Studies on some oxidation reactions using a Ru(III) supported catalyst

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A metal catalyst has been prepared by supporting Ru(III) onto zirconium molybdate to catalyze oxidation reactions. The material has been characterised and the catalytic activity has been studied via hydrogen peroxide decomposition. Further, oxidation of a few organic substrates such as norbornene, cis-cyclooctene, styrene, cyclohexene and cyclohexane have been carried out.

The selective oxidation of organic compounds has gained importance in the chemical and petrochemical industries in recent years. Among these, epoxidation of olefins, in particular, has received much attention. Epoxidation reaction is an important reaction in organic synthesis because the formed epoxides are intermediates that can be converted into a variety of products.

Among the transition metals, ruthenium and its complexes are extremely versatile oxidation catalysts, both homogenous and heterogenous for a wide range of organic substrates. Ruthenium and its complexes have been successfully employed as catalysts in a number of reactions. This is mainly because of the fact that ruthenium exhibits a wide range of oxidation states with a facile interconversion of these, from one oxidation state to another. Ruthenium catalytic systems used so far in the experimental work seem to offer a low energy reaction pathway for the reactants leading to a fairly large turnover number of the product and the conditions for ruthenium catalysed systems are very mild.

Catalysis by supported metal ions is an area of intense interest. The metal ions have usually been affixed to polymer, silica or alumina surfaces. Recently, ruthenium has been supported on to different supports like polyoxometallates and zirconia. These catalysts are found to be highly active for reactions such as oxidation and hydrogenation. The ion exchange method of catalyst immobilization is simple when compared to the procedures required for the attachment of complexes to polymers. The synthesis and ion exchange properties of crystalline and amorphous zirconium molybdate have been studied earlier. Efforts have not been made to examine the catalytic properties of zirconium molybdate. Increasing interest in supported metal catalysts, as well as the commercial importance of epoxidation of olefins, prompted the preparation of a supported metal catalyst which could be used in oxidation reactions. The present work consists of preparation of a catalyst in which Ru(III) is supported onto zirconium molybdate (ZM). The compound has been characterised for elemental analysis, thermogravimetric analysis, surface area measurement (BET method) and Fourier transform infrared (FTIR). The catalytic activity has been studied through hydrogen peroxide decomposition. Further, oxidation reactions of a few organic substrates such as norbornene, cis-cyclooctene, styrene, cyclohexene and cyclohexane have been investigated.

**Experimental Procedure**

**Materials** — Zirconium oxychloride and ammonium molybdate (BDH), ruthenium trichloride and cyclohexane (Fluka), styrene, cis-cyclooctene, cyclohexene and norbornene (Aldrich) were used as received. Water used was double distilled, while dioxan was purified by a known method. The purities of anisole (used as an internal standard) and chlorobenzene was ascertained by gaschromatography. High purity nitrogen was used. Sodium hypochlorite (NaOCl) was synthesized by a reported method.

**Preparation of the support (ZM) — Zirconium molybdate (ZM) was prepared by the ammonium molybdate method as reported earlier.**

**Preparation of the catalyst [Ru(III) supported on ZM; RuZM]**

The acid treated ion exchanger (1 g) was placed
in a glass conical flask fitted with a stopper and 25 mL of known concentration of ruthenium trichloride solution was added. The exchanger was kept in contact with the metal ion solution for 24 h with intermittent shaking. It was finally filtered, washed with conductivity water till the complete removal of the adhering metal ion and dried at 100°C. All washings were collected with the filtrate to determine the remaining quantity of Ru(III) ion. The concentration of Ru(III) ion present on the exchanger was calculated from the difference between the initial and final concentration of the solution.

**Catalytic test reaction**

*Hydrogen peroxide decomposition* — A weighed quantity of the catalyst was shaken with 10 mL (4 vol) of H$_2$O$_2$ at 25°C. The desired concentration of H$_2$O$_2$ was obtained by successive dilution from the stock solution. The volume of O$_2$ evolved was measured at various time intervals and also after complete decomposition of the H$_2$O$_2$ using a gas burette$^{32}$. Experiments were carried out at different temperatures within a range of 25-40°C. The influence of various quantities of the catalyst used (0.025-0.075 g) and the effect of varying the concentration of H$_2$O$_2$ were studied at 35°C.

