

## Supported Catalysts

Ruthenium Nanoparticles Supported on Hydroxyapatite as an Efficient and Recyclable Catalyst for *cis*-Dihydroxylation and Oxidative Cleavage of Alkenes\*\*

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The development of osmium-catalyzed alkene dihydroxylation and its asymmetric variants represents an important milestone in modern organic synthesis.<sup>[1]</sup> While this technology has been widely applied to the synthesis of pharmaceuticals and fine chemicals, the high cost and possible product contamination by toxic osmium metal have restricted its use for large-scale reactions in industry. Currently, there is considerable interest in the search for alternative metal catalysts for alkene dihydroxylations.<sup>[2]</sup> Ruthenium and its complexes, being isoelectronic to its osmium counterparts, are well-known for their catalytic activities for oxidative transformations.<sup>[3,4]</sup> And indeed,  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  has been demonstrated to catalyze *cis*-dihydroxylation<sup>[5]</sup> and oxidative cleavage<sup>[6]</sup> of alkenes.

Application of nanosized metal particles as catalysts for organic transformations is an area of growing interest.<sup>[7,9a]</sup> Because of its high surface area and high density of active sites, nanosized metal particles exhibit superior catalytic activities compared with the corresponding bulk materials. Herein, we report that ruthenium nanoparticles immobilized on hydroxyapatite<sup>[8]</sup> are an effective catalyst for *cis*-dihydroxylation and oxidative cleavage of alkenes. With ethyl *trans*-cinnamate as substrate, the supported catalyst has been recycled for successive *cis*-dihydroxylation reactions without significant deterioration of catalytic activities. Prior to this work, there are no precedent examples in the literature of recyclable ruthenium catalysts for *cis*-dihydroxylation and oxidative cleavage of alkenes.<sup>[9,10]</sup>

One approach to obtain supported catalysts with well-defined metal particles is to immobilize metal colloids onto solid supports.<sup>[7]</sup> Based on the Fiévet's protocol,<sup>[11a]</sup> stable ruthenium colloids can be prepared by the reduction of  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  (0.32 mmol) in 1,2-propanediol (100 mL) in the presence of sodium acetate (1 mmol) at 150°C. Reduction of

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the Ru<sup>3+</sup> salt was considered complete upon the disappearance of the band at about 400 nm in the corresponding UV/Vis spectrum (see Supporting Information). The ruthenium colloid (3.2 mM) prepared in this manner exhibited excellent stability against agglomeration since no precipitation of metal powder was evident upon standing the colloidal solution at room temperature for 7 days. Successful immobilization of the ruthenium nanoparticles was achieved by treating the colloidal solution with calcium hydroxyapatite (0.4 g) and H<sub>2</sub>O (50 mL) for 24 h.<sup>[12]</sup> Ruthenium nanoparticles that were grafted onto hydroxyapatite (nano-RuHAP) were obtained as a dark-grey solid after centrifugation, washing with deionized water, and drying under vacuum at 110 °C overnight. By means of inductively coupled plasma mass spectrometry ICPMS, the Ru content of nano-RuHAP was determined to be 5 wt % (0.5 mmol g<sup>-1</sup>) and the Ca:P molar ratio was 1.66; the latter agrees with the reported value of 1.67,<sup>[10d]</sup> thus indicating no significant exchange of the constituent Ca<sup>2+</sup> ions. Attempts to immobilize the ruthenium nanoparticles on some common inorganic supports such as silica gel and alumina were not successful, since the resulting materials contained <0.1 wt % Ru based on ICP analysis.

