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Niobium peroxo compounds as catalysts for liquid-phase oxidation with hydrogen peroxide

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Abstract

The sodium tetraperoxo niobate, $Na_3[Nb(O_2)_4] \cdot 13H_2O$ (**1**) was prepared by fusing Nb_2O_5 with NaOH followed by reacting with aqueous H_2O_2 and characterised by single-crystal X-ray analysis and TGA. **1** was tested for the epoxidation of cyclohexene and oxidation of alcohols with hydrogen peroxide as a homogeneous catalyst. The $[Nb(O_2)_4]^{3-}$ anion was found to catalyse the epoxidation of cyclohexene with 30% aqueous H_2O_2 in homogeneous solution giving cyclohexene oxide in a 73% selectivity and 7% cyclohexene conversion at 45°C. It also showed some catalytic activity for the homogeneous oxidation of alcohols (ethanol, isopropanol, 1- and 2-butanol) with H_2O_2. The $[Nb(O_2)_4]^{3-}$ anion immobilised on a quaternary ammonium polystyrene resin was much less active in the above reactions than the homogeneous catalyst. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Catalysis by niobium compounds is a field of growing interest [1]. Niobic acid, niobium pentoxide and Nb-containing mixed oxides have been studied as catalysts and supports for a wide range of heterogeneously catalysed reactions [1–4]. On the other hand, peroxo niobium(V) compounds have attracted considerable attention recently as catalysts for oxidations with hydrogen peroxide in the liquid phase. For example, peroxo niobium(V) complexes have been reported to catalyse the homogeneous oxidation of benzyl alcohol by H_2O_2 [5]. Another approach to utilise the potential of peroxoniobates for selective oxidation is to incorporate them into polyoxometalates, which are the efficient catalysts for peroxide oxidations (for a review, see Refs. [6,7]). Recently several peroxo niobium(V) polytungstosilicates [8,9] and polytungstophosphates [10], e.g., $[(NbO_2)_3SiW_9O_{37}]^{7-}$ and $[(NbO_2)_3PW_9O_{37}]^{6-}$, have been prepared and structurally characterised. These have been found to catalyse selectively the oxidation of olefins to glycols by H_2O_2. However, instead of a niobium species, a tungsten compound seems to be the active catalyst in these reactions [8–11].

In this paper we present the results of our study on tetraperoxoniobate, $[Nb(O_2)_4]^{3-}$, as a homogeneous catalyst for the epoxidation of cyclohexene with hydrogen peroxide. The synthesis and X-ray structure of sodium tetraperoxo niobate $Na_3[Nb(O_2)_4] \cdot 13H_2O$ (**1**) are reported. Additionally, the peroxide oxidation of some aliphatic alcohols in the presence of $[Nb(O_2)_4]^{3-}$ is examined.

2. Experimental

2.1. Materials

All chemicals were from Aldrich and used as purchased, without further purification. $Na_3[Nb(O_2)_4] \cdot 13H_2O$ (**1**) was synthesised by fusing 13 g of NaOH and 7.0 g of Nb_2O_5 in a nickel crucible at 700°C. After cooling down the solid obtained was dissolved in 100 ml of 1 M aqueous hydrogen peroxide. Unreacted Nb_2O_5 was filtered off and the clear solution collected was allowed to crystallise at 5°C and for 24 h to yield 3.0 g (11%) of **1**. From this sample crystals suitable for single-crystal X-ray structure determination were collected. IR (KBr): 1645, 1450, 1412, 865, 845, 812, 546 and 475 cm^{-1}.

2.2. Techniques

IR spectra were obtained on a Perkin-Elmer 883 Infrared Spectrophotometer in KBr pellets. Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer TGA7 analyser. The powder X-ray diffraction pattern was collected using a Hiltonbrooks modified Philips 1050-W diffractometer with CuK_α source.

