Rh-TPPTS Intercalated Layered Double Hydroxides as Hydroformylation Catalyst

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Trans-RhCl(CO)(TPPTS)2 [TPPTS, trisodium salt of tri-(m-sulfophenyl)-phosphine] and TPPTS ligands have been cointercalated into zinc–aluminum-layered double hydroxides (ZnAl-LDHs) by in situ complexation, and the catalytic performances of the resulting materials for 1-hexene hydroformylation have been investigated. The intercalated materials were characterized by means of XRD, FTIR, ICP, and 31P MAS NMR. The rhodium complex and TPPTS ligands coexist in the interlayer galleries of LDH (denoted as RhP2-P-ZnAl-LDH, where n denotes as the molar ratio Zn/Al), with an interlayer spacing of ca. 1.58 nm. Compared with the catalytic properties of the corresponding water-oil biphasic catalyst under similar reaction conditions, RhP2-P-Zn3Al-LDH showed better reusability and activity. Furthermore, compared with a related material prepared by ion exchange, the RhP2-P-ZnAl-LDH showed better activity and selectivity towards aldehyde. The influence of the Zn/Al molar ratio in RhP2-P-ZnAl-LDH has also been studied, and it was found that higher selectivity to aldehydes and lower activity were obtained with increasing Zn/Al molar ratio. © 2007 American Institute of Chemical Engineers AIChE J, 53: 2916–2924, 2007

Keywords: trans-RhCl(CO)(TPPTS)2, layered double hydroxide, intercalation, hydroformylation, in situ complexation

Introduction

Hydroformylation, the addition of synthesis gas (CO and H2) to alkenes, is one of the most important syngas-related reactions.1 The hydroformylation reaction was first discovered using a heterogeneous Fischer-Tropsch catalyst.2 As one of the mildest and cleanest methods to produce aldehydes, it is widely applied in the petrochemical industry. All current commercial processes are based on homogeneous catalysts, mostly using rhodium. Over the past few decades, however, development and application of immobilized homogeneous catalysts have been attracting widespread interest,3–5 since such catalysts can combine the high activity and selectivity of homogeneous catalysts with the long lifetime and ease of separation of heterogeneous catalysts.6 A large number of papers and patents concerning alkene hydroformylation catalyzed by rhodium or other noble metal complexes supported on silica or other oxide supports have been published7,8 and, moreover, the encapsulation of such complexes in microporous and mesoporous supports,9 construction through a “ship-in-the-bottle” process in zeolites,10 and entrapment in sol-gel structures11 or “host-guest” structures12 have also...
been studied. It has been reported that some of these catalysts are highly effective hydroformylation catalysts.

Layered double hydroxides (LDHs) are a class of synthetic anionic clays whose structure is based on brucite (Mg(OH)2)-like layers in which some of the divalent cations have been replaced by trivalent ions giving positively-charged sheets.11-15 This charge is balanced by intercalation of anions in the hydrated interlayer regions. LDHs can be represented by the general formula [M2n−2n+1(MIII(OH)2)n+1]+(A−)x+y·2n+1H2O. The identities of the di- and trivalent cations (MII and MIII, respectively) and the interlayer anion (A−) together with the value of the stoichiometric coefficient (x) may be varied over a wide range, giving rise to a large class of isostructural materials. These layered solids have received considerable attention because of their many practical applications, including as nanocomposite materials,16 functional materials,17 and catalysts.13,18,19 One attractive feature of such materials is that they serve as a template for the formation of supramolecular structures,20 and many new species can be assembled by reaction of guest compounds in the LDH matrices.13,17 There have been some reports of intercalation of transition metal complexes in LDHs giving materials with expanded interlayer spacing, which have shown good catalytic activity. Examples include dioxomolybdenum (VI) complexes,21 cobalt (II) macrocyclic complexes,22 and manganese (III) complexes of Schiff base ligands.23 In other cases, catalytic activity was observed with no expansion of interlayer spacing, suggesting that the catalytically active anion was adsorbed on edge sites as in the case of WO42–18 or PdCl42–.24