The powder X-ray diffraction (XRD) pattern [Philips PW1830 (2 kW), Cu<sub>Kα</sub>, 40 kV, 40 mA, 25 °C] of nano-RuHAP showed prominent peaks at 2θ = 25.90°, 31.85°, 32.25°, 32.95° and 49.55°, which are indexed to the [002], [211], [112], [300], and [213] reflections of the hexagonal crystal system of hydroxyapatite (JCPDS card no: 09-0432), respectively (see Supporting Information). It should be noted that free hydroxyapatite (i.e., without Ru particles) exhibits an almost identical XRD pattern, thus indicating that the crystallinity of hydroxyapatite was retained after immobilization of ruthenium nanoparticles. The TEM image of nano-RuHAP shows randomly dispersed particles, and energy-dispersive X-ray (EDX) and selected-area electron diffraction (SAED) analyses confirmed that the particles corresponded to ruthenium with an average diameter of about 4 nm. X-ray photoelectron spectroscopy (XPS) analysis of the freshly prepared nano-RuHAP catalyst revealed the binding energy of Ru 3p<sub>3/2</sub> at 462.7 eV (see Supporting Information). This value is slightly larger than the reported value (462 eV) for a bulk ruthenium metal.<sup>[13]</sup> There is a small increase in the surface area of nano-RuHAP (25 m<sup>2</sup> g<sup>-1</sup>) compared to its parent hydroxyapatite (17 m<sup>2</sup> g<sup>-1</sup>) as determined by the N<sub>2</sub> adsorption isotherms. This is accounted for by the physical adsorption of ruthenium nanoparticles on the solid support.

The nano-RuHAP catalyst was tested for *cis*-dihydroxylation of ethyl *trans*-cinnamate.<sup>[5a]</sup> In the presence of nano-RuHAP (1 mol % Ru), ethyl *trans*-cinnamate (2 mmol) was treated with NaIO<sub>4</sub> (3.0 mmol) and H<sub>2</sub>SO<sub>4</sub> (20 mol %) in EtOAc/MeCN/H<sub>2</sub>O (3:3:1 v/v) at 0 °C for 30 min with complete substrate consumption. After workup and chromatographic purification, (±)-*threo*-ethyl 2,3-dihydroxy-3-phenylpropanoate was isolated in 70% yield, and benzaldehyde (18%) and benzoic acid (6%) were obtained as minor products (Table 1, entry 1). By centrifugation, the supported ruthenium catalyst was recovered and was used for the second, third, and fourth runs under identical reaction conditions. No apparent loss of catalytic activity was

**Table 1:** Nano-RuHAP-catalyzed *cis*-dihydroxylation of ethyl *trans*-cinnamate.<sup>[a]</sup>

$\text{Ph}-\text{CH}=\text{CH}-\text{CO}_2\text{Et} \xrightarrow[\text{EtOAc/MeCN/H}_2\text{O}]{\text{Ru catalyst, NaIO}_4, \text{H}_2\text{SO}_4} \text{Ph}-\text{CH}(\text{OH})-\text{CH}(\text{OH})-\text{CO}_2\text{Et}$			
Entry	Catalyst	Reaction run	Yield [%] <sup>[b]</sup>
1	nano-RuHAP	first	70
2		second	80
3		third	82
4		fourth	66
5 <sup>[c]</sup>	nano-RuHAP		67
6	RuHAP <sup>[d]</sup>	first	80
7 <sup>[e]</sup>		second	50

[a] Reaction conditions: ethyl *trans*-cinnamate (2 mmol), nano-RuHAP (40 mg, 1 mol %), NaIO<sub>4</sub> (1.5 equiv) and H<sub>2</sub>SO<sub>4</sub> (20 mol %) in EtOAc/MeCN/H<sub>2</sub>O 3:3:1 at 0 °C, time = 30 min. [b] Yield of isolated product based on complete alkene consumption. [c] Ethyl *trans*-cinnamate (10 mmol). [d] Kaneda's catalyst, see reference [12]. [e] Conversion = 80%.

observed, and the product, *cis*-diol, was isolated in 80, 82, and 66% yields (entries 2–4, respectively). A total product turnover of 298 was attained over four consecutive runs. No alkene conversion to *cis*-diol or any oxidized products was detected in the absence of the nano-RuHAP catalyst. It is noteworthy that when the ethyl *trans*-cinnamate (2 mmol) oxidation was performed by using commercially available ruthenium metal powder (1 mol % Ru) as catalyst [reaction conditions: NaIO<sub>4</sub> (1.5 equiv) and H<sub>2</sub>SO<sub>4</sub> (20 mol %) in an EtOAc/MeCN/H<sub>2</sub>O mixture (3:3:1)], neither *cis*-1,2-diol nor benzaldehyde was obtained, and the starting alkene was recovered quantitatively.

