

Preparation of Rh-TPPTS complex intercalated layered double hydroxide and influences of host and guest compositions on its catalytic performances in hydroformylation reaction

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Based on the concept of intercalation chemistry of layered double hydroxides (LDHs), RhCl(CO)-(TPPTS)₂ (TPPTS: P(*m*-C₆H₄SO₃Na)₃) and TPPTS co-intercalated LDHs were successfully synthesized by *in situ* complexation method. Characterizations of structure and composition of composite materials by powder XRD, FT-IR, and ICP-AES techniques confirmed the supramolecular structures of the catalytic species intercalated LDHs. The correlation between catalytic performance of intercalated catalyst and the composition of both host layers and interlayer guest species was also investigated.

layered double hydroxides, hydroformylation, supported catalyst, RhCl(CO)(TPPTS)₂

Hydroformylation reaction, the addition of synthesis gas (CO and H₂) to alkenes, is one of the most important syngas-related reactions^[1]. Hydroformylation of alkenes performed by using transition metal catalysts is widely applied into petrochemical industry for the production of aldehydes (*ca.* 7 million tones per year)^[2]. Over the past few decades, development and application of immobilized hydroformylation catalysts have been attracting widespread interest^[3,4], since such catalysts can combine the high activity and selectivity of homogeneous catalysts with the long lifetime and ease of separation of heterogeneous catalysts^[5]. A large number of papers and patents concerning alkene hydroformylation reactions catalyzed by rhodium or other noble metal complexes supported on silica or other oxide supports have been published^[6,7], with some showing high performance.

Layered double hydroxides (LDHs) are a class of synthetic anionic clays, whose structures can be described as positively-charged brucite (Mg(OH)₂)-like layers with some divalent cations being replaced by trivalent ions. The charge is balanced by the intercalated anions in the hydrated interlayer regions. LDHs can be

represented by the general formula [M^{II}_{1-x}M^{III}_x(OH)₂]^{x+}(Aⁿ⁻)_{x/n}·yH₂O. Many divalent and trivalent cations (M^{II} and M^{III}, respectively) and the anion (Aⁿ⁻) can form LDHs structures, and the concentration of M^{II} cation^[8-10] may vary over a wide range, giving rise to a large class of isostructural functional materials. These layered solids have received considerable attention due to their many practical applications, such as ion-exchangeable absorbents^[11], molecular container^[12], medication^[13,14] and catalysts. There were some reports on intercalation of transition metal complexes in LDHs which have shown good catalytic activity. Examples include reusable OsO₄²⁻ on ion-exchangers for asymmetric dihydroxylation of olefins^[15], LDHs-host catalysts for stereoselective epoxidation^[16] and LDHs-

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WO_4^{2-} for mild oxidative bromination^[17].

In our previous work^[18], *trans*- $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ [TPPTS: trisodium salt of tri-(*m*-sulfophenyl)-phosphine] and TPPTS ligands were co-intercalated into zinc-aluminum-layered double hydroxides (ZnAl-LDHs) by *in situ* complexation method, and the catalytic performances of the resulting materials for 1-hexene hydroformylation were investigated.

Based on our previous work, the aim of this work is to investigate the influences of the composition of both host layers (M^{2+} species) and interlayer inorganic anions species on the catalytic behavior, and thus give a detailed understanding for the relationship between host-guest interactions and the catalytic performances.

1 Experimental

1.1 Reagents

TPPTS was provided by Sichuan University. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (Rh: 40 wt%) was purchased from General Research Institute of Nonferrous Metals. All the chemicals used in this synthesis were of analytical grade and without further purification. All solutions were prepared by using distilled and decarbonated water.

1.2 Synthesis of precursors

The ion-exchange precursors: $[\text{Zn}_2\text{Al}(\text{OH})_6](\text{NO}_3) \cdot 4\text{H}_2\text{O}$ ^[19], $[\text{Ni}_2\text{Al}(\text{OH})_6](\text{NO}_3) \cdot 4\text{H}_2\text{O}$ ^[20], $[\text{Zn}_2\text{Al}(\text{OH})_6](\text{Cl}) \cdot 4\text{H}_2\text{O}$ ^[21], $[\text{Zn}_2\text{Al}(\text{OH})_6](\text{SO}_4)_{0.5} \cdot 4\text{H}_2\text{O}$ ^[22] were synthesized by the literature procedure. TPPTS pre-intercalated LDHs precursor was prepared by ion exchange method, in which a mixture of precursor and the aqueous solution of TPPTS was heated at 80°C under nitrogen atmosphere for 72 h. The resulting precipitate was separated, washed with water and dried *in vacuo* at room temperature for 48 h.