2.3. X-ray crystallography

The crystal data for **1** were collected on a STOE-IPDS diffractometer at 193(2) K using MoK_α radiation ($\lambda = 0.71073$ Å). Crystal structure determination details: Triclinic space group $P\bar{1}$, $a = 7.6449(14)$, $b = 8.7726(16)$, $c = 9.1643(16)$ Å, $\alpha = 64.103(19)$, $\beta = 81.83(2)$, $\gamma = 69.80(2)°$, $V = 518.85(16)$ Å^3, $Z = 1$, $\rho_{calc} = 1.735$ g cm^{-1}, μ (MoK_α) = 0.734 mm^{-1}, $2\theta_{max} = 48°$, refined against all 1528 unique data using F^2 (SHELX97), $R1(F > 4\sigma(F)) = 0.043$, $wR2$ (all data) = 0.105. Nb–O distances range between 1.954(6) and 2.057(5) Å and O–O distances within peroxo groups between 1.568(6) and 1.632(6) Å. However, these distances should be handled with caution due to the disorder within the $[Nb(O_2)_4]^{3-}$ anion (see below).
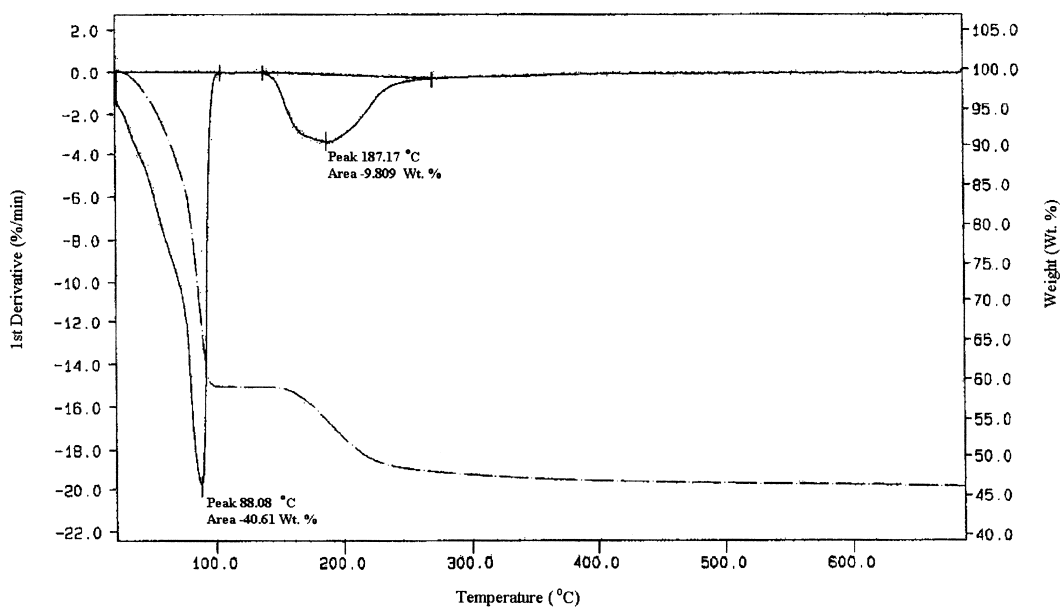
2.4. Reactions

The oxidations were carried out at 45°C in a 100-ml round-bottom flask fitted with a coil condenser and a magnetic stirrer and topped with a rubber balloon. In a typical oxidation experiment, the flask was loaded with 0.2 mmol of the catalyst, 10 ml of aqueous 30% H_2O_2 (88 mmol), 10 ml of *tert*-butanol and 1 ml (9 mmol) of cyclohexene. Alternatively, acetonitrile or dioxane were also used as co-solvents. The products were identified by GC-MS and ^{1}H NMR and quantified by GC (a Varian 3380 Gas Chromatograph, BP5 15 m $\times$ 0.3 mm capillary column).

3. Results and discussion

3.1. Preparation and characterisation of **1**

Synthesis of soluble niobium(V) compounds is not easy due to the very low solubility of the common starting material Nb_2O_5. We prepared **1** by a relatively simple procedure in a fairly good yield of 11% which may be improved by further optimisation. **1** is stable in air, losing the hydration water after several days. TGA shows that all the water of hydration in **1** is lost at 80°C, with the peroxo compound decomposition taking place at 180°C (Fig. 1). The anhydrous **1** is just as stable as the $13H_2O$ hydrate, also

Fig. 1. TGA for **1**.