The nano-RuHAP-catalyzed protocol is equally effective on a larger scale. For example, the reaction of ethyl *trans*-cinnamate (10 mmol) in the presence of nano-RuHAP (0.2 mol %) gave the corresponding *cis*-1,2-diol in 67% isolated yield (product turnover = 330; Table 1, entry 5).

During our catalyst recycling study, we observed about 20–30% weight loss of the nano-RuHAP catalyst after each reaction run. The observed weight loss was attributed to slow dissolution of the HAP support in the acidic reaction medium. After centrifugation, the supernatant solution was subject to ICPMS, and the Ru content in solution was measured to be <5 ppm. Both recovered and freshly prepared catalysts exhibited similar TEM images (i.e., metal particles with an average diameter ca. 4 nm). By XPS analysis, the binding energy of Ru 3p<sub>3/2</sub> of the recovered catalyst was found to be 463.3 eV, which is different from the 462.7 eV value found for the freshly prepared catalyst sample (see Supporting Information). Similar SAED patterns of the ruthenium particles were obtained for the recovered and the freshly prepared catalysts, thus revealing that the crystal packing structure of the metal particles did not exhibit any significant changes after the oxidation reaction (see Supporting Information).

Previously Kaneda and co-workers reported that an Ru<sup>3+</sup>-exchanged hydroxyapatite, prepared by treating hydroxyapatite with methanolic RuCl<sub>3</sub>, is an efficient heterogeneous catalyst for aerobic alcohol oxidations.<sup>[10d]</sup> In the work presented herein, we found that Kaneda's catalyst is also

effective for dihydroxylation of ethyl *trans*-cinnamate under the reaction conditions: alkene (2 mmol), Ru (1 mol %), NaIO<sub>4</sub> (3.0 mmol), H<sub>2</sub>SO<sub>4</sub> (20 mol %) in EtOAc-MeCN-H<sub>2</sub>O (3:3:1) at 0 °C for 30 min, and (±)-*threo*-ethyl 2,3-dihydroxy-3-phenylpropanoate was isolated in 80 % yield (Table 1, entry 6). However, when the recovered Kaneda's catalyst (by centrifugation) was subjected to a second reaction run, a mixture of *cis*-1,2-diol (50 %) and benzaldehyde (28 %) was obtained (Table 1, entry 7).

Dihydroxylations of other alkenes were examined by using the nano-RuHAP-catalyzed protocol, and the results are depicted in Table 2; a family of  $\alpha,\beta$ -unsaturated alkenes, including ethyl crotonate, dimethyl fumarate, dimethyl maleate, and isophorone can be converted into their corresponding *cis*-1,2-diols in 65, 53, 50, and 64 % isolated yields, respectively (Table 2, entries 2–5). The lower yields obtained for the dihydroxylations of dimethyl fumarate and dimethyl maleate are probably due to the high aqueous solubility of the *cis*-diol products. Under the Ru-catalyzed conditions, oxidation of 1-dodecene and styrene gave the respective dodecene glycol (75 %) and styrene glycol (85 %) in good yields (entries 6 and 7). Likewise, dihydroxylation of 1,2-disubstituted alkenes such as 1,4-diacetoxy-*cis*-but-2-ene and phenanthrene afforded the corresponding *cis*-1,2-diols in 61 and 60 % yields (entries 8 and 9). With 1-acetoxy-2-cyclohexene as substrate, the Ru-catalyzed dihydroxylation furnished 1-acetoxy-2,3-*cis*-dihydroxycyclohexane in 75 % yield (entry 10) with the *anti*-isomer being the major product (*anti:syn* = 9:1). Yet, the catalytic dihydroxylation of trisubstituted alkenes such as (3-benzloxy)-1-methylbut-1-ene appeared to be less effective, and the corresponding *cis*-1,2-diol was obtained in only 45 % yield (entry 11).