In our previous work, the intercalation of trans-RhCl(CO)(TPPTS)2 [TPPTS: trisodium salt of tri-(n-sulfophenyl)phosphine, P(m-C6H4SO3Na)3] into zinc–aluminum-layered double hydroxides (ZnAl-LDHs) was performed by the method of ion-exchange, and the resulting composite material was structurally characterized.25 To the best of our knowledge, except for this work, there has been only one other reported attempt to immobilize a water soluble phosphine transition metal complex on an LDH viz. reaction of cis-Pd(TPPPTS)2Cl2 and Mg-Al-Cl-LDH afforded a material with unchanged interlayer spacing, indicating that the palladium complex was immobilized on the edge of the crystallites.26 At the start of the work reported here, we studied the catalytic performance of trans-RhCl(CO)(TPPTS)2 intercalated LDH in hydroformylation, but found that its catalytic properties were somewhat disappointing. As a result, the aim of this work is to prepare heterogenized rhodium complex catalysts based on composites of trans-RhCl(CO)(TPPTS)2 and intercalated ZnAl-LDHs with improved catalytic performance in hydroformylation. In particular, trans-RhCl(CO)(TPPTS)2 has been intercalated into ZnAl-LDHs in the presence of free TPPTS as the cointercalated component (to give materials denoted as RhP2−P-Zn2Al-LDH, n = 2, 3, and 4) by a method of in situ complexation. The catalytic performance of the new cointercalated material was compared with that of the corresponding biphasic catalyst system under similar reaction conditions, in which trans-RhCl(CO)(TPPTS)2 and TPPTS were untethered, and trans-RhCl(CO)(TPPTS)2 intercalated ZnAl-LDH prepared via ion-exchange. Therefore, this work provides a new Rh-phosphine complex-inorganic layered material with prospective application.

**Experimental Section**

**Catalyst preparation**

*Synthesis of Trans-RhCl(CO)(TPPTS)2.* TPPTS was prepared according to a standard literature procedure.27 Trans-RhCl(CO)(TPPTS)2 was prepared as a pale yellow powder according to the procedure described in a Chinese patent25,28 and characterized by microanalysis; found (calculated) wt.%: P 4.67 (4.76), S 15.04 (14.74), Rh 7.58 (7.91); P/Rh 1.9 (2.0), S/P 2.9 (3.0).

*Preparation of Trans-RhCl(CO)(TPPTS)2 Intercalated ZnAl-LDHs. Ion-Exchange Method.* The precursor [Zn5Al3(OH)8(NO3)4H2O, (denoted as NO3-Zn3Al-LDH) was synthesized by a literature procedure.29 Intercalation of trans-RhCl(CO) (TPPTS)2 into LDH was carried out by the method of ion-exchange as reported previously.25 The sample is denoted as RhP2−Zn3Al-LDH.

*In Situ Complexation Method.* A TPPTS preintercalated ZnAl-LDH precursor (denoted as TPPTS-Zn3Al-LDH) was first prepared by the method of ion exchange, in which a mixture of the precursor NO3-Zn3Al-LDH (5.00 g, 1.80 mmol) and an aqueous solution of TPPTS (1.02 g, 1.80 mmol) was heated at 80°C under a nitrogen atmosphere for 72 h. A solution of RhCl3·3H2O (0.02 g, 6.90 × 10−2 mmol) in pure ethanol (10 ml) was held at 78°C under a carbon monoxide atmosphere for 50 min. A suspension of TPPTS-Zn3Al-LDH (1.00 g, 0.42 mmol) in distilled, deionized water (5 ml) was then added dropwise quickly. The mixture was held at 78°C for 40 min, after which pure ethanol was added to cool the mixture. The resulting precipitate was separated, washed with pure ethanol, and dried in vacuo at 60°C. The product is denoted as RhP2−P-Zn3Al-LDH. Other intercalates with different Zn/Al molar ratios were obtained by the same method (denoted as RhP2−P-Zn2Al-LDH and RhP2−P-Zn4Al-LDH, respectively). It was found that the color of the composite material changed from white in the case of the precursor (TPPTS-ZnAl-LDH, n = 2, 3, 4) to pale yellow in the cases of the resulting RhP2−P-ZnAl-LDH (n = 2, 3, 4), indicating the formation of the Rh-phosphine complex via in situ complexation.

**Characterization**

XRD measurements were performed on a Rigaku XRD-6000 diffractometer, using Cu Kα radiation (λ = 0.154 nm) at 40 kV, 30 mA, a scanning rate of 0.02 °/s, in the 2θ range 3° to 70°.

FTIR spectra were recorded using a Bruker Vector22 spectrophotometer in the range 4000–400 cm−1 with 2 cm−1 resolution. The standard KBr disk method (1 mg of sample in 100 mg of KBr) was used.

31P MAS NMR spectra were recorded on a Bruker AV300 spectrometer operating at a frequency of 121.497 MHz for 31P at a spinning rate of −8000 Hz with a 10 s pulse delay.

