to multi-carbonyl coordination with rhodium center. No peaks around 1700 and 1400–1600 $cm^{-1}$ were observed during CO adsorption experiments. These peaks appeared only under reaction conditions, indicating that the peaks around 1700 and 1400–1600 $cm^{-1}$ were not related to molecular CO-derived adspecies. The intensity of the peaks around 1700 and 1400–1600 $cm^{-1}$ was increased with proceeding hydroformylation. In order to assign the peak around 1700 $cm^{-1}$, $N_2$ was introduced again into the system and the peak at 1700 $cm^{-1}$ was gradually purged away in this case. The results suggest the peak is assignable to the molecularly adsorbed propanal.

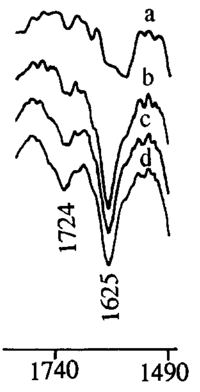

Fig. 3. In situ spectra of ethene hydroformylation on SAP rhodium catalyst; reaction temperature 393 K; total pressure 0.8 MPa; $C_2H_4/CO/H_2 = 0.5/1/1$ (v/v); Rh 0.04 mmol/g-$SiO_2$. (a) 1 min; (b) 3 min; (c) 10 min; (d) 20 min.

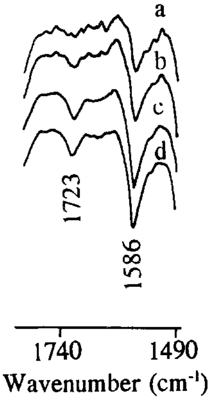

Fig. 4. In situ spectra of ethene hydroformylation on KCl-modified SAP rhodium catalyst; reaction temperature 373 K; total pressure 0.8 MPa; $C_2H_4/CO/H_2 = 0.5/1/1$ (v/v); Rh 0.04 mmol/g-$SiO_2$. (a) 1 min; (b) 5 min; (c) 15 min; (d) 25 min.

The peaks around 1400–1600 $cm^{-1}$ may be assigned to bridge-type propionate species, judging from the peak frequencies and peak separation. The changes in stretching frequency of the bridge-type propionate species were observed in the spectra, which appeared at ca. 1625 $cm^{-1}$ for non-modified SAP catalyst samples and at ca. 1586 $cm^{-1}$ for KCl-modified ones, as shown by figs. 3 and 4. The in situ IR experimental results also revealed that the peaks of acyl species at ca. 1625 $cm^{-1}$ for non-modified SAP catalyst and at 1586 $cm^{-1}$ for KCl-modified catalyst can be immediately detected during ethene hydroformylation and the intensity of these acyl species is stronger than that of aldehyde appearing at around 1700 $cm^{-1}$.

### 3.4. DEUTERIUM INVERSE ISOTOPE EFFECT IN ALDEHYDE FORMATION OVER SAP RHODIUM CATALYST

The effect of deuterium isotope on the rate of a hydrogenation reaction is often used to ascertain whether hydrogen is involved in the rate-determining step (r.d.s.) or not. It is generally accepted that the hydrogenolysis of acyl intermediate to form aldehyde product is the r.d.s. in olefin hydroformylation on homogeneous Rh complexes and heterogeneous supported Rh catalyst systems, as evidenced by noticeable inverse deuterium isotope effects observed in several experiments [19,29]. A series of investigations of olefin hydroformylation with substitution of $CO/D_2$ for $CO/H_2$ to study the isotope effects of deuterium on SAP rhodium catalysts have been carried out by us. Table 2 shows the results of hydroformylation of several olefins over SAP rhodium catalysts under $CO/D_2$ and $CO/H_2$ respectively. The reaction conversions and rates of aldehyde formation (TOF) in $CO/D_2$ atmosphere are about 1.3 times faster than that in $CO/H_2$, whereas this is not the case for the selectivity of *n*/*b* aldehyde. These results indicate

Table 2
$H_2/D_2$ isotope effect in olefin hydroformylation over SAP catalysts [a]

| Substrate | $C^D/C^H$ | $Y^D/Y^H$ | $n^D/n^H$ |
|---|---|---|---|
| 1-hexene | 1.36 | 1.31 | 1.01 |
| 1-heptene | 1.31 | 1.30 | 1.00 |
| 1-octene | 1.33 | 1.29 | 1.03 |

[a] $C$: conversion (%); $Y$: STY ($h^{-1}$); $n$: normal aldehyde (%); reaction condition: $T = 373$ K; feed-rate for liquid reactant 2.0 ml/h; Rh 0.04 mmol/g-$SiO_2$; $CO/H_2$ or $CO/D_2$ (v/v = 1); pressure 0.1 MPa; syngas flow-rate 10.0 ml/min.

that the aldehyde formation shows a noticeable inverse isotope effect, but no isotope effects are observed on the formation rates of normal aldehyde, in olefin hydroformylation over the SAP rhodium catalysts.

The steps of hydride migration, CO insertion and acyl hydrogenation are involved in the two possible mechanisms, namely the dissociative and the associative mechanism, proposed by Wilkinson et al. [15]. From the kinetic results of the deuterium isotope effect study it may be inferred that the r.d.s. involved in aldehyde formation is, most probably, related with hydrogen (e.g., hydride migration or acyl hydrogenolysis).

However, the evidence that the in situ IR bands of acyl species appeared very quickly and their peak intensity is stronger than that of propanal during ethene hydroformylation on SAP catalysts (figs. 3 and 4) strongly supports that the r.d.s. should be unlikely the step of hydride migration, but the acyl hydrogenolysis.

### 3.5. THE ROLE OF ALKALI METAL SALT

From the in situ IR spectroscopy data of ethene hydroformylation and the kinetic results of liquid-olefin hydroformylation over alkali metal salt modified SAP rhodium catalysts, it is expected that alkali metal salts in SAP rhodium catalysts may assist CO insertion into alkyl ligands and lower the potential energy of formation of acyl intermediates by stabilizing the acyl intermediate, as reflected by the changes in stretching frequency of the carbonyl species in in situ IR spectra, probably due to dipole–charge interaction and the bonding action between the carbonyl species or CO and the alkali metal cation. As a result, it is reasonable to deduce that the concentration of the acyl intermediate in the steady state may be increased with proper KCl content in the catalyst, in turn, leading to the enhancement in TOF and STY for aldehyde formation because of the mass transfer, although the hydrogenolysis of the acyl intermediate has been inferred to be the r.d.s. of hydroformylation.

In fact, the catalysts were prepared with addition of excessive ligand (L/Rh = 10, mol/mol) under the present experimental condition. However, it was found in our experiments that the hydroformylation TOF was decreased with almost no selectivity change in $n/b$ ratio when the L/Rh mole ratio was over 10.

Also, a few increments in $n/b$ ratio in the hydroformylation product were obtained on the salt modified SAP rhodium catalyst (fig. 2), in which the salt may serve as a highly hydrophilic electrolyte to increase the interfacial tension between the oleophobic catalyst surface and oleophilic substrate. These results seem to imply that the rapid reorientation of reactant molecules at the interface should occur at the temperatures investigated.

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