*Epoxidation of alkenes* — All reactions were carried out in a schlenk tube, in nitrogen atmosphere. The substrate and catalyst were added in a dioxan-water (7:3) mixture in which the substrate is soluble and the solvent was deaerated by bubbling nitrogen for 10 min. To this mixture, the substrate followed by the internal standard were added. The total volume of the system was 10 mL. Sodium hypochlorite (NaOCl) was added as an oxidant. The time at which sodium hypochlorite was added was considered as the initial time of the reaction. The mixture was stirred at ambient temperature for 2 h. Aliquots (1 mL) were withdrawn from the reaction mixture with the help of a Hamilton syringe and were injected into the gas chromatograph. A Shimadzu GC 15 A, equipped with an integrator, detector (TCD) and flame ionization detector (FID) was used to monitor the progress of the reaction.

**Characterization methods**

The samples were analysed for zirconium and molybdenum. Zirconium was determined gravimetrically as zirconium oxide while molybdenum was determined gravimetrically as molybdenum oxide by the $\alpha$-benzoin oxime method$^{33}$. Ru(III) was estimated spectrophotometrically by the Ruthenium-Thiourea method$^{34}$.

Thermogravimetric analysis of samples were performed on a Shimadzu DT$\alpha$-30 at a heating rate of 10°C/min under air. FTIR spectra of the samples were obtained using a KBr-wafer on a Perkin Elmer FTIR model 1720X, with Epson Hi 80 printer/plotter. The surface area of the materials was measured by the nitrogen adsorption BET method and recorded on a Carlo-Erba sorptomatic series-1800, at −196°C.

**Results and Discussion**

Chemical analysis indicates the composition of ZM, Zr:Mo to be 1:1. The number of water molecules have also been calculated using Alberti's$^{35}$ formula. From chemical analysis and thermogravimetric analysis, the proposed formula for ZM is ZrO$_2$.MoO$_4$.15H$_2$O.

TGA of ZM shows sharp change within the temperature range of 100-180°C, corresponding to the loss of external water molecules. After this, a slow change in weight loss is observed, which may be due to the condensation of structural hydroxyl groups. TGA of Ru-ZM shows additional weight loss within the temperature range of 360-424°C probably due to the removal of ruthenium from the support.

The FTIR spectra of ZM shows broad bands in the region $\sim$ 3400 cm$^{-1}$ corresponding to asymmetric and symmetric hydroxo $-\text{OH}$ and aquo $-\text{OH}$ stretches. A medium band at $\sim$ 1620 cm$^{-1}$ and broad shoulder at $\sim$ 935 cm$^{-1}$ indicates the presence of aquo $-[\text{H-O-H}]$ bending and zirconium-oxygen stretching respectively. FTIR of Ru-ZM shows an additional band at $\sim$ 620 cm$^{-1}$ which may be attributed to Ru-O stretching.

The surface area of Ru-ZM is 143 m$^2$/g against ZM which is 25 m$^2$/g.

In the present investigation, the kinetic analysis is based on the initial rate data because the reaction rate approaches equilibrium after a lapse of time.

For Ru-ZM, it was found that the rate was independent of initial concentration of H$_2$O$_2$ (Table 1a, Fig. 1), while an increase in the amount of the catalyst increased the rate of reaction (Table 1b, Fig. 2). An increase in the reaction temperature increases the rate of decomposition (Table 1c, Fig. 3).

The colour of the surface adsorbed metal ion changes from dark brown to light brown when it comes in contact with H$_2$O$_2$. The colour persisted as long as any residual H$_2$O$_2$ remained in the system. After complete decomposition of the hydrogen peroxide, the catalyst regained its original...
Table I—Catalytic activity of Ru(III) sorbed on zirconium molybdate

a — Influence of concentration of hydrogen peroxide

<table>
<thead>
<tr>
<th>Concentration of H₂O₂ (vol).</th>
<th>Specific reaction rate 10⁴K, min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>2.97</td>
</tr>
<tr>
<td>7.50</td>
<td>2.97</td>
</tr>
<tr>
<td>10.00</td>
<td>2.96</td>
</tr>
</tbody>
</table>

