(54) Title: OXIDATION PROCESS AND CATALYSTS FOR USE THEREIN

(57) Abstract: The invention concerns a catalyst, suitable for use in the oxidation of alcohols to aldehydes, comprising a binary oxide of ruthenium (IV) with either cobalt (III) or copper (II), optionally also including a support material.
Oxidation process and catalysts for use therein

This specification relates to ruthenium compounds, their use as catalysts and in particular to the oxidation of alcohols using such catalysts.

The catalytic conversion of primary alcohols to aldehydes is essential for the preparation of fragrances and food additives as well as of many organic intermediates. Traditional methods for the synthesis of aldehydes generally involve the use of stoichiometric amounts of inorganic oxidants, such as Cr(VI), and generate large quantities of waste. Hence, the development of effective and environmentally benign catalytic systems for the aerobic oxidation of alcohols using oxygen or air is commercially desirable.

The aerobic oxidation of alcohols using catalysts based on platinum group metals is well known. Supported platinum and palladium catalysts have long been used for alcohol oxidation. More recently, ruthenium compounds have attracted significant interest for use as oxidation catalysts, either as soluble complexes or solid materials. For example, M. Matsumoto and N. Watanabe, (J. Org. Chem., 1984, 49, 3435) have used RuO₂. T. Matsushita, K. Ebitani and K. Kaneda, (Chem. Commun., 1999, 265) demonstrate the use of Ru-Co-Al hydrotalcite. B. Hinzen R. Lenz and S.V. Ley, (Synthesis, 1998, 977) show the use of perruthenate supported on an ion exchange resin and A. Beloch, B.F.G. Johnson, S.V. Ley, A.J. Priece, D.S. Shephard and A.W. Thomas, (Chem. Commun., 1999, 1907) on MCM-41 molecular sieve. Frequently, these catalysts are sufficiently selective to avoid over-oxidation of aldehydes to acids and are tolerant towards many other functional groups that may be present in the alcohol molecules. Most work has so far been done on oxidation of benzylic and allylic alcohols that are easier to selectively oxidise to the corresponding aldehydes than primary aliphatic alcohols.

It is an object of the present invention to provide an alternative catalyst for use in oxidation of alcohols to aldehydes and which is relatively simple to prepare.

According to the invention we provide a catalyst, suitable for use in the oxidation of alcohols to aldehydes, comprising a binary oxide of ruthenium (IV) with either cobalt (III) or copper (II).

According to a second aspect of the invention, we provide a process for the oxidation of an alcohol to form an aldehyde comprising contacting, in the liquid phase, said alcohol with a gaseous source of oxygen in the presence of a catalyst comprising a binary oxide of ruthenium (IV) with either cobalt (III) or copper (II).
The Ru/Co binary oxide catalyst of the invention differs from the Ru/Co/Al hydrotalcite used by Kaneda et al., in that the hydrotalcite structure requires the use of a divalent metal cation to replace the magnesium in the Brucite layer of the hydrotalcite structure and so Co(II) must be used.

The catalyst of the invention may be prepared by coprecipitation of the oxides from an aqueous solution of a ruthenium (III) compound, for example a chloride, and either a cobalt (II) compound or a copper (II) compound (e.g. a chloride). The precipitant may be any suitable alkali such as NaOH or Na₂CO₃ for example. The resulting precipitated solid oxide is then separated from the remaining solution, washed, and dried in air. The drying process brings about the oxidation of the Ru(III) to Ru (IV) and of the Co(II) to Co(III) oxides. The washing is preferably continued until the chloride ions are no longer detectable in the wash water.

The catalyst may be subjected to a process to form shaped pieces such as by granulation, tabletting, extrusion or other known methods, optionally with the addition of processing aids such as lubricants or binders. Alternatively it may be used in powdered form in slurry reactions.