Elemental analysis was performed by ICP emission spectroscopy on a Shimadzu ICP-7500 instrument using solutions prepared by dissolving the samples in dilute HCl.

Thermogravimetric analysis and differential thermal analysis (TG/DTA) were measured in air using a PCT-1A thermal analysis system with a heating rate of 10°C/min.
Catalytic testing

Hydroformylation of 1-hexene was conducted under 1.6 MPa of an equimolar CO and H₂ mixture at 100°C in a stainless steel autoclave with a magnetic stirrer. The rhodium-containing catalyst (Rh/1-hexene = 4.0 × 10⁻⁴), 1-hexene (1.5 ml), toluene (3 ml), and triethylamine (0.05 ml) were first transferred to the autoclave. The reaction system was purged with the CO-H₂ mixture and subsequently charged to the working pressure. When a reaction cycle was completed, the reactor was allowed to cool to room temperature and depressurized. The solid catalyst was reclaimed in a sealed tube by centrifugal separation for 3 min and the cycle repeated. The products of hydroformylation were analyzed by GC-MS using a Shimadzu 2010 instrument.

Results and Discussion

Structure of the catalysts and their precursors

The powder XRD patterns of NO₃-Zn₃Al-LDH, (b) RhP₂-Zn₃Al-LDH, (c) TPPTS-Zn₃Al-LDH, (d) RhP₂-P-Zn₂Al-LDH, (e) RhP₂-P-Zn₃Al-LDH, and (f) RhP₂-P-Zn₄Al-LDH are shown in Figure 1. In each case, the reflections can be indexed to a hexagonal lattice with R-3m rhombohedral symmetry, commonly used for the description of LDH structures. However, as is often the case, several of the (hkl) reflections disappear or broaden in the samples prepared by the method of both ion-exchange and in situ complexation. The NO₃-Zn₃Al-LDH precursor has an XRD pattern (Figure 1a) similar to those reported previously, with a basal spacing (d₀₀₃) of 0.88 nm (Table 1). After reaction with trans-RhCl(CO)(TPPTS)₂ by the method of ion exchange, the basal reflection in the XRD pattern of RhP₂-Zn₃Al-LDH (Figure 1b) was observed at 4.96 nm, corresponding to an expanded basal spacing of 1.78 nm (Table 1). The XRD pattern of the precursor TPPTS-Zn₃Al-LDH (Figure 1c) indicates that the material has a basal spacing of 1.63 nm. After the in situ complexation reaction however, the 003 reflections of RhP₂-P-Zn₂Al-LDH, RhP₂-P-Zn₃Al-LDH, and RhP₂-P-Zn₄Al-LDH appear at 5.60, 5.64, and 5.66 nm, with the corresponding basal spacings (d₀₀₃) of 1.57, 1.58 and 1.56 nm, respectively, representing a contraction of the interlayer distance compared with the precursor. This is rather interesting and is consistent with the occurrence of a chemical reaction and the reorientation of the interlayer guests. A significant decrease in the reflection intensity as well as increase in the peak width at half height were observed as the Zn/Al ratio in RhP₂-P-ZnᵣAl-LDH increased from r = 1.9 to 2.6 to 3.9 (Figures 1d–f). A small amount of an impurity phase was also found in RhP₂-P-Zn₄Al-LDH. The basal spacing of the material prepared by ion-exchange is much larger than that of the materials prepared by in situ complexation (1.78 and 1.56–1.58 nm, respectively), which suggests that different spatial orientation of the interlayer anions are involved. This will be further discussed in the ³¹P MAS NMR section below.

The FTIR spectra of TPPTS, trans-RhCl(CO)(TPPTS)₂, and their intercalates in the LDHs are shown in Figure 2. The spectra of TPPTS and trans-RhCl(CO)(TPPTS)₂ (Figures 2a and b) are similar to those reported in the literature. In the case of the intercalated materials, the broad bands at around 3443 cm⁻¹ (Figures 2c–g) can be attributed to O-H stretching vibrations of surface and interlayer water molecules, which are found at lower frequency in LDHs compared with the O-H stretching vibrations of free water at 3600 cm⁻¹. This suggests the presence of hydrogen bonding between interlayer water and the guest anions as well as the layer hydroxide groups. The bands at 1196, 1040, and 628 cm⁻¹ of TPPTS (Figure 2a) and trans-RhCl(CO)(TPPTS)₂ (Figure 2b) can be attributed to the stretching