b — Influence of catalyst on decomposition of hydrogen peroxide

<table>
<thead>
<tr>
<th>Quantity of Ru(III)</th>
<th>Specific reaction rate 10⁴K, min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.50 × 10⁻³</td>
<td>2.06</td>
</tr>
<tr>
<td>7.00 × 10⁻³</td>
<td>2.96</td>
</tr>
<tr>
<td>1.05 × 10⁻²</td>
<td>3.10</td>
</tr>
</tbody>
</table>

c — Influence of temperature on decomposition of hydrogen peroxide

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Specific reaction rate 10⁴K, min⁻¹</th>
<th>Energy of activation kcal mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.28</td>
<td>13.00</td>
</tr>
<tr>
<td>30</td>
<td>2.06</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>2.96</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>4.20</td>
<td></td>
</tr>
</tbody>
</table>

*Quantity of catalyst = 0.05 g; reaction temperature = 35°C

**Volume of hydrogen peroxide = 10 mL (4 vol); reaction temperature = 35°C

'Quantity of catalyst = 0.05 g; volume of hydrogen peroxide = 10 mL (4 vol)

colour. This could be due to the formation of a peroxo species.

Based on the above observations the following reaction mechanism has been suggested, as proposed earlier.

It is known that H₂O₂ dissociates to

\[ H₂O₂ \rightarrow HO₂⁻ + H^+ \]  \hspace{1cm} (1)

The surface Ru(III) may interact with HO₂⁻ ions to form an intermediate complex.

Surface - Ru³⁺ + HO₂⁻ \rightarrow

Surface - [Ru(HO₂)⁺²⁺] \hspace{1cm} (2)

A second molecule of H₂O₂ may then interact with the intermediate complex to form the products

Surface - [Ru(HO₂)]²⁺ + H₂O₂ \rightarrow

Surface - Ru³⁺ + H₂O + O₂ + OH⁻ \hspace{1cm} (3)

During the course of decomposition of H₂O₂, pH increases, which is in keeping with the above mechanism. From the Arrhenius plot (Fig. 4) the energy of activation calculated is 13 kcal/mol.
The above reactions, suggest the probable use of Ru-ZM as an oxidation catalyst. In order to confirm this, some oxidation reactions of alkenes and alkanes such as norbornene, styrene, cis-cyclooctene, cyclohexene and cyclohexane were carried out using Ru-ZM as a catalyst. It was found that alkenes or alkanes used did not undergo oxidation in absence of either catalyst or an oxidant. Thus catalyst and oxidant are both essential for the epoxidation reactions.

Generally, the above mentioned substrates yield the following products on oxidation.

Norbornene → Norbornene oxide
Norbornenol exo
Norbornenol endo

cis-cyclooctene → Cyclooctene oxide
Styrene → Styrene oxide
Phenylacetaldehyde
Acetophenone
Benzaldehyde

Cyclohexene → Cyclohexene oxide
2-Cyclohexene-1-one
2-cyclohexene-1-ol

Cyclohexane → Cyclohexanol
Cyclohexanone

The results of oxidation of alkenes and alkanes with sodium hypochlorite using Ru-ZM as catalyst are shown in Table 2. As seen from Table 2 norbornene and cis-cyclooctene give the respective oxides selectively. Oxidation of styrene also selectively gives benzaldehyde as a major product while styrene oxide is found to be less. This is due to the oxidative cleavage of styrene. Oxidation of cyclohexene is accompanied by a large amount of allylic hydroxylation and subsequent formation of ketone, 2-Cyclohexene-1-ol is found in large amount as compared to cyclohexene oxide and 2-cyclohexene-1-one. Oxidation of cyclohexane gives cyclohexanone selectively.

A phase transfer catalyst could transfer ions, free radicals and molecules from the aqueous to the organic phase. Since the present reactions
were carried out in dioxan-water media, it was thought of interest to carry out the reactions using a phase transfer catalyst, in order to observe any change in the yields of the products obtained. The reactions were carried out under same conditions except making use of cetyl tetra ammonium bromide (CTAB) as a phase transfer catalyst. The yields observed are however, almost the same. This study shows that the use of a phase transfer catalyst does not have much effect on the yields of the products obtained and confirms the use of Ru-ZM as an oxidation catalyst.

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References