

## Clean Aerobic Liquid Oxidation of Aldehydes with Solid Catalyst

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**Abstract:** Clean liquid oxidation of aldehydes can be accomplished using solid catalyst in the presence of molecular oxygen at room temperature, which is a valuable alternative to traditional counterparts.

**Keywords:** Clean oxidation, aldehydes, solid catalyst.

Oxidation of aldehydes into the corresponding carboxylic acids is one of the important methods in organic synthesis as the carboxylic acids are versatile intermediates in a variety of synthetic transformations<sup>1</sup>. Many processes with different reagents have been reported for this purpose including stoichiometric<sup>2,3</sup> and catalytic methods<sup>4,5</sup>. Those stoichiometric procedures employ oxidation reagents containing poisonous metals, such as hexavalent chromium, or explosive reagents, such as organic peroxides, and are snubbed with increasingly stringent environmental laws. Therefore, from the environmental point of view, using clean oxidants such as molecular oxygen/air<sup>4,6,7</sup>, hydrogen peroxide<sup>5,8</sup> and ozone<sup>9</sup> towards green oxidations of aldehydes is of great importance. Other reinforcing method such as sonication<sup>10</sup> was also reported. Undoubtedly, molecular oxygen/air would be an encouraging alternative owing to its readily availability and cost-effectiveness.

There has been many research for aldehydes oxidation using molecular oxygen as oxidant, including aerobic homogeneous catalyst systems, such as [Ni(acac)<sub>2</sub>]<sup>11</sup>, Keggin-type heteropolyanion [PW<sub>9</sub>O<sub>37</sub>(Fe<sub>3-x</sub>Ni<sub>x</sub>(OAc)<sub>3</sub>]<sup>(9+x)-</sup> (x=predominantly 1)<sup>12</sup>, and aerobic heterogeneous catalyst systems, such as Au/C<sup>4</sup>, Cs<sub>6</sub>H<sub>2</sub>P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>Co·OH<sub>2</sub>/SiO<sub>2</sub><sup>6</sup> and Ru/CeO<sub>2</sub><sup>7</sup>. The use of heterogeneous systems would be superior to homogeneous counterparts owing to easier separation of product and easier reuse of catalyst<sup>1</sup>.

In our earlier study, a novel heterogeneous ruthenium catalyst combined with microcrystals of cobalt hydroxide and cerium oxide was found to be a more efficient catalyst for oxidation of various types of alcohols including inactive alcohol such as primary aliphatic alcohols<sup>13</sup>. To the best of my knowledge, this Ru-Co(OH)<sub>2</sub>-CeO<sub>2</sub> is the most effective catalyst for the one-pot oxidation of primary aliphatic alcohols into

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carboxylic acids using atmospheric O<sub>2</sub> as a sole oxidant. Inspired by the result, recently, we have developed its catalytic activity towards aldehydes oxidation using molecular oxygen as a sole oxidant at room temperature.

Wet chemical method was used to prepare Ru-Co(OH)<sub>2</sub>-CeO<sub>2</sub> catalyst and the typical example was as follows: 3-neck round bottle flask equipped with a thermometer, reflux condenser and mechanical stirrer were charged with 30 mL of deionized water, 13.3 mmol of Na<sub>2</sub>CO<sub>3</sub> and 46.4 mmol of NaOH pellets. A second solution containing 10.2 mmol of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 5.1 mmol of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 1.53 mmol of RuCl<sub>3</sub>·xH<sub>2</sub>O (Aldrich-Sigma Co.), and 20 mL of water was prepared and added dropwise to the first solution while stirring. The resultant mixture was heated for 18 h at 65°C. The dark brown slurry was filtrated, washed with distilled water and dried at 110 °C for 12 h, yielding 2.3 g of black powder [Anal. Co, 33.6; Ce, 25.7; Ru, 6.4 (wt%). XPS: Ru 3p<sub>3/2</sub>, 464.4 eV; Co 2p<sub>3/2</sub>, 780.8 eV; Ce 3d<sub>5/2</sub>, 883.4 eV].

A typical procedure for the aerobic heterogeneous oxidation of octanal is as follows. A mixture of octanal (2 mmol), Ru-Co(OH)<sub>2</sub>-CeO<sub>2</sub> (0.30 g), and benzotrifluoride (5 mL) was stirred at room temperature under an atmospheric O<sub>2</sub> pressure. After 40 min, the solid catalyst was separated by filtration. GC analysis of the filtrate showed a quantitative yield of product. **Table 1** gives the result of octanal oxidation in the presence and absence of Ru component under atmospheric O<sub>2</sub> pressure.

**Table 1** Aerobic oxidation of octanal in the presence and absence of Ru <sup>a</sup>

Entry	Catalyst	Conv. <sup>b</sup>	Yield (%) <sup>b</sup>
1	Ru-Co(OH) <sub>2</sub> -CeO <sub>2</sub>	100	93
2	Co(OH) <sub>2</sub> -CeO <sub>2</sub>	<2	<1
3	No catalyst	<2	<1

<sup>a</sup>Reaction conditions: catalyst (0.3 g); octanal (2 mmol); benzotrifluoride (5 mL); O<sub>2</sub>; room temperature; reaction time (40 min). <sup>b</sup>Conversions and yields were determined by GC using *p*-dichlorobenzene as an internal standard.