decomposing at 180°C. The powder X-ray diffraction pattern for an anhydrous sample of **1** is shown in Fig. 2. Interestingly, the potassium–magnesium tetraperoxoniobate $KMg[Nb(O_2)_4] \cdot 7H_2O$ (**2**), prepared by reacting MgO and $KNbO_3$ with aqueous H_2O_2, was reported to
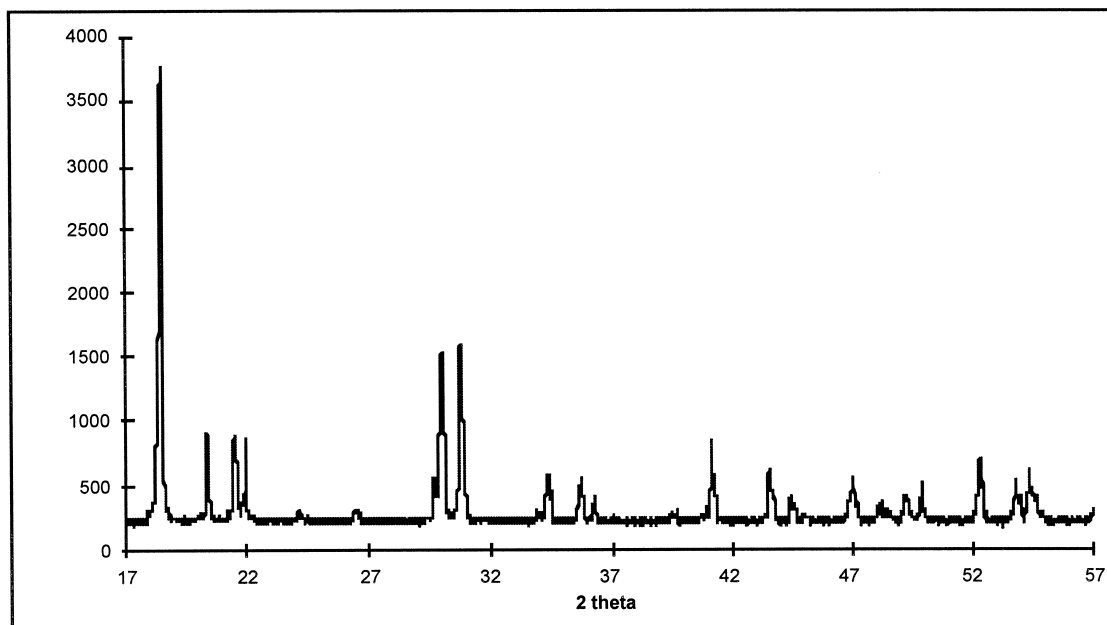
Fig. 2. Powder X-ray diffractogram for $Na_3[Nb(O_2)_4]$.

decompose explosively at 80°C [12]. It was also **2** that was first used to determine the structure of the $[Nb(O_2)_4]^{3-}$ peroxoanion [12]. Recently, the rubidium peroxoniobate, $Rb_3[Nb(O_2)_4]$ has also been structurally characterised [13]. Water-soluble peroxoniobate **1** may be useful as a starting material to synthesise various niobium compounds, e.g., Nb-containing catalysts, which otherwise are difficult to make.

3.2. Crystal structure of *1*

Our single crystal X-ray studies revealed significant structural differences between **1** and **2**. The principal structure of the peroxoanion $[Nb(O_2)_4]^{3-}$ is similar in **1** and **2**, as expected, although in **1** it is disordered (Fig. 3). The crystal packing of **1** and **2** is even more different. In **2**, the $[Mg(H_2O)_6]^{2+}$ cation forms intercalated layers with $[Nb(O_2)_4]^{3-}$, with K^+ occupying sites between them. The K^+ ion coordinates to the oxygen atoms of $[Nb(O_2)_4]^{3-}$ and $[Mg(H_2O)_6]^{2+}$, creating a rigid environment that holds the conformation of $[Nb(O_2)_4]^{3-}$ [12]. In **1**, the Na^+ cations are represented by the trimers $[Na_3(H_2O)_{12}]^{3+}$, which join together to form one-dimensional chains, intercalated by

Fig. 4. Crystal packing for the $Na_3[Nb(O_2)_4]\cdot 13H_2O$.