Table 1. XRD Data and Lattice Parameters of NO₃-Zn₃Al-LDH and the Intercalated Materials

<table>
<thead>
<tr>
<th></th>
<th>NO₃-Zn₃Al-LDH</th>
<th>RhP₂-Zn₃Al-LDH</th>
<th>TPPTS-Zn₃Al-LDH</th>
<th>RhP₂-P-Zn₂Al-LDH</th>
<th>RhP₂-P-Zn₃Al-LDH</th>
<th>RhP₂-P-Zn₄Al-LDH</th>
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<tbody>
<tr>
<td>d₀₀₃/nm</td>
<td>0.88</td>
<td>1.78</td>
<td>1.63</td>
<td>1.57</td>
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<td>1.56</td>
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<tr>
<td>d₀₀₆/nm</td>
<td>0.44</td>
<td>0.90</td>
<td>0.80</td>
<td>0.78</td>
<td>0.79</td>
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<tr>
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<td>0.53</td>
<td>0.52</td>
<td>0.52</td>
<td>0.53</td>
</tr>
<tr>
<td>d₁₁₀/nm</td>
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<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Lattice parameter a/nm</td>
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<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Lattice parameter c/nm</td>
<td>2.64</td>
<td>5.34</td>
<td>4.89</td>
<td>4.71</td>
<td>4.74</td>
<td>4.68</td>
</tr>
</tbody>
</table>
vibrations $\nu_{o-o}$, $\nu_{s-o}$, and $\nu_{as}$, respectively. After intercalation into the LDH host, these three bands move to lower frequency, being observed at 1184, 1036, and 615 cm$^{-1}$ (Figures 2c–g), respectively. It is known that the coordination of the oxygen atom in the sulfonate group decreases the force constant in the $S$–O bond and accordingly results in a shift of the $S$–O vibration band to lower frequency$^{36}$, this has been previously reported in the FTIR spectra of the intercalates of naphthalene-2,6-disulfonate$^{37,38}$ and 9,10-anthraquinone-1,2-dihydroxy-3-sulfonate (Alizarin red S anion) in LDHs$^{39}$. Therefore, it can be concluded that the observed shift of these bands results from the interaction between the oxygen atom in the sulfonate group of the interlayer trans-RhCl(CO)(TPPTS)$_2$, or TPPTS and the host lattice. The $\nu_{C=O}$ stretching vibration of the pristine trans-RhCl(CO)(TPPTS)$_2$ (Figure 2b) appears at 1977 cm$^{-1}$, while this band in RhP$_2$-Zn$_3$Al-LDH (Figure 2c) and RhP$_2$-Zn$_3$Al-LDH (Figures 2e–g) was observed at 1996 and 1990 cm$^{-1}$, respectively, representing shifts of 19 and 13 cm$^{-1}$ to higher frequency compared with the free complex. The frequencies of all the other main absorption bands of RhP$_2$-Zn$_3$Al-LDH (Figure 2c) and RhP$_2$-P-Zn$_3$Al-LDH (Figures 2e–g), such as the bands centered at 1466 and 1400 cm$^{-1}$ corresponding to phenyl ring vibrations and at 797 and 690 cm$^{-1}$ attributed to C–H out-of-plane bending vibrations of phenyl rings, closely resemble those in the spectra of both free trans-RhCl(CO)(TPPTS)$_2$ (Figure 2b) and TPPTS (Figure 2a). These data confirm that trans-RhCl(CO)(TPPTS)$_2$ can be intercalated between the layers of LDHs by both ion-exchange and in situ complexation methods.