The catalyst optionally comprises a support such as silica, alumina, silica-alumina mixtures, carbon, graphite. The support may be used in the form of a powder or a shaped particle such as a tablet, sphere, cylinder, ring or shaped extrudate, e.g. having a lobed cross-section. Such shaped particles may be made by known methods such as granulation, extrusion or tabletting. A supported catalyst of the invention may be prepared by known methods such as impregnation, precipitation in the presence of a solid support or by coprecipitation with the support. A preferred preparation method is by impregnation onto solid particles of the support material using the incipient wetness technique, i.e. by introducing a measured volume of a solution of soluble compounds of ruthenium and cobalt onto the support, the volume of the solution being measured to be sufficient to fill the pore volume of the support.

The catalyst very preferably comprises hydrous oxides of Ru and Co. We have found that anhydrous, crystalline RuO₂ is relatively inactive compared with the hydrated forms. Suitable hydrous Ru oxides preferably have an amorphous form and contain from 3 to 5 molecules of water for each Ru atom. The Ru and Co or Ru and Cu are present in the catalyst at a molar ratio in the range of about 1 – 6 Ru : 1 – 10 Co or Cu, more preferably from about 1 – 3 Ru : 1 – 4 Co or Cu. The molecular formula of a suitable binary oxide for the catalyst of the invention is therefore RuO₂·2CoO(OH)·3 – 5H₂O which is believed to include the amorphous RuO₂ hydrate and crystalline cobaltic acid, CoO(OH).
The oxidation process of the invention may be carried out at room temperature, but is preferably performed at elevated temperature, for example from 25 – 200 °C and under conditions of pressure which keep the reactants in the liquid phase, e.g. atmospheric pressure or higher pressures if required. The catalyst is used at a suitable amount so as to provide a molar ratio of Ru to alcohol of 1:5 to 1:100, preferably about 1:10.

The process may be performed in the presence of a radical scavenger. We have found that the presence of a radical scavenger improves the selectivity of the reaction to aldehyde and reduces the likelihood of over-oxidation which converts the desired aldehyde product to the corresponding acid. A suitable radical scavenger is 2,6-di-t-butyl-p-cresol. The process may be carried out in the presence of a solvent such as toluene, for example. The process may be carried out in a fixed bed reactor system or in a slurry process.

The process of the invention may be used to oxidise both saturated and unsaturated alcohols to their corresponding aldehydes or ketones. We have observed that unsaturated alcohols may be oxidised using the catalyst of the invention without migration of the double bond so that selectivity to the desired aldehyde is thereby increased. Both primary and secondary alcohols may be oxidised using the process of the invention to make aldehydes and ketones respectively. It is particularly useful for oxidising C₆ – C₂₀ alcohols to the corresponding aldehydes and ketones. The oxidation of primary alcohols to aldehydes is of particular importance in the manufacture of fragrances and is a preferred use of the process. Examples of alcohols which may be oxidised using the process of the invention include linear and branched alcohols, which may be substituted such 1-decanol, 1-dodecanol, 9 decenol, 1-cyclohexanol, 3-methyl-5-phenyl- pentanol, 2,2-dimethyl-1-phenyl-1-propanol and cinnamyl alcohol, although this is not an exhaustive list of suitable substrate alcohols.

A particular advantage of using the catalyst and process of the invention is that the catalyst may be isolated from the reaction mixture after reaction and re-used, optionally after a suitable washing and drying procedure.

The invention will be illustrated in the following examples and the accompanying drawing which is:

Fig. 1 – a graph of yield of cinnamaldehyde vs. time for the aerobic oxidation of cinnamyl alcohol (2.5 mmol) catalysed by RuO₂ or by Ru-Co (1:2) oxide with and without radical scavenger (0.11 mmol) in toluene (10 ml) at 110 °C (alcohol/Ru = 10:1).

