1. Introduction

Supported molecular metal complexes continue to attract significant interest in the field of catalysis [1–3]. The uniformly distributed catalytic species on the surface are regarded as molecular analogues, the structure of which can be determined more precisely than those of supported metal catalysts containing particles or crystallites [3]. In addition, supported molecular catalysts offer advantages such as high selectivity and uniform accessibility (similar to molecular catalysts in solution), as well as ease of separation (characteristic of solid catalysts). Supported molecular catalysts continue to draw interest in the field of olefin hydroformylation, catalysis and many examples have been reported to-date. Supports such as zeolites [4], amorphous silica-alumina [5], oxides [6], as well as organic polymers [7,8], all have been exploited for hydroformylation catalysts.

Hydroxyapatite [HAP-x, Ca_{10-x}(PO_4)_{6-x}(OH)_{2-x}, x = 0, 1] is an important class of biomaterial, which is chemically similar to the mineral component of mammalian bones [9]. HAP adopts a hexagonal structure in the P6_3/m space group. The structure can be viewed as consisting of unconnected PO_4^{3-} tetrahedrons with Ca^{2+} in the space between and a chain of OH^- ions along the c-axis to balance the charge [10]. Hydroxyapatites possess a number of interesting properties such as ion-exchange capability, adsorption capacity, acid–base properties, non-toxicity, and thermal stability [9]. These properties make them attractive for catalytic applications. For example, substituting or partially substituting Ca^{2+} (with Ni^{2+} [11] or Cu^{2+} [12]) or P^{5+} (with V^{5+} [13]) makes HAP-type materials active catalysts for a range of reactions. Recently, HAP-supported Pd [14] and Ru [15] made from molecular metal precursors have been reported as efficient catalysts for aerobic oxidation of alcohols.

Using Rh(CO)_2(acac) as precursor for supported Rh catalysts is not new [3]. For example, Wrzyszcz et al. reported Rh(CO)_2(acac) supported on zinc aluminate spinel in a study for olefin hydroformylation [6]. However, no catalytic activity for 1-hexene hydroformylation was observed in the absence of added PPh_3. Here we report the first example using hydroxyapatite as support for rhodium hydroformylation catalyst, its structural characterization and catalysis for 1-hexene hydroformylation.
[Rh(CO)$_2$(acac), Strem Chemicals], all other chemicals were purchased from Aldrich.

Elemental analysis was obtained by Inductively Coupled Plasma/Atomic Emission Spectroscopy (ICP/AES). BET surface area was measured on a Micromeritics Tristar N$_2$ sorption instrument employing the ASTM D4263-10 standard method. Powder X-ray diffraction patterns were obtained on a Bruker D8 diffractometer. Transmission IR (Nujol mull) was obtained on a Mattson Sirius100 IR spectrometer.

Magic angle spinning (MAS) $^1$H NMR spectra were recorded on a 4.7 T Varian InfinityPlus 400 spectrometer corresponding to a $^1$H Larmor frequency of 400 MHz. Details of the quantitative $^1$H MAS NMR experimental procedures are described elsewhere [16].

The $^{31}$P MAS NMR spectra were recorded on an 11.7 T Varian InfinityPlus 500 spectrometer corresponding to a $^{31}$P Larmor frequency of 202 MHz. The $^{31}$P MAS spectra were obtained with a $\pi/4$ rad pulse length, $^1$H decoupling during acquisition, a recycle delay of 300 s, and averaging 8 scans. All MAS NMR measurements were done at room temperature with samples that were loaded in 4 mm (o.d.) MAS rotors and spun at the magic angle at rates of 10–16 kHz. The $^1$H and $^{31}$P chemical shifts are referenced with respect to external solutions of TMS ($\delta_H = 0.0$ ppm) and 85% H$_3$PO$_4$ ($\delta_P = 0.0$ ppm), respectively.