Figure 3 shows the $^{31}$P MAS NMR spectra of pristine TPPTS (Figure 3a), trans-RhCl(CO)(TPPTS)$_2$ (Figure 3b), the ion-exchange product RhP$_2$-Zn$_3$Al-LDH (Figure 3c), the TPPTS intercalated LDH precursor TPPTS-Zn$_3$Al-LDH (Figure 3d), and the in situ complexation product RhP$_2$-P-Zn$_3$Al-LDH (Figure 3e). The spectra of the pristine TPPTS (Figure 3a) and trans-RhCl(CO)(TPPTS)$_2$ (Figure 3b) show resonances at $-5.5$ and $32.3$ ppm, respectively, which compare well with the literature values of $-5.2$ ppm for TPPTS and $32.5$ ppm for trans-RhCl(CO)(TPPTS)$_2$. In the case of RhP$_2$-Zn$_3$Al-LDH obtained by ion-exchange (Figure 3c), the broad signal at about $30.5$ ppm can be assigned to the trans-RhCl(CO)(TPPTS)$_2$ in the interlayer galleries of the LDHs. Comparison of Figures 3a and d indicates that the $^{31}$P resonance shifts from $-5.5$ ppm for free TPPTS (Figure 3a) to $-20.2$ ppm for its intercalated composite with LDH (Figure 3d). To determine whether this remarkable shift is indicative of decomposition of TPPTS during the intercalation process, a sample of TPPTS-Zn$_3$Al-LDH was subsequently stirred with an aqueous solution of sodium carbonate heated at 40°C under a nitrogen atmosphere for 24 h. Since carbonate anions have a very strong affinity for LDH layers and would be expected to displace the interlayer guest anions in TPPTS-Zn$_3$Al-LDH. After filtration of the mixture, the $^{31}$P NMR spectrum of the filtrate showed an intense peak at $-5.9$ ppm, characteristic of TPPTS, together with a weak peak at 34.0 ppm, which is indicative of a small amount of TPPTS oxide, with no peak in the region around $-20$ ppm. Since the TPPTS was recovered essentially unchanged, the large difference in TPPTS chemical shift before and after intercalation is therefore a result of the host-guest interactions in the intercalate, rather than decomposition. The additional weak resonance at $-7.2$ ppm in Figure 3d may be attributed to a small amount of TPPTS adsorbed on the surface of LDH. As for the intercalated material RhP$_2$-P-Zn$_3$Al-LDH obtained by in situ complexation (Figure 3e), in addition to the two resonances at $-20.6$ and $-7.2$ ppm corresponding to intercalated and surface adsorbed TPPTS, respectively, another resonance was observed at 24.0 ppm, which can be assigned to the chemical shift of trans-RhCl(CO)(TPPTS)$_2$. This indicates that trans-RhCl(CO)(TPPTS)$_2$ is formed in the interlayer gallery of the precursor LDH (TPPTS-Zn$_3$Al-LDH) via in situ complexation, resulting in cointercalation of residual TPPTS and the rhodium complex. The difference between the $^{31}$P chemical shifts of the in situ complexation product (24.0 ppm) and the ion-exchange product (30.5 ppm) is indicative of different...
interlayer micro-environments of the phosphorus atom in the two complex-LDH composites, which can be related to the different spatial orientations of the interlayer anions. This is in consistent with the results of XRD, in which two different $d_{003}$ values were obtained.

On the basis of elemental analysis data, key elemental molar ratios in trans-RhCl(CO)(TPPTS)$_2$ and the intercalated materials are listed in Table 2. It can be seen that the Zn/Al molar ratios of the intercalated materials are close to the value expected. The P/Rh molar ratio of RhP$_2$-Zn$_3$Al-LDH prepared by ion-exchange is the same as that of pristine trans-RhCl(CO)(TPPTS)$_2$, while this value in RhP$_2$-P-Zn$_n$Al-LDH prepared by in-situ complexation is much higher. This is in accordance with the cointercalation of TPPTS and trans-RhCl(CO)(TPPTS)$_2$, which has been demonstrated by $^{31}$P MAS NMR. The P/Rh molar ratios in RhP$_2$-P-Zn$_n$Al-LDH are close to each other. The Rh loading in RhP$_2$-P-Zn$_n$Al-LDH is much higher than that in RhP$_2$-P-Zn$_n$Al-LDH, as a result of the presence of cointercalated TPPTS in the case of RhP$_2$-P-Zn$_n$Al-LDH. The difference in Rh content of the samples prepared by in situ complexation will be discussed in the next section.

The TG/DTA curves for RhP$_2$-P-Zn$_3$Al-LDH are shown in Figure 4 to study the thermal stability of the new catalyst. The thermal decomposition of RhP$_2$-P-Zn$_3$Al-LDH is characterized by four steps (Figure 4): the first loss event (50–150 °C) corresponds to the dehydration of both the surface and interlayer water molecules with an endothermic peak at 100 °C in the DTA curve; the second event (150–285 °C) is due to the decomposition of the interlayer anions, and the corresponding endothermic peak is observed at 275 °C; the third (285–460 °C) is a consequence of dehydroxylation of the brucite-like layers and continued decomposition of interlayer anions; the fourth stage (460–580 °C) is attributed to the further decomposition and combustion of interlayer materials with a strong exothermic peak at 540 °C. The thermal decomposition process of RhP$_2$-P-Zn$_3$Al-LDH in this work is similar to that of trans-RhCl(CO)(TPPTS)$_2$ intercalated LDH materials in our previous report$^{25}$ except that the fourth loss event extends to a higher temperature (580 °C). This might be related to the difference in both component and spatial orientations of the interlayer anions.