**Example 1** Preparation of binary Ru (IV)-Co(III) oxide and Ru (IV)-Cu(II) oxide catalyst.
The Ru\textsuperscript{IV}-Co\textsuperscript{III} and Ru\textsuperscript{IV}-Cu\textsuperscript{II} (1:2) binary oxides were each prepared by co-precipitation of 0.2 M RuCl\textsubscript{3} solutions containing 0.4 M CoCl\textsubscript{2} or CuCl\textsubscript{2} with 1 M NaOH at pH 10. The resulting suspensions were aged with stirring for 2 hours, filtered off, washed with water until Cl\textsuperscript{-} removed (test with AgNO\textsubscript{3}) and finally dried at 60\textdegree{}C at 0.5 Torr for 2 hours. During the preparation, Ru\textsuperscript{III} oxidised to Ru\textsuperscript{IV} and Co\textsuperscript{III} to Co\textsuperscript{II} with air.

Example 2 (comparative catalyst preparation)
Ru dioxide hydrate was prepared by precipitation from 0.2 M aqueous solution of RuCl\textsubscript{3} with 1 M NaOH at pH 10 and the precipitate was separated, washed and dried as above.

Example 3 Oxidation of alcohols
All alcohols were used as received without further purification. The solvents were dried over a 4 Å molecular sieve.

A mixture of an alcohol (2.5 mmol), Ru catalyst (as specified in Table 1) and decane (as a GC internal standard) in toluene (10 ml) was charged at a ratio of alcohol/Ru of 10:1 mol : mol, into a 50 ml round-bottom reactor fitted with a reflux condenser and a magnetic stirrer. Air or oxygen was allowed to bubble through the mixture via a gas inlet at a flow of 25 ml/min. The mixture was saturated with oxygen at room temperature for 5 min while intensely stirred. Then the reactor was placed into a preheated oil bath to maintain a reaction temperature of 110 °C to start the reaction. Samples of the reaction mixture were taken out at appropriate time intervals to monitor the reaction by gas chromatography (GC). Conversions and selectivities to the indicated aldehyde were measured by gas chromatography using the internal standard. The results are shown in Table 1. The catalyst and reaction conditions were varied as set out below:

In example 3b air (at 25 ml/min) was used in place of oxygen.
Example 3c was carried out at 80 °C instead of 110 °C with the addition of a 4Å molecular sieve for the removal of water.
Example 3d, 3e, 3f and 3g (shown with asterisk in the table) were run in the presence of a radical scavenger (2,6-di-t-butyl-p-cresol, 0.11 mmol). The conversions and selectivities shown in brackets correspond to the maximum yields obtained in the absence of radical scavenger in about one hour.

The results show that the activity and selectivity of the Ru-Co and Ru-Cu binary oxides of the invention are more active and selective in the oxidation of cinnamyl alcohol to cinnamaldehyde than the comparison catalysts which contain no copper or cobalt.

The catalyst used in example 3a was isolated and re-used in two further reactions. The yield of cinnamaldehyde was 23% and 58% after 30 minutes and 120 minutes respectively in the second reaction and 25, 47 and 79% after 30, 120 and 240 minutes respectively in the third reaction.
A comparison of examples 3d and 3e and the graph shown in Fig 1, show that the addition of the radical scavenger maintains a high selectivity to aldehyde over a greater time.

