

# Colloid-catalysed arene hydrogenation in aqueous/supercritical fluid biphasic media†

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**Hydrogenation of arenes, including the lignin model compound 2-methoxy-4-propylphenol, has been effected using a Rh colloid in biphasic aqueous/supercritical ethane reaction media; this is the first successful example of an unsupported colloid-catalysed hydrogenation of a substrate in a supercritical fluid; the same reaction does not proceed in aqueous/supercritical carbon dioxide or ionic liquid/supercritical fluid media.**

Catalysis performed in aqueous/organic biphasic media, with the catalyst in the aqueous phase and hydrophobic substrates and products in the organic phase, is appealing for industry because the products can be separated cleanly and easily from the catalyst with negligible loss of catalyst.<sup>1</sup> However, given the ability of water to retain high levels of organic solvent residues, the disposal of the aqueous phase can be problematic. A more environmentally benign alternative is to use aqueous/supercritical fluid (SCF) biphasic media for catalysis. In such a scheme the catalyst resides in the aqueous phase and the non-polar SCF phase dissolves and transports the substrates, reagent gases (if any) and products. The advantages of using SCFs such as carbon dioxide (scCO<sub>2</sub>) or ethane (scC<sub>2</sub>H<sub>6</sub>) over liquid organic solvents include lower environmental impact, enhanced diffusion rates of H<sub>2</sub>, ease of recycling, and facile removal of the SCF solvent from the product and from the aqueous phase.<sup>2</sup> Aqueous/SCF biphasic media have been found to be effective for several types of catalysts, including enzymes,<sup>3</sup> antibodies,<sup>4</sup> and water-soluble homogeneous catalysts.<sup>5,6</sup> We now report the use of aqueous/SCF biphasic media for arene hydrogenation with a colloidal catalyst.

Hydrogenation of arenes, an important chemical process in the synthesis of fine chemicals,<sup>7</sup> can be catalysed by Raney nickel, supported palladium or nickel catalysts, homogeneous catalysts or colloidal catalysts. Many of the "homogeneous" catalysts that have been reported for arene hydrogenation are in fact catalytically active colloidal metal particles.<sup>8</sup> Such particles are known to be quite active and are usually prepared *in situ* in biphasic aqueous/organic reaction media.<sup>9</sup> Hydrogenations with this type of catalyst can be achieved at room temperature and low hydrogen pressure.<sup>10,11</sup>

Colloid-catalysed reactions in SCFs or aqueous/SCF biphasic media have not been much studied in the past. Zemanian *et al.* reported minimal conversion (0.25–1%) in the hydrogenation of naphthalene to tetralin using a colloidal CoMoO<sub>3</sub> catalyst in reverse micelles in supercritical butane at 135–155 °C.<sup>12</sup> In our laboratory we have tested the hydrogenation of a series of arenes in a biphasic, aqueous/SCF using Rh colloids generated *in situ* from the complex [RhCl(cod)]<sub>2</sub>.

The first tests in this series were of the hydrogenation of 2-methoxy-4-propylphenol. This compound was selected because results published earlier<sup>13</sup> showed it to be particularly

difficult to hydrogenate and because it is a model for the phenolic groups in lignin; the hydrogenation of the aromatic rings in lignin has been proposed as a method of preventing the yellowing of mechanical pulps.<sup>13,14</sup> The reactions were performed in 1.5 mL aqueous buffer and 29.5 mL of supercritical fluid, with the catalyst precursor, surfactant (tetrabutylammonium hydrogen sulfate, THS) and arene typically in a Rh:THS:arene ratio of 1:3:50.