1.3 Synthesis of Rh-TPPTS complex intercalated LDHs by *in-situ* complexation method

Rh-TPPTS complex intercalated LDHs were synthesized by *in-situ* complexation method^[18]. A solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in absolute ethanol (10 mL) was held at 78°C under carbon monoxide atmosphere for 50 min. A suspension of TPPTS pre-intercalated LDHs precursor in water (5 mL) was then added dropwise quickly. The mixture was held at 78°C for 90 min, after which absolute ethanol was added to cool the mixture. The resulting precipitate was separated, washed with absolute ethanol

and dried *in vacuo* at 60°C. The product is denoted as $\text{RhP}_2/\text{P/A-M}_2\text{Al-LDHs}$ ($\text{RhCl}(\text{CO})(\text{TPPTS})_2$ is denoted as RhP_2 , and TPPTS is denoted as P; A: NO_3^- , Cl^- , SO_4^{2-} ; M: Zn, Ni). The white TPPTS pre-intercalated LDHs precursors turned to pale yellow $\text{RhP}_2/\text{P/A-M}_2\text{Al-LDHs}$, which indicates the formation of the Rh-phosphine complex via *in situ* complexation.

1.4 Catalyst evaluation

Hydroformylation reaction of 1-hexene was conducted under 1.6 MPa of an equimolar CO and H_2 mixture at 100°C in a stainless steel autoclave for 6 h. The intercalated LDHs catalyst ($\text{Rh}/1\text{-hexene} = 4.0 \times 10^{-4}$), 1-hexene (1.0 mL), toluene (2.0 mL) and triethylamine (0.05 mL) were first transferred into the autoclave. The reaction system was purged with an equimolar CO and H_2 mixture and subsequently charged to the working pressure. When the reaction was completed, the reactor was allowed to cool to room temperature and depressurized. The solid catalyst was filtered off from the reaction mixture in air. The products of hydroformylation were analyzed by GC-MS.

1.5 Characterization

XRD measurements were performed on a Rigaku XRD-6000 diffractometer, using Cu K α radiation ($\lambda = 0.154184$ nm) at 40 kV, 30 mA, a scanning rate of 0.02°/s, with the 2θ range of 3° to 70°. FT-IR spectra were recorded using a Bruker Vector 22 spectrophotometer in the range of 4000 to 400 cm^{-1} with 2 cm^{-1} resolution. The standard KBr disk method (1 mg of sample in 100 mg of KBr) was used.

Elemental analysis was performed by ICP atomic emission spectroscopy (ICP-AES) on a Shimadzu ICPS-7500 instrument and the analyzed solutions were prepared by dissolving the sample in dilute HCl solution. The products of hydroformylation were separated and analyzed with programmed heating method by using a Shimadzu 2010 GC-MS instrument.

2 Results and discussion

2.1 Effect of varied M^{2+} species of host layers on catalytic performances

Two samples, $\text{RhP}_2/\text{P-Zn}_2\text{Al-LDHs}$ and $\text{RhP}_2/\text{P-Ni}_2\text{Al-LDHs}$, were prepared by the method of *in situ* complexation through varying the M^{2+} cation in the host layers. The structure and composition of the composite

materials were analyzed by powder XRD, FT-IR and ICP-AES. The catalytic performances of the intercalated catalysts as well as the correlation between the M^{2+} species of host layers and the catalytic performances were investigated.