<table>
<thead>
<tr>
<th>Example</th>
<th>Catalyst</th>
<th>Alcohol</th>
<th>Time (min)</th>
<th>Aldehyde</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>Ru-Co (1:2)</td>
<td>cinnamyl</td>
<td>30</td>
<td>Cinnamaldehyde</td>
<td>100</td>
<td>92</td>
</tr>
<tr>
<td>3b (air)</td>
<td>Ru-Co (1:2)</td>
<td>cinnamyl</td>
<td>30</td>
<td>Cinnamaldehyde</td>
<td>72</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>Ru-Co (1:2)</td>
<td>cinnamyl</td>
<td>60</td>
<td>Cinnamaldehyde</td>
<td>91</td>
<td>95</td>
</tr>
<tr>
<td>3c (80°C)</td>
<td>Ru-Co (1:2)</td>
<td>cinnamyl</td>
<td>30</td>
<td>Cinnamaldehyde</td>
<td>90</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>Ru-Co (1:2)</td>
<td>cinnamyl</td>
<td>60</td>
<td>Cinnamaldehyde</td>
<td>100</td>
<td>86</td>
</tr>
<tr>
<td>3d</td>
<td>Ru-Co (1:2)*</td>
<td>cinnamyl</td>
<td>30</td>
<td>Cinnamaldehyde</td>
<td>100 (100)</td>
<td>95 (92)</td>
</tr>
<tr>
<td>3e</td>
<td>Ru-Co (1:2)*</td>
<td>cinnamyl</td>
<td>60</td>
<td>Cinnamaldehyde</td>
<td>100 (100)</td>
<td>95 (47)</td>
</tr>
<tr>
<td>3f</td>
<td>Ru-Co (1:2)*</td>
<td>1-dodecanol</td>
<td>240</td>
<td>Dodecanol</td>
<td>54</td>
<td>93</td>
</tr>
<tr>
<td>3g</td>
<td>Ru-Co (1:2)*</td>
<td>9-decenol</td>
<td>240</td>
<td>9-decanal</td>
<td>66 (60)</td>
<td>76 (40)</td>
</tr>
<tr>
<td>3h</td>
<td>Ru-Cu (1:2)</td>
<td>cinnamyl</td>
<td>120</td>
<td>Cinnamaldehyde</td>
<td>100</td>
<td>85</td>
</tr>
<tr>
<td>4a</td>
<td>Ru-Co (4:1)</td>
<td>cinnamyl</td>
<td>60</td>
<td>Cinnamaldehyde</td>
<td>89</td>
<td>89</td>
</tr>
<tr>
<td>4b</td>
<td>Ru-Co (4:1)</td>
<td>cinnamyl</td>
<td>120</td>
<td>Cinnamaldehyde</td>
<td>100</td>
<td>85</td>
</tr>
</tbody>
</table>

Example 4
A binary Ru (IV)/Co(III) oxide catalyst was made according to the procedure in Example 1, using a ratio of ruthenium to cobalt of 4:1. The catalyst was used in the oxidation of cinnamyl alcohol according to the procedure of Example 3. The results are shown in Table 1.

Example 5
The oxidation of cinnamyl alcohol in oxygen or air was carried out as described in Example 3 using comparison catalysts comprising single oxides of Ru, Co and Cu. The results are shown in Table 2. The RuO₂ was made according to Example 2. In Example 5b, the catalyst was recovered from the reaction at 5a and reused.

<table>
<thead>
<tr>
<th>Example</th>
<th>Catalyst</th>
<th>Alcohol</th>
<th>Time (min)</th>
<th>Aldehyde</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>RuO₂ (comp)</td>
<td>cinnamyl</td>
<td>120</td>
<td>Cinnamaldehyde</td>
<td>100</td>
<td>79</td>
</tr>
<tr>
<td>5b</td>
<td>RuO₂ (comp)</td>
<td>cinnamyl</td>
<td>120</td>
<td>Cinnamaldehyde</td>
<td>80</td>
<td>79</td>
</tr>
<tr>
<td>5c (air)</td>
<td>RuO₂ (comp)</td>
<td>cinnamyl</td>
<td>120</td>
<td>Cinnamaldehyde</td>
<td>50</td>
<td>80</td>
</tr>
<tr>
<td>5d</td>
<td>CoO(OH)</td>
<td>cinnamyl</td>
<td>240</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5e</td>
<td>CuO</td>
<td>cinnamyl</td>
<td>240</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Example 6
A supported Ru-Co binary oxide was prepared by impregnation using incipient w wetness methodology. An impregnation solution was prepared by dissolving RuCl₃ and CoCl₂ in a 1:2 molar ratio in water and stirring for 0.5h. The total volume of the solution was calculated to fill the absorption volume of the support. The mixed metal solution was impregnated onto a gamma-Al₂O₃ support, having a mean particle size (d50) of 45 μm, with vigorous mixing to achieve a homogeneous distribution of metal on the support. The impregnated support was then mixed gradually into an agitated 1M NaOH solution, whilst ensuring that the pH was maintained at >10, to precipitate the metal compounds onto the support. The slurry was stirred for 30 minutes, filtered from the supernatant solution, washed with water until no chloride ions were detected when tested with AgNO₃ and then dried at 60°C for 2 hours under atmospheric conditions.