Hydroformylation reactions were carried out in a batch mode in a 70-mL Hastelloy C autoclave fitted with a glass liner and a magnetic stirrer. To avoid possible contaminations, a new glass liner was used for each run. Neat 1-hexene was used as the reaction medium, toward which the catalyst was mixed and loaded into the autoclave inside a N$_2$-filled dry-box. The autoclave was attached to a gas manifold and purged three times with syngas (H$_2$/CO = 1), charged with 300 psi of syngas and heated to 100 °C for 17 h; after which the autoclave was cooled down to room temperature and vented. The soluble rhodium catalyst was removed by running the product mixture through a column of silica. The liquid products were analyzed by GC and GC–MS using n-decane as an internal standard.

2.3.1. 1-Hexene hydroformylation using Rh(CO)$_2$(acac)

An amount of 0.0093 g (0.035 mmol) Rh(CO)$_2$(acac) was dissolved in 20 mL of 1-hexene in a glass liner and loaded into the autoclave. The autoclave was charged with 300 psi of syngas and heated to 100 °C for 17 h; after which the autoclave was cooled down to room temperature and vented. The soluble rhodium catalyst was removed by running the product mixture through a column of silica. The liquid products were analyzed by GC and GC–MS using n-decane as an internal standard.

2.3.2. Hydroformylation of 1-hexene using Rh(CO)$_2$(acac) in the presence of PPh$_3$

An amount of 0.0093 g (0.035 mmol) of Rh(CO)$_2$(acac) was mixed with 0.092 g of PPh$_3$ (0.35 mmol, Rh/P = 1/10), dissolved in 20 mL of 1-hexene in a glass liner, and loaded into the autoclave. The autoclave was charged with 300 psi of syngas and heated to 100 °C for 17 h; after which the autoclave was cooled down to room temperature and vented. The soluble rhodium catalyst was removed by running the product mixture through a column of silica. The liquid products were analyzed by GC and GC–MS using n-decane as an internal standard.

2.3.3. 1-Hexene hydroformylation using supported Rh(CO)$_2$(acac) on hydroxyapatite

An amount of 0.50 g of the supported catalyst (0.035 mmol Rh) was mixed with 20 mL of 1-hexene in the autoclave. The autoclave was charged with 300 psi of syngas and heated to 100 °C for 17 h, after which the autoclave was cooled down to room temperature and vented. The solid catalyst was removed by filtration and the liquid analyzed by GC and GC–MS using n-decane as an internal standard.

3. Results and discussion

3.1. Preparation of hydroxyapatite and hydroxyapatite-supported Rh(CO)$_2$(acac)

The chemical composition of hydroxyapatite can be varied from the stoichiometric Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ (HAP-0) to the Ca-deficient form Ca$_9$(HPO$_4$)$_5$(PO$_4$)$_2$(OH) (Ca/P = 1.50, HAP-1) by using an appropriate Ca/P ratio during synthesis. ICP/AES analysis of the hydroxyapatite synthesized here reveals a Ca/P atomic ratio of 1.6, suggesting it is close to the stoichiometric form HAP-0. The co-precipitation method employed here generates hydroxyapatite with a BET surface area of 105 m$^2$/g, which is far greater than that of a commercial sample from Aldrich (22 m$^2$/g). Adsorption--desorption isotherm of nitrogen at 77 K and the pore size distribution for the hydroxyapatite are given in Fig. 1. The isotherm is similar to the type H1 adsorption isotherm in the IUPAC classification, suggesting the material contains cylindrical pores of nearly uniform size and shape. Pore size distribution (insert in Fig. 1) shows a pore diameter between 10 and 30 nm, with a maximum centered around 20 nm. Scanning electron microscopy (SEM) reveals a granular (0.2 μm × 0.5 μm dimension) morphology for the particles (Fig. 2). Significant peak broadening was observed in the powder XRD pattern (Fig. 3), consistent with the small particle sizes observed in SEM.