The hydrogenation did not proceed in aqueous/scCO<sub>2</sub> biphasic media (Table 1); the likely reason being the low pH due to the dissolution of CO<sub>2</sub> in the aqueous phase (see ESI†). Rh colloidal catalysts are particularly sensitive to pH, with optimum activity at pH 7.4–7.6.<sup>10</sup> In order to bypass the pH problem, attempts were made to use a non-aqueous polar solvent in place of the water.‡ For example, the ionic liquid [bmim]BF<sub>4</sub> (bmim = 1-butyl-3-methylimidazolium cation) is insoluble<sup>15</sup> in scCO<sub>2</sub> and therefore is an appropriate substitute. Unfortunately, the colloidal catalyst in the present experiments was not active for hydrogenation in [bmim]BF<sub>4</sub>/scCO<sub>2</sub>, [bmim]BF<sub>4</sub>/scC<sub>2</sub>H<sub>6</sub>, or [bmim]BF<sub>4</sub>/pentane mixtures. The catalyst may have been inactivated by the ionic liquid itself or by trace chloride ions<sup>16</sup> remaining from the preparation of the ionic liquid.

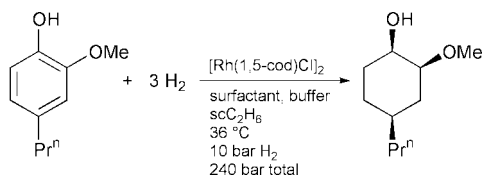
In an aqueous/supercritical ethane (scC<sub>2</sub>H<sub>6</sub>) biphasic medium, excellent results were obtained (Scheme 1 and Table 1). At a substrate:Rh ratio of 10:1, complete conversion was obtained, while at 50:1, the reaction was 88% complete (Table 1). This is the first successful example of the use of an aqueous-phase colloidal catalyst for the hydrogenation of a substrate in a supercritical phase. Hydrogenations using liquid C<sub>2</sub>H<sub>6</sub> as the non-polar phase were also achieved. In all cases, the major

**Table 1** Reaction conditions for the hydrogenation of 2-methoxy-4-propylphenol<sup>a</sup>

Non-polar Phase	S/Rh <sup>b</sup>	Surfactant	Buffer pH	<i>P</i> <sub>total</sub> /bar	<i>t</i> /h	Conv. (%)
At room temp. and 4 bar H <sub>2</sub>						
liq. C <sub>5</sub> H <sub>12</sub>	10	THS	7.5	4	46	100
liq. C <sub>2</sub> H <sub>6</sub>	10	THS	7.5	49	64	100
liq. CO <sub>2</sub>	50	THS	7.5	74	66	0
At 36 °C and 10 bar H <sub>2</sub>						
liq. C <sub>5</sub> H <sub>12</sub>	50	THS	7.5	10	72	100
scC <sub>2</sub> H <sub>6</sub>	10	THS	7.5	240	72	100
scC <sub>2</sub> H <sub>6</sub>	50	THS	7.5	240	72	88
scC <sub>2</sub> H <sub>6</sub>	50	AOT <sup>c</sup>	7.5	240	96	4
scCO <sub>2</sub>	10	None	None	240	78	0
scCO <sub>2</sub>	50	THS	7.5	210	50	0
scCO <sub>2</sub>	50	THS	11.2 <sup>d</sup>	210	60	8
scCO <sub>2</sub>	50	THS	7.2 <sup>e</sup>	220	72	0

<sup>a</sup> The catalyst precursor [RhCl(1,5-cod)]<sub>2</sub> was used for all reactions. The buffer is 0.1 M Na<sub>3</sub>PO<sub>4</sub>, 0.05 M citric acid, and 0.2 M boric acid except where noted. The buffer pH refers to the pH at room pressure. <sup>b</sup> Substrate / rhodium mole ratio. <sup>c</sup> 1 M AOT, conversion determined by GC. <sup>d</sup> 0.5 M Na<sub>3</sub>PO<sub>4</sub>, 0.05 M citric acid and 0.2 M boric acid. <sup>e</sup> 1 M MOPS solution.