The powder XRD patterns of $RhP_2/P-Zn_2Al-LDHs$ and $RhP_2/P-Ni_2Al-LDHs$ are shown in Figure 1. Table 1 lists the corresponding basal spacing and lattice parameters. The reflections of the materials show the characteristic features of LDHs^[24,25]. However, as is often the case^[26], several (*hkl*) reflections disappear or broaden. The basal spacing (d_{003}) of $RhP_2/P-Zn_2Al-LDHs$ and $RhP_2/P-Ni_2Al-LDHs$ is 1.579 and 1.595 nm, respectively (Table 1), which increases by 0.701 and 0.697 nm compared with their ion-exchange precursor $[Zn_2Al(OH)_6](NO_3) \cdot 4H_2O$ and $[Ni_2Al(OH)_6](NO_3) \cdot 4H_2O$, respectively. The expansion of the basal spacing resulted from the intercalation of bulky organic anions into the LDHs, indicating that the *in situ* complexation reaction occurred in the interlayer region of TPPTS pre-intercalated LDHs. Moreover, a decrease in the reflection intensity as well as increase in the peak width at half maximum were observed in the XRD pattern of $RhP_2/P-Ni_2Al-LDHs$ compared with that of $RhP_2/P-$

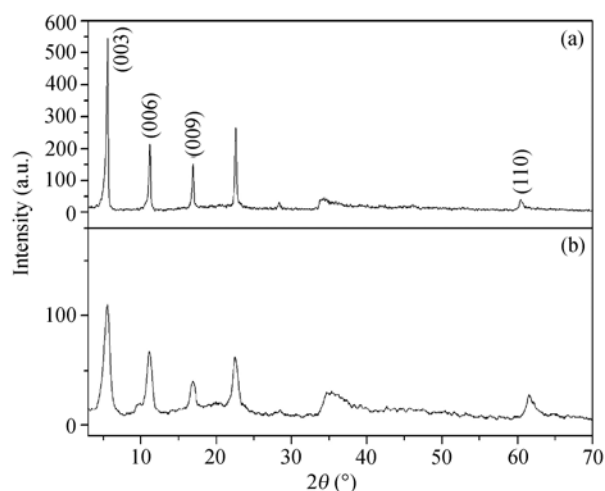


Figure 1 XRD patterns for (a) $RhP_2/P-Zn_2Al-LDHs$ and (b) $RhP_2/P-Ni_2Al-LDHs$.

Table 1 Lattice parameters of $RhP_2/P-Zn_2Al-LDHs$ and $RhP_2/P-Ni_2Al-LDHs$

Sample	$RhP_2/P-Zn_2Al-LDHs$	$RhP_2/P-Ni_2Al-LDHs$
d_{003} (nm)	1.579	1.595
d_{110} (nm)	0.153	0.151
Lattice parameter a (nm)	0.306	0.302
Lattice parameter c (nm)	4.737	4.785

$Zn_2Al-LDHs$, which indicates that the crystallinity of the latter is higher than that of the former.

The FT-IR spectra of the TPPTS, $RhCl(CO)(TPPTS)_2$ and their intercalation into the LDHs are presented in Figure 2. The spectra of TPPTS and $RhCl(CO)(TPPTS)_2$ (Figure 2(a) and (b)) are similar to those reported in ref. [26]. The bands at 1207/1196, 1040 and 628 cm^{-1} of TPPTS (Figure 2(a)) and $RhCl(CO)(TPPTS)_2$ (Figure 2(b)) can be attributed to the stretching vibrations ν_{oso} , ν_{so} and ν'_{so} , respectively. After intercalation reaction, these three bands of $RhP_2/P-Zn_2Al-LDHs$ moved towards lower frequency, observed at 1182, 1036 and 619 cm^{-1} (Figure 2(c)), respectively. The electrostatic force between the host layers and the sulfonate group of guest anions leads to the shift of the three bands to lower energy. On the other hand, the coordination of the oxygen atom in the sulfonate group decreases the force constant of the S–O bond and accordingly results in a shift of the S–O vibration band to lower frequency. This was previously reported in the FT-IR spectra of the intercalation of naphthalene-2,6-disulfonate^[27] and 9,10-anthraquinone-1,2-dihydroxy-3-sulfonate (Alizarin red S anion) in LDHs^[28]. Therefore, it can be concluded that the observed shifts of these bands result from the interaction between the sulfonate group of the interlayer organic anions and the host lattice. However, compared with $RhP_2/P-Zn_2Al-LDHs$, the stretching vibrations ν_{oso} , ν_{so} and ν'_{so} of $RhP_2/P-Ni_2Al-LDHs$ moved to much lower frequency: 1178, 1035 and 618 cm^{-1} (Figure 2(d)), respectively. This can be explained by the different electrostatic force between the host layers and TPPTS, which is related to the electronegativity of the divalent