The supported catalyst was prepared by stirring the HAP-0 support in an acetonitrile solution containing Rh(CO)$_2$(acac). Physically adsorbed Rh complex on the surface was washed off to give a light yellow solid (yield 2.5 g). ICP/AES reveals the Rh level is 7270 ppm on the hydroxyapatite support.
using excess acetone. Targeting at 1 wt% rhodium level on HAP-0 using Rh(CO)2(acac) resulted in a supported catalyst with 7270 ppm Rh. This supported rhodium catalyst is referred as Rh(CO)2(acac)/HAP-0, which was used for characterization and 1-hexene hydroformylation in this study.

3.2. IR characterization of Rh(CO)2(acac)/HAP-0

Since perturbations to the P–OH resonance in IR are too small to be detected due to the very low Rh concentration in Rh(CO)2(acac)/HAP-0, we focused on the carbonyl stretch region in IR as shown in Fig. 4. Two carbonyl stretches at 2089 cm\(^{-1}\) (\(\nu_{as}\)) and 2007 cm\(^{-1}\) (\(\nu_{as}\)), respectively were revealed for Rh(CO)2(acac)/HAP-0, consistent with the two carbonyls bound to Rh in a cis-fashion [18]. Both peaks are fairly sharp and symmetrical, suggesting the supported catalyst adopts only one major structure. The carbonyl bands observed here are also consistent with those reported for Rh(CO)2+ supported on ZnAl2O4 [6] and zeolites [19]. For comparison, two peaks at 2082 cm\(^{-1}\) (\(\nu_{as}\)) and 2012 cm\(^{-1}\) (\(\nu_{as}\)) are present in Rh(CO)2(acac). In addition, three resonances (1526, 1557, and 1581 cm\(^{-1}\)) in the ketone vibration region were also observed for Rh(CO)2(acac), which disappear upon supporting on HAP-0, consistent with the acac\(^{-}\) ligand being protonated (by surface P–OH) to acetylacetone (acacH). The weak band around 1700 cm\(^{-1}\) in Rh(CO)2(acac)/HAP-0 may be attributed to acacH either bound to Rh or physically adsorbed on HAP-0 surface (free acacH: 1719, 1617 cm\(^{-1}\) [17]). Based on the IR results, we propose that the Rh on the supported catalyst is bound to two carbonyls in a cis-fashion; and that the acac\(^{-}\) ligand in the precursor is protonated to acacH and stays coordinated to Rh. This proposal for the supported catalyst structure is corroborated by NMR (vide infra).

3.3. Solid state NMR characterization of hydroxyapatite-supported Rh(CO)2(acac)

The structure of Rh(CO)2(acac)/HAP-0 was further probed using solid state NMR. Due to the low concentration of Rh relative to the bulk phosphorus, perturbations to phosphorus were undetectable by \(^{31}\)P NMR. By contrast, \(^{1}\)H NMR readily detects the P–OH group in the HAP-0 support and was used to monitor changes in the supported catalyst (Fig. 5). In addition to the P–OH group (\(\delta_H = 0.3\) ppm), \(^{1}\)H NMR also reveals a broad peak near 7 ppm in HAP-0, which is attributed to residual water. The proton density associated with the P–OH group in HAP-0 is 1.98 mmol/g by \(^{1}\)H NMR, agreeing with the theoretical value of 1.99 mmol/g for Ca10(PO4)6(OH)2, again confirming the hydroxyapatite pre-
Scheme 1. Proposed formation pathway and structure for Rh(CO)$_2$(acac)/HAP-0.

pared here is the stoichiometric form. For Rh(CO)$_2$(acac)/HAP-0, no change in the chemical shift for the P–OH peak is detected; but the concentration of the P–OH group decreases. In addition, a peak at ~2.2 ppm appears. The broad peak associated with residual water in HAP-0 shifts its center slightly upfield, suggesting other proton sources in addition to residual water exist in the supported sample.