If without catalyst, the conversion of octanal was poor (entry 3). That the catalyst lack of Ru element, *i.e.*, Co(OH)<sub>2</sub>-CeO<sub>2</sub>, also presented poor conversion of octanal hints that Ru element is indispensable towards octanal oxidation at room temperature in the presence of molecular oxygen (entry 2). Although the existence of only Co and Ce components in the heterogeneous catalyst was examined to be unactive for octanal oxidation, the addition of Co component was key to achieve mild reaction in comparison with another heterogeneous Ru/CeO<sub>2</sub> catalyst<sup>7</sup>, which was also reported as an effective catalyst for oxidation of primary alcohols and aldehydes to carboxylic acids. Wherein, 6 h of reaction time and 140°C were necessary for oxidation of octanal and benzaldehyde. Furthermore, lower dissociation energy of Co-O and effective aldehydes-to-acids Co-mediated catalysts<sup>6,14</sup> could explain the importance of existence of Co component. That a combination of Ru with both Co and Ce elements is necessary to achieve high yield of the carboxylic acid indicated a concerted synergism among the Ru, Co, and Ce components.

Various aldehydes including primary aliphatic, allylic and benzylic aldehydes were

investigated at room temperature in the presence of molecular oxygen using Ru-Co(OH)<sub>2</sub>-CeO<sub>2</sub> catalyst as shown in **Table 2**.

**Table 2** Aerobic oxidation of aldehydes by Ru-Co(OH)<sub>2</sub>-CeO<sub>2</sub> catalyst at room temperature <sup>a</sup>

Entry	Substrate	Product	Conv. (%) <sup>b</sup>	Yield (%) <sup>b</sup>
1	octanal	octanoic acid	100	93
2	2-ethylhexanal	2-ethylhexanoic acid	84	67
3	trimethylacetaldehyde	trimethylacetic acid	100	92
4	cinnamaldehyde	cinnamic acid	-	-
5	benzaldehyde	benoic acid	95	94
6	4-methylbenzaldehyde	4-methylbenzoic acid	90	85

<sup>a</sup>Reaction conditions: substrate (2 mmol), Ru-Co(OH)<sub>2</sub>-CeO<sub>2</sub> (0.3 g, Ru: 6.4 (wt%)), benzotrifluoride (5 mL), O<sub>2</sub>; room temperature; 40 min. <sup>b</sup>Conversions and yields were determined by GC or LC using an internal standard method.

Primary aliphatic aldehydes were smoothly oxygenated to the corresponding acids with good yield at room temperature (entries 1-3). However, the conversion of 2-ethylhexanal was less selective. The possible reaction intermediate, *i.e.*, tertiary carbonic ion was formed easily and rather stable, this could explain more paths towards by-products *via* intermediate and less selectivity for generating the corresponding carboxylic acid (entry 2). The analogous phenomena could also be found in the oxidation of 2-ethyl hexanol, in which water is necessary for improving the selectivity. This phenomenon has been noticed and will be further studied. Benzaldehyde and its derivatives were also readily oxygenated to their carboxylic acids under room temperature, showing the strong oxidative activity of Ru-Co(OH)<sub>2</sub>-CeO<sub>2</sub> (entries 5-6). However, for allylic aldehyde, such as cinnamyl alcohol, no conversion can be attained at the same condition and even at the elevated temperature like 60°C (entry 4). We have characterized that Ru component in this catalyst system was in higher oxidation state (Ru<sup>4+</sup>) and had thicker electrophilicity, showing some tendency adhering to allylic group. It seems that this temporary Ru complex made its electrophilicity weaker by forming temporary metallorganic complex *via* attraction between active Ru and olefinic group. Ru in this complex becomes more difficult to contact with aldehyde group. In the result the conversation of allylic aldehyde was zero.

Leaching experiment was performed and this reaction appears to be truly heterogeneous. The evidence is as follows: 1-octanol oxidation reacting at 60°C was used as probe reaction. The oxidation of 1-octanol could be smoothly performed at 60°C catalyzed by Ru-Co(OH)<sub>2</sub>-CeO<sub>2</sub> catalyst, stoichiometrically generating octanoic acid in 4 h; however, when the reaction was stopped after 3 h and the Ru-Co(OH)<sub>2</sub>-CeO<sub>2</sub> catalyst was filtrated from the reacting system, no further oxidation could continue at room temperature. This result presented heterogeneous catalysis in this reaction system.

As to reaction mechanism of aldehydes oxidation, there were two possible types of paths, one is geminal diol process, the other is radical chain process. A radical scavenger, *i.e.*, 2,6-di-*tert*-butyl-*p*-cresol was employed to determine the reaction path of octanal oxidation catalyzed by Ru-Co(OH)<sub>2</sub>-CeO<sub>2</sub> at room temperature in the presence of molecular oxygen. After 40 min no octanoic acid was formed, it might propose the

reaction mechanism to be a free radical process.

In a word, aldehydes oxidation using solid catalyst in the presence of molecular oxygen may prove to be green alternative to traditional aldehydes oxidation.

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