**Catalytic performance in hydroformylation of 1-hexene and catalysis mechanism**

Figure 5 depicts the catalytic results for four consecutive 10 h reaction cycles for the three catalyst systems studied,

Table 2. Key Elemental Molar Ratios in Trans-RhCl(CO)(TPPTS)$_2$ and the Intercalated Materials

<table>
<thead>
<tr>
<th>Sample</th>
<th>Trans-RhCl (CO)(TPPTS)$_2$</th>
<th>RhP$_2$-Zn$_3$Al-LDH</th>
<th>TPPTS-Zn$_3$Al-LDH</th>
<th>RhP$_2$-P-Zn$_2$Al-LDH</th>
<th>RhP$_2$-P-Zn$_3$Al-LDH</th>
<th>RhP$_2$-P-Zn$_4$Al-LDH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar ratio Zn/Al</td>
<td>2.4</td>
<td>2.4</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
<td>3.9</td>
</tr>
<tr>
<td>Molar ratio P/Rh</td>
<td>1.9</td>
<td>1.9</td>
<td>–</td>
<td>7.8</td>
<td>7.8</td>
<td>7.3</td>
</tr>
<tr>
<td>Rh (w/w) (%)</td>
<td>7.58</td>
<td>3.44</td>
<td>–</td>
<td>0.90</td>
<td>0.48</td>
<td>0.60</td>
</tr>
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</table>

Figure 5. Activity (A) and selectivity (B) of (a) RhP$_2$-P-Zn$_3$Al-LDH, (b) corresponding biphasic system (RhP$_2$ and TPPTS)$_2$, and (c) RhP$_2$-Zn$_3$Al-LDH catalyst$^*$ in hydroformylation$^*$ for 1-hexene.

$^*$Rh/1-hexene = 4.0 × 10$^{-4}$; $^*$TOF: mol aldehyde·mol$^{-1}$Rh·h$^{-1}$; $^*$Reaction conditions: 1.5 ml of 1-hexene, 1.6 MPa, 100 °C, H$_2$/CO = 1, 10 h per cycle.
The catalytic performance of RhP₂-P-Zn₃Al-LDH prepared by the new method of in situ complexation, in which free TPPTS ligands are intercalated into LDH (P/Rh molar ratio: 7:8), is shown in Figure 5a. In the four consecutive cycles, the RhP₂-P-Zn₃Al-LDH catalyst displayed high selectivity towards aldehydes of 70–80%, low selectivity for 2-hexene of around 20–30%, and n/i-aldehyde ratios of 2.6–3.0; moreover, the activity toward aldehyde formation of RhP₂-P-Zn₃Al-LDH was rather high [Figure 5Aa, turnover frequency (TOF) = 80–150 h⁻¹]. Based on the elemental analysis data, the Rh loading for the sample of RhP₂-P-Zn₃Al-LDH after 4 cycles used is 0.44% (w/w). Compared with the Rh content before use (0.48%, Table 2), the loss of Rh in this catalyst after 4 cycles is 8.3%.

For comparative purposes, a mixture of trans-RhCl(CO)(TPPTS)₂ and TPPTS (with the same P/Rh molar ratio as that in RhP₂-P-Zn₃Al-LDH) in a water-oil biphasic catalytic system was also studied. Compared with hydroformylation over RhP₂-P-Zn₃Al-LDH, the catalyst in the water-oil biphasic catalytic system exhibited lower total conversion (10–26%). Furthermore, the value of TOF towards aldehyde of around 20–25 h⁻¹ in this system was much lower than that in the RhP₂-P-Zn₃Al-LDH system, although the value of n/i-aldehyde ratio (3.5–5.7) was higher than that for RhP₂-P-Zn₃Al-LDH.