The weight-corrected density for the P–OH group decreases from 1.98 to 1.81 mmol/(g HAP-0) upon supporting Rh(CO)$_2$(acac), suggesting protons associated with the P–OH are partially consumed. Assuming each Rh(CO)$_2$(acac) reacts with one P–OH, the amount of Rh (7270 ppm) in Rh(CO)$_2$(acac)/HAP-0 (0.46 mmol H/g) is approximately the same as expected from the acac$^-$ ligand in the Rh(CO)$_2$(acac) precursor (0.07 mmol Rh/g x 6 H per Rh = 0.42 mmol H/g). We therefore assign the peak at 2.2 ppm in Rh(CO)$_2$(acac)/HAP-0 to the –CH$_3$ group in acacH, formed via protonation of the acac$^-$ anion by the surface P–OH group. The –CH$_2$– group in acacH could overlap with the residual water peak, shifting the center of this broad peak upfield. We also acquired $^{13}$C CPMAS (cross-polarization magic angle spinning) NMR spectra for both Rh(CO)$_2$(acac) and Rh(CO)$_2$(acac)/HAP-0, and confirmed the presence of –CH$_3$ on the supported catalyst.

3.4. Proposed formation path and structure of Rh(CO)$_2$(acac)/HAP-0

Based on the characterization results discussed so far, we propose a formation pathway for Rh(CO)$_2$(acac)/HAP-0 (Scheme 1). Upon mixing with HAP-0, the acac$^-$ ligand in Rh(CO)$_2$(acac) reacts with the proton in the P–OH group on the surface, forming acacH and anchoring the Rh dicarbonyl species Rh(CO)$_2$º on the surface via the resulting P–O$^-$ site, with coordination from the P=O group on the same phosphorus atom.

Three possibilities for the fate of the resulting acacH can be considered: (1) as free acacH in solution; (2) physically adsorbed on HAP-0 surface; and (3) coordinated to Rh. After the supported catalyst was filtered, the supernatant in acetone was analyzed by GC/MS. Trace amount of acetylacetone (acacH) was detected. However, free acacH was also observed by GC/MS for a separately prepared Rh(CO)$_2$(acac) solution (1000 ppm in acetone, similar to the residual level of Rh in the supernatant). Clearly, Rh(CO)$_2$(acac) decomposes in the GC injector forming acacH. Therefore the acacH observed in the supernatant may very well be due to un-reacted Rh(CO)$_2$(acac), not necessarily supporting that the existence of free acacH in solution is a result of anchoring as argued by Wrzyszcz et al. [6]. The possibility of physically adsorbed acacH on HAP-0 can also be ruled out. The supported catalyst had been washed extensively with acetone and dried under vacuum for 24 h. Further, the NMR sample had been dried under vacuum at an elevated temperature (50°C for 10 h). Physically adsorbed acacH (bp 140°C) is expected to be largely removed after these treatments. Residual acacH left on the surface after these treatments is not expected to give the –CH$_3$ count in $^1$H NMR matching the Rh concentration in the supported catalyst. Consequently, the most logical proposal is that the acacH stays coordinated to Rh, resulting in a six-coordinated Rh species as shown in Scheme 1.