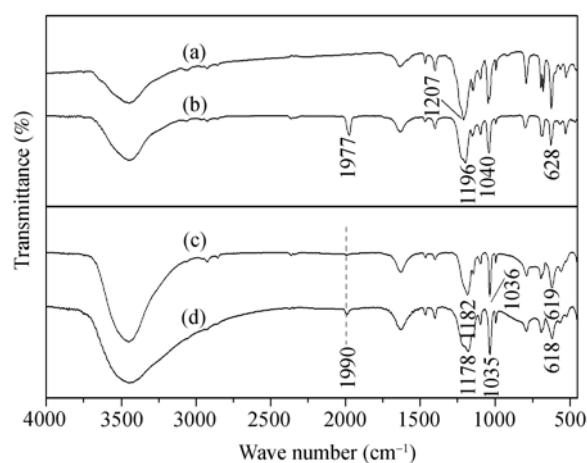


Figure 2 FT-IR spectra for (a) TPPTS, (b) $RhCl(CO)(TPPTS)_2$, (c) $RhP_2/P-Zn_2Al-LDHs$, and (d) $RhP_2/P-Ni_2Al-LDHs$.

metal^[29,30]. It is known that the values of electronegativity for zinc and nickel are 1.6 and 1.9^[31], respectively. The electron donating ability of M^{2+} in the host layers decreases with the increase of electronegativity, and thus leads to an increase in hydrogen bonding force between the M^{2+} and guest anions. Moreover, it also results in an increase in positive charge density around the neighbouring M^{3+} , which conduces to an increase in electrostatic attraction between M^{3+} and TPPTS. Consequently, the interactions between the host layers and TPPTS in $RhP_2/P-Ni_2Al$ -LDHs are stronger than those in $RhP_2/P-Zn_2Al$ -LDHs, accounting for the different basal spacing of the two samples shown in Table 1. The ν_{CO} stretching vibration of the pristine $RhCl(CO)-(TPPTS)_2$ (Figure 2(b)) appears at 1977 cm^{-1} , while this band in $RhP_2/P-Zn_2Al$ -LDHs and $RhP_2/P-Ni_2Al$ -LDHs (Figure 2(c) and (d)) is observed at 1990 cm^{-1} , with a shift of 13 cm^{-1} to higher frequency. This can be attributed to the interaction between the sulfonate group of TPPTS and the host layers. The frequencies of all the other main absorption bands of $RhP_2/P-Zn_2Al$ -LDHs and $RhP_2/P-Ni_2Al$ -LDHs (Figure 2(c) and (d)), such as the vibrations bands of phenyl ring centered at 1464 and 1398 cm^{-1} as well as C-H out-of-plane bending vibrations of phenyl ring at 788 and 692 cm^{-1} , closely resemble those in the spectra of pristine $RhCl(CO)(TPPTS)_2$ and TPPTS (Figure 2(a) and (b)).

According to elemental analysis data, the key elemental molar ratios in the intercalated LDHs are listed in Table 2. These data combining with XRD and FT-IR results confirm that $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ and TPPTS have co-intercalated into the interlayer region of LDHs by *in-situ* complexation method.

Table 3 depicts the catalytic performances for the two

catalyst systems, *viz.* the RhP₂/P-Zn₂Al-LDHs-catalyzed and RhP₂/P-Ni₂Al-LDHs-catalyzed systems. The effect of different M²⁺ in the intercalated samples on catalytic performances was studied in detail.

Table 2 Key elemental content and molar ratios in RhP₂/P-Zn₂Al-LDHs and RhP₂/P-Ni₂Al-LDHs

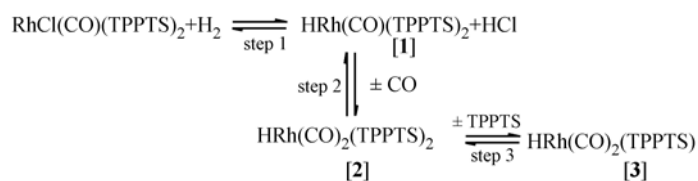
Sample	RhP ₂ /P-Zn ₂ Al-LDH	RhP ₂ /P-Ni ₂ Al-LDH
Molar ratio M/Al	2.0	1.6
Molar ratio P/Rh	18.4	16.2
Rh (%) (w/w)	0.36	0.31