Comparison of the catalytic performance of RhP₂-P-Zn₃Al-LDH and the corresponding water-oil biphasic catalytic system reveals three main points. First, trans-RhCl(CO)(TPPTS)₂ has a much higher activity when intercalated in an LDH than in solution. For aldehyde formation under identical reaction conditions, the value of TOF is enhanced four to six times by immobilization between the sheets of the positively charged LDH layers. The generally accepted mechanism for hydroformylation proposed by Evans et al. is shown in Scheme 1. The higher activity of RhP₂-P-Zn₃Al-LDH may be ascribed to the basic nature of LDHs, which facilitates the formation of a rhodium hydride complex by removing the HCl formed (step 1 in Scheme 1A). It is also possible that the large positive electrical potential experienced by HRh(CO)(TPPTS)₂ in the interlayer galleries may be responsible for the superior performance. Similar observations have been reported for Heck arylation catalyzed by LDH-Pd(TPPTS)₂ oxidative bromination catalyzed by LDH-WO₃ and asymmetric dihydroxylation catalyzed by LDH-OsO₄. Secondly, it can be concluded that the reusability of RhP₂-P-Zn₃Al-LDH is much better than the corresponding water-oil biphasic system. This is because of the little leaching of active species from the carrier because of the strong electrostatic interaction between the oxygen atoms in the sulfonate groups of the interlayer trans-RhCl(CO)(TPPTS)₂ and the host lattice, which has been confirmed by FTIR spectroscopy (Figure 2f). The activity of the RhP₂-P-Zn₃Al-LDH showed a statistically significant increase on reuse, as seen in Figure 5A. It is well-known that there is an induction period during which the rhodium precursor becomes an active 16-electron complex such as HRhCO(TPPTS)₂ or HRh(CO)₅(TPPTS) under catalytic conditions, as shown in Scheme 1A. It is therefore possible that the amount of active species derived from the tethered catalyst precursor increases slowly with reaction time. Finally however, it must also be noted that the value of n/i aldehyde ratio (3.5–5.7) for the water-oil biphasic system was higher than that for RhP₂-P-Zn₃Al-LDH (2.6–3.0), so that the selectivity of the water-oil biphasic system for n-aldehydes is better than that of RhP₂-P-Zn₃Al-LDH. This may be rationalized using the catalytic cycle (Scheme 1B), which has been taken from the literature. The different ways of inserting an alkene into a metal-hydrogen bond, as shown by Route (2)→(3) and (2)→(3'), are called anti-Markovnikov and Markovnikov addition, respectively. The relative rates of these two reactions are considered to be primarily determined by the degree of steric crowding around the metal center. The normal alkyl intermediate requires less space and is therefore formed more easily than the branched one in the presence of bulky ligands. Comparing HRhCO(TPPTS)₂ with HRh(CO)₂(TPPTS), the former favors high selectivity to n-aldehyde. In the water-oil biphasic system, TPPTS is more mobile and may be more available for coordination to Rh compared with the RhP₂-P-Zn₃Al-LDH system, in spite of the P/Rh molar ratios being the same in the two systems. Consequently, the catalytically active species HRhCO(TPPTS)₂ (Scheme 1A) can form more readily than HRh(CO)₂(TPPTS) in the water-
oil biphasic system, and may be responsible for the higher \( n/i \) ratios observed in this system.

As shown in Figure 5B, the sample of \( \text{RhP}_2\text{-P-Zn}_3\text{Al-LDH} \) prepared by the method of ion-exchange exhibited low selectivity for the hydroformylation of 1-hexene. Isomerization of \( \text{C}==\text{C} \) bonds was predominant and the value of aldehyde \( n/i \) ratio was a little lower than that for hydroformylation with the \( \text{RhP}_2\text{-P-Zn}_3\text{Al-LDH} \) catalyst. The lower amount of TPPTS in the \( \text{RhP}_2\text{-P-Zn}_3\text{Al-LDH} \) catalyst system compared with that in \( \text{RhP}_2\text{-P-Zn}_3\text{Al-LDH} \) should result in the formation of less \( \text{HRhCO(TPPTS)}_2 \) and more \( \text{HRh(CO)}_2\text{(TPPTS)} \) (steps 2 and 3 in Scheme 1A), which leads to lower selectivity towards both total aldehyde and \( n \)-aldehyde in the \( \text{RhP}_2\text{-Zn}_3\text{Al-LDH} \) catalytic system, as discussed above. However, it can be seen from Figure 5A that the sample of ion-exchange (\( \text{RhP}_2\text{-Zn}_3\text{Al-LDH} \)) exhibited higher activity than that of \( \text{RhP}_2\text{-P-Zn}_3\text{Al-LDH} \) prepared by in situ complexation. The main reason is that the Rh loading in the former sample is much higher than that of the latter (3.44 and 0.48%, respectively, Table 2).