Further to alkene dihydroxylation, we examined the catalytic activity of nano-RuHAP for oxidative cleavage of alkenes, which is also a synthetically useful transformation.<sup>[14]</sup>

With *trans*-stilbene as the model substrate, treatment of the alkene (0.5 mmol) with NaIO<sub>4</sub> (1 mmol) and nano-RuHAP (4 mol % Ru) in a 1,2-dichloroethane-H<sub>2</sub>O (5:1 v/v) at room temperature for 2 h gave benzaldehyde in 81 % yield based on capillary GC analysis (Table 3, entry 1). The catalyst was recycled for repetitive *trans*-stilbene oxidations, and benzaldehyde was formed in comparable yields: 75 % (2nd run), 71 % (3rd run) and 72 % (4th run). No significant weight loss of the catalyst was observed under the reaction conditions for the oxidative C=C cleavage reactions.

Oxidative cleavages of other stilbene derivatives such as *cis*-stilbene and 1-methyl-1,2-diphenylethylene under the nano-RuHAP catalyzed conditions also proceeded efficiently, and the carbonyl products were produced in excellent yields (> 85 %, Table 3 entries 2 and 3). Styrene,  $\alpha$ -methylstyrene, and *trans*- $\beta$ -methylstyrene were found to undergo oxidative cleavage by using the “nano-RuHAP + NaIO<sub>4</sub>” protocol, and benzaldehyde was obtained in 66–92 % yield (entries 4–6). When dihydronaphthalene was employed as substrate, the corresponding dicarbonyl product was isolated in 86 % yield with 76 % substrate conversion (entry 7). Likewise, cyclic aliphatic alkenes such as norbornene, cyclohexene, 1-*tert*-butyldimethylsiloxy-2-cyclohexene, and cyclooctene were found to undergo effective C=C bond cleavage to afford the corresponding dicarbonyl products in 51–87 % yields (Table 3, entries 8–11). Catalytic oxidative C=C bond cleavage was also achieved for linear aliphatic alkenes such as methyl oleate and 1-dodecene, giving the corresponding carbonyl products in about 80 % yields, albeit with 10–20 % substrate conversion (entries 12 and 13).












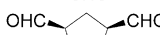

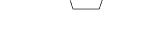








However,  $\alpha,\beta$ -unsaturated alkenes such as chalcone are poor substrates for the “nano-RuHAP + NaIO<sub>4</sub>” protocol, and only 23 % substrate conversion was attained with benzaldehyde (16 %) and benzoic acid (14 %) being formed after one day of reaction. In this work, we found that the use

**Table 2:** Nano-RuHAP-catalyzed *cis*-dihydroxylation of alkenes.<sup>[a]</sup>

Entry	Alkene	Product	Yield [%] <sup>[b]</sup>	Entry	Alkene	Product	Yield [%] <sup>[b]</sup>
1			70	6			75
2			65	7			85
3			53	8			61
4 <sup>[c]</sup>			50	9 <sup>[d]</sup>			60
5			64	10			75 ( <i>anti:syn</i> = 9:1)
				11			45

[a] Reaction conditions: alkene (2 mmol), nano-RuHAP (40 mg, 1 mol %), NaIO<sub>4</sub> (1.5 equiv) and H<sub>2</sub>SO<sub>4</sub> (20 mol %) in EtOAc/MeCN/H<sub>2</sub>O (3:3:1 v/v) at 0 °C, reaction time = 30 min. [b] Isolated yield based on complete alkene consumption. [c] Reaction time = 10 min. [d] Reaction time = 40 min.