It can be seen from Table 3 that the $\text{RhP}_2/\text{P-Zn}_2\text{Al-LDHs}$ catalyst displays higher activity than $\text{RhP}_2/\text{P-Ni}_2\text{Al-LDHs}$ with similar M^{2+}/Al and P/Rh molar ratios. The values of total conversation are 76% and 32 % and the turnover frequencies (TOF) towards aldehyde are 267 h^{-1} and 54 h^{-1} , respectively (Table 3). The generally accepted hydroformylation catalytic mechanism of $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ is shown in Scheme 1^[32,33]. The Rh-TPPTS complex undergoes an induction period before it turns to $\text{HRh}(\text{CO})_m\text{L}_n$ [$\text{L} = \text{TPPTS}$, m , $n = 1, 2, 3$] including active 16-electron complex, $\text{HRhCO}(\text{TPPTS})_2[1]$ and $\text{HRh}(\text{CO})_2(\text{TPPTS})[3]$ (Scheme 1) under the catalytic conditions. The structure of LDHs support is based on brucite-like layers in which $[\text{M}(\text{OH})_6]$ coordinating octahedra share all edges to form infinite sheets. As a basic support^[34,35], LDHs facilitate the formation of a rhodium hydride complex by removing the HCl formed (step 1 in Scheme 1). The basicity of LDHs support is comparable to that of $\text{M}(\text{OH})_2$, which is determined by the electronegativity of M^{2+} . Therefore, the $\text{RhP}_2/\text{P-Zn}_2\text{Al-LDHs}$ catalyst showed higher activity than the $\text{RhP}_2/\text{P-Ni}_2\text{Al-LDHs}$ one, due to the high basicity of $\text{Zn}_2\text{Al-LDHs}$ support. Similar observations were reported for oxida-

Table 3 Effect of different M^{2+} in $RhP_2/P-M_2Al-LDHs$ ^{a)} on its catalytic performances in hydroformylation ^{b)} for 1-hexene

Sample	Conversion (%)	TOF (h ⁻¹) (mol aldehyde · mol ⁻¹ Rh · h ⁻¹)	Aldehyde selectivity (%)	<i>n</i> / <i>i</i>
RhP ₂ /P-Zn ₂ Al-LDH	75.94	266.97	84.38	2.19
RhP ₂ /P-Ni ₂ Al-LDH	32.38	54.31	40.27	1.58

a) Rh/1-hexene= 4.0×10^{-4} ; b) reaction conditions: 1 mL of 1-hexene, 1.6 MPa, 100 °C, H₂/CO=1, 6 h reaction time.



Scheme 1 The equilibrium between $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ and catalytic active species.

tive bromination catalyzed by LDH-WO₄^[17], Heck arylation catalyzed by LDH-Pd(TPPTS)₂^[36] and asymmetric dihydroxylation catalyzed by LDH-OsO₄^[37].

Significant difference in product selectivity for the two intercalated catalysts was also observed. The selectivity towards aldehyde for RhP₂/P-Zn₂Al-LDHs and RhP₂/P-Ni₂Al-LDHs is 84% and 40%, and *n*/*i*-aldehyde ratio is 2.2 and 1.6, respectively. It has been concluded from the FT-IR analysis that the host-guest interaction in RhP₂/P-Ni₂Al-LDHs was stronger than that of RhP₂/P-Zn₂Al-LDHs. Therefore, it can be speculated that the strong host-guest interaction restricts the TPPTS-substitution reaction of HRh(CO)₂(TPPTS) (complex [3] in Scheme 1) to form the product of HRhCO(TPPTS)₂ (complex [1] in Scheme 1) that is an important catalytic active species for improving the selectivity to both aldehyde and *n*-aldehyde. As a result, the selectivity towards *n*-aldehyde and *iso*-aldehyde in the RhP₂/P-Ni₂Al-LDHs-catalyzed system is lower than that in the RhP₂/P-Zn₂Al-LDHs-catalyzed system.

2.2 Effect of guest inorganic anions species on catalytic performances

It has been reported that the rhodium catalyst system containing inorganic salt gives increased reaction activity and selectivity in the hydroformylation process under two-phase reaction conditions^[38]. Combined with the structural feature of LDHs, the inorganic anion species intercalated into LDHs varied in the samples of RhP₂/P/NO₃-Zn₂Al-LDHs, RhP₂/P/Cl-Zn₂Al-LDHs and RhP₂/P/SO₄-Zn₂Al-LDHs through changing the ion-exchange precursors. The structure and composition of the composite materials were detected by XRD, FT-IR and ICP-AES. The catalytic performances of the intercalated catalyst as well as the effect of co-intercalated inorganic anion were studied.