† Electronic supplementary information (ESI) available: experimental details, description of the effect of changing the buffer, plot of pH of aqueous buffers under 10 atm H<sub>2</sub> and varying pressures of CO<sub>2</sub>. See <http://www.rsc.org/suppdata/cc/a9/a907193h/>



**Scheme 1**

product was *cis*-2-methoxy-*cis*-4-propylcyclohexanol. The minor product, which had been observed in small amounts in earlier studies, was *cis*-2-methoxy-*trans*-4-propylcyclohexanol. The ratio of products was 8:1 in all runs, regardless of whether  $scC_2H_6$  or an organic liquid was used. This high selectivity indicates that the hydrogenation of the arene ring takes place without the partially-hydrogenated substrate dissociating from the catalyst.<sup>14</sup>

Switching the surfactant from THS (0.04 M) to AOT (dioctylsulfosuccinate, sodium salt, 1 M), which has been used previously for the preparation of aqueous/ $scC_2H_6$  emulsions,<sup>17–20</sup> resulted in a dramatic drop in the catalytic activity.<sup>§</sup>

The extension of the method to the hydrogenation of simpler arenes was also explored (Table 2). In these experiments, an even higher substrate:Rh ratio of 100:1 was used. Conversions were high in all cases. The hydrogenation of 4-phenylbutanone was essentially complete and highly selective for hydrogenation at the arene ring only. *p*-Xylene was primarily converted to *cis*-1,4-dimethylcyclohexane, although it is interesting that the selectivity for hydrogenation on a single face was greater for 2-methoxy-4-propylphenol than xylene. One could speculate that the hydroxy and methoxy groups help anchor the substrate to the metal surface.

Catalytic activity in this system may be related to the solubility of the substrates. The range of arenes tested encompasses hydrophilic and hydrophobic arenes. Phenol, which is very soluble in water and essentially insoluble in alkanes, was completely hydrogenated. It is tempting to

**Table 2** The hydrogenation of other arenes in  $H_2O/scC_2H_6$ <sup>a</sup>

Substrate	TON	Products (%)
	100	(100%)
	110 <sup>b</sup>	(73%)
	99	(97%) (2%)
	77	(77%)
	79	(53%) (26%)
	96	(96%)

<sup>a</sup> Conditions: 36 °C, 62 h, 31 mL vessel, 240 bar total pressure (10 bar  $H_2$ , balance ethane), 9.5  $\mu$ mol  $[RhCl(1,5-cod)]_2$ , 76  $\mu$ mol THS, and 1.9 mmol arene (arene:Rh ratio of 100:1) were used for all reactions. The buffer is 0.1 M  $Na_3PO_4$ , 0.05 M citric acid and 0.2 M boric acid (buffer volume 1.7 mL, pH at atmospheric pressure 7.5). TON = turnover number = mol product per mol Rh. <sup>b</sup> Arene:Rh ratio of 150:1.

conclude that solubility in water is a requirement for efficient hydrogenation by this method, but the conversion of *p*-xylene, which is far more soluble in alkanes than it is in water, was still fair. Unfortunately, the literature does not contain solubility data for these arenes in  $scC_2H_6$ , but the solubility is expected to be similar to that in  $scCO_2$ . Xylene<sup>21</sup> and anisole<sup>22</sup> are completely miscible with  $scCO_2$  but benzyl alcohol<sup>23</sup> and phenol<sup>24</sup> have limited solubilities of 1–2 mol% at 36–40 °C and elevated pressures (above 140 bar). Despite this wide range of solubilities, the extent of hydrogenation was satisfactory for all substrates.

In conclusion, arene hydrogenation is catalysed by Rh colloids with high conversion in an aqueous/ $scC_2H_6$  biphasic medium. The same reaction in aqueous/ $scCO_2$  biphasic medium does not proceed, probably due to pH problems which could not be alleviated by the use of buffers. These results are new examples of transition-metal catalysed reactions in aqueous/SCF biphasic solvent mixtures.

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## Notes and references

‡ This is complicated by the fact that most polar organic solvents are quite soluble in  $scCO_2$ . For example, using a methanol or methoxyethanol solution of the Rh catalyst precursor gave no conversion, presumably because the organic solvent entirely dissolved in the supercritical phase.  
§ The effect of applying shear to create an emulsion was not tested.

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