The hydroxyapatite-supported catalyst Rh(CO)$_2$(acac)/HAP-0 was tested for 1-hexene hydroformylation and the results are listed in Table 1. A total turnover number (TON) of 1330 was achieved using Rh(CO)$_2$(acac)/HAP-0 in 17 h (100°C, 300 psig, H$_2$/CO = 1, neat 1-hexene). The products contained internal hexenes, n-heptanal, 2-methyl-hexanal, and 2-ethyl-pentanal, with an n/i ratio of 0.8 for the aldehydes [n/i = n-heptanal/(2-Me-hexanal + 2-Et-pentanal)]; Scheme 2]. For comparison, a homogeneous system containing the same concentration of Rh(CO)$_2$(acac) (0.035 mmol) alone gave only 167 TON (n/i=1.8) under similar conditions, an order of magnitude lower than that of Rh(CO)$_2$(acac)/HAP-0. To gauge the activity of this supported catalyst relative to other rhodium catalysts, a homogeneous HRh(CO)(PPH$_3$)$_3$ system was generated in situ by mixing Rh(CO)$_2$(acac) (0.035 mmol) with 10 molar equiv. PPH$_3$ [20]. Under similar reaction conditions, this Rh/PPH$_3$ system gave a TON of 3220 (n/i=0.9), roughly two and half times that of Rh(CO)$_2$(acac)/HAP-0. Similar n/i

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rh (mmol)</th>
<th>Product composition (mol%)</th>
<th>TON$^b$</th>
<th>n/i$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(CO)$_2$(acac)</td>
<td>0.035</td>
<td>22</td>
<td>3.2</td>
<td>1.9</td>
</tr>
<tr>
<td>Rh(CO)$_2$(acac) + 10 eq PPh$_3$</td>
<td>0.035</td>
<td>0.8</td>
<td>46</td>
<td>1.2</td>
</tr>
<tr>
<td>Rh(CO)$_2$(acac)/HAP-0</td>
<td>0.035</td>
<td>2</td>
<td>13</td>
<td>69</td>
</tr>
<tr>
<td>Rh(CO)$_2$(acac)/HAP-0 (re-used)</td>
<td>0.034</td>
<td>6</td>
<td>10</td>
<td>72</td>
</tr>
</tbody>
</table>

$^a$ Sum of 2-hexenes and 3-hexenes.

$^b$ Total turnover number (TON) is defined as moles of aldehydes formed per mole of Rh during the total run time.

$^c$ n/i = n-heptanal/(2-Me-hexanal + 2-Et-pentanal).

Scheme 2. Aldehyde isomers formed in 1-hexene hydroformylation.
Rhodium-based catalysts are known to be very active for olefin isomerization [21]. Consistently, large amounts of internal hexenes were observed. Although hydroformylation of internal olefins is slower than that for terminal olefins [21], contributions of internal hexenes to the low n/i ratio (0.8) for Rh(CO)$_2$(acac)/HAP-0 are significant here due to the large amounts of internal hexenes formed, which only give iso-aldehydes, reducing the n/i ratio as reaction time increases.

The low n/i ratio for Rh(CO)$_2$(acac)/HAP-0 resembles those for simple rhodium compounds [22], suggesting a sterically unhindered coordination environment around Rh, which is consistent with the proposed catalyst structure. Under reaction conditions, the weak coordination of acacH to Rh may dissociate and open up coordination sites for the Rh center for hydroformylation. The higher activity compared to the homogeneous system may be attributed to the effects of the phosphate ligand on the HAP-0 surface. Hydroformylation mechanism on this supported catalyst is not yet clear and will be a topic for future studies.

4. Summary

In summary, a high surface area hydroxyapatite [Ca$_{30}$PO$_4$]$\cdot$OH$_2$ was prepared and used as support for Rh(CO)$_2$(acac). The supported catalyst was characterized using IR and solid state NMR. The proton in the P–OH group of hydroxyapatite reacts with the acac– ligand forming acetylacetone (acacH); and the Rh dicarbonyl species was anchored on the surface via the resulting P–O– group. It is proposed that acacH stays coordinated with Rh in the supported catalyst. The supported catalyst is active in catalyzing 1-hexene hydroformylation without the need of an auxiliary ligand such as phosphine. Activity for the supported Rh catalyst is an order of magnitude higher than that for un-supported Rh(CO)$_2$(acac). The supported catalyst was separated from the reaction medium and re-used, giving a slightly lower activity.

Future work will focus on mitigating Rh leaching, understanding the reaction mechanism, and expanding the scope of reaction to other olefins.

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References