Figure 3 shows the powder XRD patterns of RhP₂/P/NO₃-Zn₂Al-LDHs, RhP₂/P/Cl-Zn₂Al-LDHs and RhP₂/P/SO₄-Zn₂Al-LDHs, and Table 4 lists the corresponding basal spacing and lattice parameters. The XRD patterns for the composite materials exhibit the characteristic

reflections of LDHs with a series of (00*l*) peaks, which are evidence for the layered character^[23,24]. After the intercalation of Rh-TPPTS complex, the interlayer distance (*d*₀₀₃) of RhP₂/P/NO₃-Zn₂Al-LDHs, RhP₂/P/Cl-Zn₂Al-LDHs and RhP₂/P/SO₄-Zn₂Al-LDHs increases to 1.571, 1.555 and 1.566 nm, which is larger than that of ion-exchange precursors [Zn₂Al(OH)₆](NO₃)·4H₂O, [Zn₂Al(OH)₆](Cl)·4H₂O, [Zn₂Al(OH)₆](SO₄)_{0.5}·4H₂O by 0.693, 0.785 and 0.496 nm, respectively (Table 4). The expansion of the basal spacing is due to the intercalation of Rh-TPPTS complex into the LDHs lamella. A significant decrease in the reflection intensity as well as increase in the peak width at half maximum are observed in XRD patterns of RhP₂/P/Cl-Zn₂Al-LDHs and RhP₂/P/SO₄-Zn₂Al-LDHs in comparison with those of RhP₂/P/NO₃-Zn₂Al-LDHs.

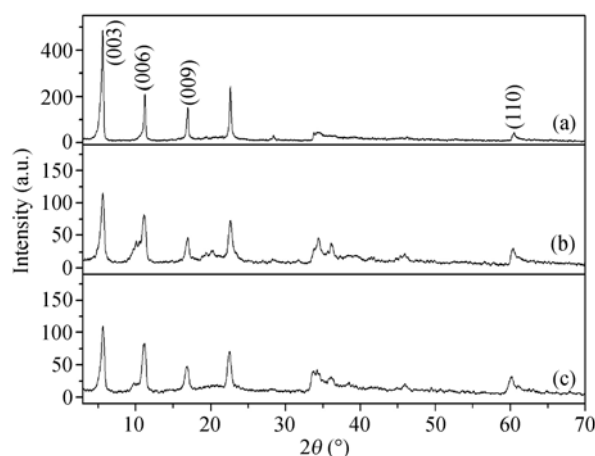


Figure 3 XRD patterns for (a) RhP₂/P/NO₃-Zn₂Al-LDHs, (b) RhP₂/P/Cl-Zn₂Al-LDHs, and (c) RhP₂/P/SO₄-Zn₂Al-LDHs.

Figure 4 displays the FT-IR spectra of RhP₂/P/NO₃-Zn₂Al-LDHs, RhP₂/P/Cl-Zn₂Al-LDHs and RhP₂/P/SO₄-Zn₂Al-LDHs. The bands of the three samples observed at around 1182, 1036 and 619 cm⁻¹ (Figure 4), respectively, can be attributed to the stretching vibrations ν_{oso} , ν_{so} and ν'_{so} , which move to lower frequency compared with those of TPPTS and RhCl(CO)(TPPTS)₂ (Figure 2(a) and (b)). This is due to the interactions between the

Table 4 Lattice parameters of intercalated materials

Sample	RhP ₂ /P/NO ₃ -Zn ₂ Al-LDHs	RhP ₂ /P/Cl-Zn ₂ Al-LDHs	RhP ₂ /P/SO ₄ -Zn ₂ Al-LDHs
<i>d</i> ₀₀₃ (nm)	1.571	1.555	1.566
<i>d</i> ₁₁₀ (nm)	0.153	0.153	0.153
Lattice parameter <i>a</i> (nm)	0.306	0.306	0.306
Lattice parameter <i>c</i> (nm)	4.713	4.665	4.698