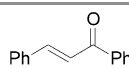
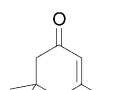
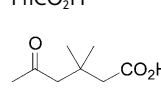
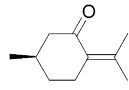
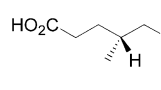

**Table 3:** Nano-RuHAP catalyzed oxidative cleavage of alkenes.<sup>[a]</sup>

Entry	Alkene	t [h]	Product	Yield [%] <sup>[b]</sup>
1		2	PhCHO	81 <sup>[c]</sup>
2		2	PhCHO	85 <sup>[c]</sup>
3		3	PhCHO	85
4		2	PhCOMe PhCHO	89 66
5		3	PhCOMe	92
6		3	PhCHO	90
7		3		86 <sup>[d,e]</sup>
8		3		72 <sup>[d]</sup>
9		3		51 <sup>[d]</sup>
10		3		79 <sup>[d,f]</sup>
11		3		87 <sup>[d]</sup>
12		12		84 <sup>[g]</sup>
13		12		79
		12		82 <sup>[h]</sup>

[a] Reaction conditions: alkene (0.5 mmol), nano-RuHAP (40 mg, 4 mol%), NaIO<sub>4</sub> (1 mmol), in ClCH<sub>2</sub>CH<sub>2</sub>Cl/H<sub>2</sub>O (5:1 v/v) at room temperature, and the products were identified and quantified by GC analysis. [b] Yield based on complete alkene consumption. [c] Yield based on 2 equiv of benzaldehyde formed. [d] Yield of isolated product. [e] 76% conversion. [f] 48% conversion. [g] 16% conversion. [h] 12% conversion.

of a “nano-RuHAP + oxone” protocol<sup>[6a,15,16]</sup> would effect oxidative cleavage of  $\alpha,\beta$ -unsaturated alkenes (Table 4). When chalcone (0.5 mmol) was treated with oxone (1.25 mmol) and nano-RuHAP (4 mol%) in a NaHCO<sub>3</sub> buffered MeCN/H<sub>2</sub>O (1.5:1 v/v) at room temperature for 4 h, benzaldehyde and benzoic acid were produced in 67 and 72% yields, respectively (Table 4, entry 1). Facile oxidative cleavages of isophorone and (+)-pulegone were also

**Table 4:** Nano-RuHAP-catalyzed oxidative cleavage of  $\alpha,\beta$ -unsaturated alkenes.<sup>[a]</sup>

Entry	Alkene	t [h]	Product	Yield [%] <sup>[b]</sup>
1		4	PhCHO PhCO <sub>2</sub> H	67 72
2		7		85
3		3		84
4 <sup>[c]</sup>		2	PhCO <sub>2</sub> H	82

[a] Reaction conditions: alkene (0.5 mmol), nano-RuHAP (40 mg, 4 mol%), oxone (2.5 equiv) and NaHCO<sub>3</sub> (7.7 equiv) in MeCN-H<sub>2</sub>O 1.5:1 at RT. [b] Yield of isolated product based on complete alkene consumption. [c] Oxone (4 equiv) and NaHCO<sub>3</sub> (12 equiv).

observed when using nano-RuHAP as catalyst and oxone as oxidant (entries 2 and 3). Notably, oxidative cleavage of C≡C bonds was also achieved using the “nano-RuHAP + Oxone” protocol. For example, when alkynes such as 1-phenyl-1-propyne were subjected to the Ru-catalyzed conditions, benzoic acid was produced in 82% yield (entry 4). Results for the catalytic oxidation of other alkenes are given in the Supporting Information.

In summary, a heterogeneous catalyst was prepared by grafting ruthenium nanoparticles onto hydroxyapatite. The supported Ru nanoparticle catalyst exhibited excellent activities for dihydroxylation and oxidative cleavage of alkenes, and the catalyst can be recycled for repeated uses. Considering that preparation of the supported catalyst involves easy chemical manipulation and the lower toxicity of ruthenium compared to OsO<sub>4</sub>, the application of the ruthenium nanoparticles-based catalyst to other catalytic transformations are being pursued.

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