To study the influence of reaction time on the performance if the \( \text{RhP}_2\text{-P-Zn}_3\text{Al-LDH} \) catalyst in hydroformylation of 1-hexene, the results at the end of four consecutive 2, 6, 10, and 14-h cycles are compared in Figure 6. The system maintained hydroformylation activity throughout the 14-h reaction time, as turnover of aldehyde increased continuously. It can also be seen that the turnover of aldehyde for the third and fourth cycles increased faster with reaction time than that in the first two cycles. This indicates that the \( \text{RhP}_2\text{-P-Zn}_3\text{Al-LDH} \) catalyst can maintain its activity unchanged during prolonged hydroformylation times. The experimental results confirm the high stability of the intercalated rhodium complex and its ability to be effectively reused.

The \( \text{Zn}/\text{Al} \) molar ratio in \( \text{RhP}_2\text{-P-Zn}_n\text{Al-LDH} \) was also varied and the catalytic behavior of the resulting composites was studied (Figure 7). It is well known that electrostatic forces give rise to strong interactions between the interlayer anions and the LDH host lattice. With the increase in \( \text{Zn}/\text{Al} \) molar ratio of the host layers, the electron density of the host lattices decreases and thus leads to a decrease in the concentration of guest anions in the interlayer galleries. This is confirmed by comparison of \( \text{RhP}_2\text{-P-Zn}_2\text{Al-LDH} \) and \( \text{RhP}_2\text{-P-Zn}_3\text{Al-LDH} \), whose rhodium loadings are 0.90 and 0.48%, respectively. As a result, the activity of the former is higher than that of the latter, represented by the sharp decrease in the conversion from 81 to 28% (as shown in Figure 7) as the \( \text{Zn}/\text{Al} \) ratio increases from 1.9 to 2.6. However, as the \( \text{Zn}/\text{Al} \) ratio increased from 2.6 to 3.9, the content of Rh increased slightly (from 0.48 to 0.60%), and the conversion increased from 28 to 35%. The slight increase in rhodium loading may result from the low crystallinity of \( \text{RhP}_2\text{-P-Zn}_4\text{Al-LDH} \) [as shown by the XRD pattern (Figure 1f)], which favors the adsorption of some rhodium complex on the surface of the LDH.

As far as catalytic selectivity is concerned, it was found that the selectivity towards both total aldehyde and \( n \)-aldehyde increased with increasing \( \text{Zn}/\text{Al} \) ratio of the samples (Figure 7). This phenomenon can be explained as follows: the lower the \( \text{Zn}/\text{Al} \) ratio, the higher the electron density of the host layers, the higher the concentration of interlayer anions, and thus the more severe the steric crowding. This leads to fewer free ligands (TPPTS) being available near the active species (\( \text{HRhCO(TPPTS)}_2 \)). On increasing the \( \text{Zn}/\text{Al} \) ratio, the content of the interlayer catalytic species decreases and the steric crowding becomes less significant, and as a result, more of the TPPTS ligands may be able to coordinate to the rhodium centers. According to the catalytic mechanism (Scheme 1A), the catalytically active species \( \text{HRhCO(TPPTS)}_2 \) (Scheme 1A1) is favored over \( \text{HRh(CO)}_2\text{(TPPTS)} \) (Scheme 1A3) in the presence of large concentration of free ligands, and the former species with its sterically crowded environment around the metal center favors anti-Markovni-
kov addition. This leads to the observed increase in selectivity towards n-aldehyde on increasing the Zn/Al ratio.

Conclusions

Cointercalation of the Rh-complex trans-RhCl(CO) (TPPTS)$_2$ and the ligand TPPTS into inorganic LDH hosts was successfully accomplished by the method of in situ complexation, and the catalytic performance of the resulting material in the hydroformylation of alkenes has been investigated. It was found that the new catalyst showed higher activity towards aldehyde formation and better reusability compared with the corresponding water-oil biphasic catalytic system under similar reaction conditions. It is suggested that the basic nature of the support, the large positive electrical potential of the host LDHs, and the spatial orientation of the intercalated guests (trans-RhCl(CO)(TPPTS)$_2$ as well as TPPTS) are responsible for the superior catalytic performance. Strong interactions occur between the LDH layers and the active rhodium species on intercalation, resulting in the good reusability. Furthermore, the catalyst prepared by the method of in situ complexation (Rh(II)-P$_2$-Zn/Al-LDH) showed much higher catalytic activity and selectivity towards aldehydes compared with that of an intercalated complex prepared by ion exchange. It was found that increasing the Zn/Al molar ratio in RhP$_2$-P$_2$-Zn/Al-LDH led to lower activity and higher selectivity to both total aldehyde and n-aldehyde, which can be related to the content of Rh and the availability of the free ligand, respectively.

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Literature Cited

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