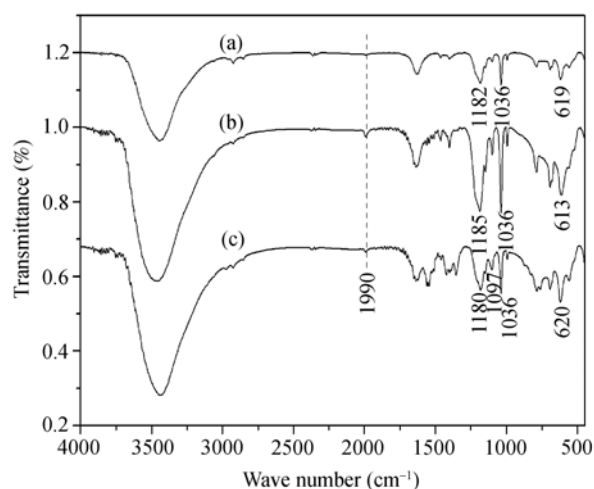


Figure 4 FT-IR spectra for (a) RhP₂/P/NO₃-Zn₂Al-LDHs, (b) RhP₂/P/Cl-Zn₂Al-LDHs, and (c) RhP₂/P/SO₄-Zn₂Al-LDHs.

sulfonate group of the interlayer RhCl(CO)(TPPTS)₂ or TPPTS and the host lattice. The ν_{CO} stretching vibration for the three samples appears at 1990 cm⁻¹, representing shifts to higher frequency compared with the pristine RhCl(CO)(TPPTS)₂ (Figure 2(b)). The frequencies of all the other main absorption bands for the three samples, such as the phenyl ring vibrations and the C–H out-of-plane bending vibrations of phenyl ring, closely resemble those of pristine RhCl(CO)(TPPTS)₂ and TPPTS (Figure 2(a) and (b)). There is also a subtle difference in their FT-IR spectra for the three samples. The band of RhP₂/P/SO₄-Zn₂Al-LDHs observed at 1097 cm⁻¹ is broader than the bands of the other two samples, due to the vibration ν_3 of the intercalated inorganic anion SO₄²⁻.

Table 5 lists the key elemental molar ratios and the rhodium content for RhP₂/P/NO₃-Zn₂Al-LDHs, RhP₂/P/Cl-Zn₂Al-LDHs and RhP₂/P/SO₄-Zn₂Al-LDHs based on

the elemental analysis data. The interlayer organic anions content can be determined from the value of Al/P molar ratio, and this value in RhP₂/P/SO₄-Zn₂Al-LDHs is much higher than the values in RhP₂/P/NO₃-Zn₂Al-LDHs and RhP₂/P/Cl-Zn₂Al-LDHs (Table 5), owing to their different ion-exchange precursors. Higher ratio of Al/P indicates higher content of interlayer SO₄²⁻ in RhP₂/P/SO₄-Zn₂Al-LDHs, which is in accordance with the result of FT-IR (Figure 4(c)). This is possibly related to the strong interaction between SO₄²⁻ and host layers and thus it is rather difficult for SO₄²⁻ to exchange with organic anions. Therefore, the content of interlayer organic anions in RhP₂/P/SO₄-Zn₂Al-LDHs is the lowest among the three samples. These data combining with XRD and FT-IR results confirm that RhCl(CO)(TPPTS)₂ and TPPTS are co-intercalated into the interlayer space of LDHs by *in-situ* complexation method.

Table 6 lists the catalytic results for the three catalyst systems studied. The effect of co-intercalated inorganic anions (NO₃⁻, Cl⁻ and SO₄²⁻ respectively) on catalytic performances was investigated.

Comparison of the catalytic performances reveals some difference in catalytic activity and selectivity of the intercalated catalyst samples. Firstly, RhP₂/P/Cl-Zn₂Al-LDH exhibits a lower total conversion than RhP₂/P/NO₃-Zn₂Al-LDHs (Table 6). The existence of interlayer Cl⁻ does not facilitate the formation of complex HRhCO(TPPTS)₂ ([1] in Scheme 1). On the other hand, the loaded weight of rhodium complex in RhP₂/P/Cl-Zn₂Al-LDHs is lower than that of RhP₂/P/NO₃-Zn₂Al-LDHs (Table 5), which is another factor for the difference in catalytic activity. As listed in Table 5, the loaded weight of rhodium complex in RhP₂/P/SO₄-Zn₂Al-LDHs is the lowest among the three samples,