Example 7 – oxidation of octanol
The catalysts made in Examples 1 and 6, i.e. an unsupported and a supported Ru/Co catalyst, were used to oxidise octanol to octanal.
A 0.5M stock solution of the substrate (1-octanol) and internal standard (mesitylene) in toluene was prepared. The catalyst was placed in a 10 ml stirred pot reactor in a measured amount quantity to provide a molar ratio of Ru to alcohol of 1:80. 5ml of the stock solution was added to the reactor pot which then contained 2.5 x 10⁻³ moles of octanol and 3.1 x 10⁻⁵ moles of Ru. The reactor pots were sealed into the reactor and pressurised up to 4 bar with air. The unit was heated to 60°C. Once the unit had attained 60°C and 4 bar, stirring commenced at 600rpm. The reaction proceeded for 8 hours, after which the reactor pots were cooled to ambient temperature before depressurisation. A samples from the reactor pot was placed into a 1ml vial and analysed by gas chromatography using a ZB Wax column. The results are shown in Table 3.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>1-Octanol Conversion (%)</th>
<th>Selectivity to octanal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 1 (unsupported)</td>
<td>8.2</td>
<td>100</td>
</tr>
<tr>
<td>Example 6 (supported)</td>
<td>16.4</td>
<td>100</td>
</tr>
</tbody>
</table>
Claims

1. A catalyst, suitable for use in the oxidation of alcohols to aldehydes, comprising a binary oxide of ruthenium (IV) with either cobalt (III) or copper (II).

2. A catalyst as claimed in claim 1 comprising hydrous oxides of Ru and Co.

3. A catalyst as claimed in claim 1 or claim 2, containing from 3 to 5 molecules of water for each Ru atom.

4. A catalyst as claimed in any of the preceding claims, wherein the Ru and Co or Ru and Cu are present in the catalyst at a molar ratio in the range 1 – 6 Ru : 1 – 10 Co or Cu.

5. A catalyst as claimed in any of the preceding claims, which is prepared by coprecipitation of the oxides from an aqueous solution of a ruthenium (III) compound, and either a cobalt (II) compound or a copper (II) compound.

6. A catalyst as claimed in any of the preceding claims, further comprising a support material.

7. A catalyst as claimed in claim 6, wherein the support is in the form of a powder or a shaped particle, including a tablet, sphere, cylinder, ring or shaped extrudate.

8. A catalyst as claimed in claim 6 or claim 7, wherein the support is selected from the group comprising silica, alumina, silica-alumina mixtures, carbon and graphite.

9. A method of preparing a catalyst which is suitable for use in the oxidation of alcohols to aldehydes, comprising:
   a) forming a solution of a Ru(III) compound and either a Co(II) compound or a Cu(II) compound,
   b) optionally adding to said solution a support material,
   c) coprecipitating the Ru and Co or Cu oxides from said solution by addition of an alkali,
   d) separating the resulting precipitate from the remaining solution,
   e) washing said precipitate, and
   f) drying the precipitate in air.

10. A process for the oxidation of an alcohol to form an aldehyde comprising contacting, in the liquid phase, said alcohol with a gaseous source of oxygen in the presence of a catalyst as claimed in any of claims 1 - 8.
11. A process as claimed in claim 10 wherein a radical scavenger is present in the reaction mixture.

12. A process as claimed in claim 10 or claim 11, which is carried out in the presence of a solvent.

13. A process as claimed in any of claims 10 to 12, wherein said alcohol is a saturated or unsaturated primary alcohol.
Fig 1

Yield, %

Time, min

- Ru dioxide
- Ru-Co oxide
- Ru-Co oxide, scavenger