Table 5 Key elemental content and molar ratios in intercalated materials

Sample	RhP ₂ /P/NO ₃ -Zn ₂ Al-LDH	RhP ₂ /P/Cl-Zn ₂ Al-LDH	RhP ₂ /P/SO ₄ -Zn ₂ Al-LDH
Molar ratio Zn/Al	2.0	2.1	2.1
Molar ratio P/Rh	12.7	10.0	11.8
Molar ratio Al/P	3.3	3.3	6.3
Rh (w/w)(%)	0.45	0.37	0.27

Table 6 Effect of co-intercalated inorganic anions in LDHs^{a)} catalyst in hydroformylation^{b)} for 1-hexene

Samples	Total Conversion (%)	TOF (h ⁻¹) (mol aldehyde · mol ⁻¹ Rh · h ⁻¹)	<i>n</i> / <i>i</i>
RhP ₂ /P/NO ₃ -Zn ₂ Al-LDHs	85.88	292.44	2.29
RhP ₂ /P/Cl-Zn ₂ Al-LDHs	76.21	171.49	2.45
RhP ₂ /P/SO ₄ -Zn ₂ Al-LDHs	41.08	133.46	3.18

a) Rh/1-hexene=4.0×10⁻⁴; b) reaction conditions: 1 mL of 1-hexene, 1.6 MPa, 100°C, H₂/CO=1, 6 h reaction time.

resulting in the lowest activity.

Secondly, $\text{RhP}_2/\text{P}/\text{SO}_4\text{-Zn}_2\text{Al-LDH}$ shows a higher selectivity towards *n*-aldehyde than the other two catalysts (Table 6). The Rh content (Rh%, in Table 5) of $\text{RhP}_2/\text{P}/\text{SO}_4\text{-Zn}_2\text{Al-LDHs}$ is the lowest among the three catalyst samples, therefore, it is advantageous to exert the steric factor of LDHs in this catalyst. The less confined interlayer region (lower content of complex and more space available) of this sample favors the formation of normal alkyl intermediate, which converts to *n*-aldehyde in the end. Consequently, the selectivity towards *n*-aldehyde is improved in the system catalyzed by $\text{RhP}_2/\text{P}/\text{SO}_4\text{-Zn}_2\text{Al-LDHs}$.

Finally, as shown in Table 6, the value of TOF towards aldehyde increases with the increase of rhodium complex loading (Rh%) of the three intercalated catalysts, and $\text{RhP}_2/\text{P}/\text{NO}_3\text{-Zn}_2\text{Al-LDHs}$ shows the highest TOF value (292 h^{-1}). Except the influence of rhodium complex loading, the different co-intercalated inorganic anions may impose some assistant catalysis. Further study is under investigation.

3 Conclusion

$\text{RhCl}(\text{CO})(\text{TPPTS})_2$ and TPPTS co-intercalated LDHs

were successfully synthesized by *in situ* complexation method. The influences of the composition of both host layers (M^{2+} species) and interlayer inorganic anions species on the catalytic behavior of the intercalated catalysts were investigated, and the relationship between host-guest interactions and the catalytic performances was revealed.

It was found that the higher the electronegativity of M^{2+} in host layers, the lower the basicity of LDHs host lattices, and the stronger the host-guest interaction. Higher electronegativity of M^{2+} leads to the decrease in both catalytic activity and selectivity towards aldehyde.

The co-intercalated inorganic anions (SO_4^{2-} , Cl^- , NO_3^-) in LDHs exhibit remarkable influence on catalytic activity. The rhodium complex loading of $\text{RhP}_2/\text{P}/\text{SO}_4\text{-Zn}_2\text{Al-LDHs}$ is the lowest among the three intercalated catalyst samples and thus leads to the lowest total conversion (41%). Since the existence of co-intercalated Cl^- does not facilitate the formation of an active rhodium complex intermediately, the total conversion is low in the system catalyzed by $\text{RhP}_2/\text{P}/\text{Cl-Zn}_2\text{Al-LDHs}$ (76%). However, the $\text{RhP}_2/\text{P}/\text{NO}_3\text{-Zn}_2\text{Al-LDH}$ shows the highest catalytic activity among the three samples (with total conversion of 86%) because of its highest rhodium complex loading.

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