the tetraperoxoniobate anions (Fig. 4). The Na^+ ions are surrounded by six water molecules and there is no direct interaction between the Na^+ cations and the $[Nb(O_2)_4]^{3-}$ anions, which makes the overall structure less rigid. However, there are hydrogen-bonding interactions between H_2O molecules and peroxo groups of $[Nb(O_2)_4]^{3-}$. As a result, the positions of the peroxo oxygen atoms of the $[Nb(O_2)_4]^{3-}$ anion in **1** are disordered. Hence two different conformations of the $[Nb(O_2)_4]^{3-}$ anion in the crystal may be assumed, which are shown in Fig. 3. The structural disorder of $[Nb(O_2)_4]^{3-}$ in **1** may be in line with the greater thermal stability of **1** compared to **2**.

3.3. Oxidations with H_2O_2

The catalytic activity of **1** was tested for the epoxidation of cyclohexene and compared to that of sodium tungstate, a well-known epoxidation catalyst (Table 1). **1** was found to be active for the catalytic conversion of cyclohexene to cyclohexene oxide in aqueous *tert*-butanol providing 73% selectivity at 7% cyclohexene conversion, with cyclohexanone and cyclohexanol as the by-products. Similar results were obtained when dioxane or acetonitrile were used as co-solvents. The small amount of cyclohexanol may be formed by the acid catalysed hydration of cyclohexene. As the reaction solution was almost neutral (pH 7.3), the Lewis acidity of **1** may be responsible for that. It should be noted that **1** showed no significant activity in the decomposition of hydrogen peroxide, as measured volumetrically by gas evolution. The
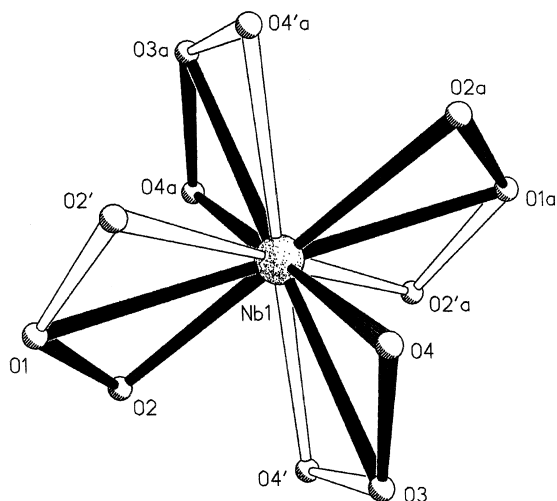

Fig. 3. The structure of the $[Nb(O_2)_4]^{3-}$ anion in **1** showing the disorder in the peroxo oxygen atom positions. Two different conformations are shown in black and white lines.
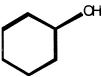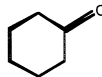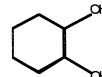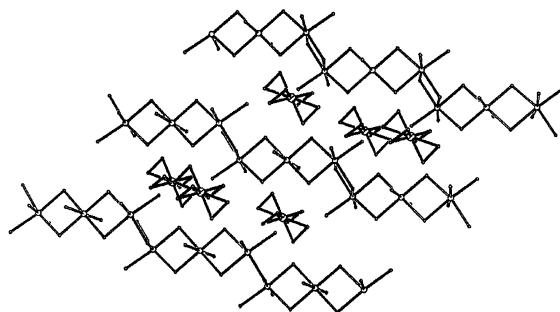
Table 1

Comparison of the performance of **1** and sodium tungstate in the epoxidation of cyclohexene

Catalyst	Conversion (%)[a]	(%)	(%)	(%)	(%)
Na$_3$[Nb(O$_2$)$_4$]	7	73	9	16	-
Na$_2$WO$_4$	53	42	9	4	42

Reaction conditions: 0.2 mmol of the catalyst, 10 ml of aqueous 30% H$_2$O$_2$ (88 mmol), 10 ml of *tert*-butanol and 1 ml (9 mmol) of cyclohexene, 45°C, 20 h with stirring.

[a] Based on cyclohexene.

sodium tungstate showed higher catalytic activity than **1**, but the selectivity to cyclohexene oxide was only 42%; a significant amount of 1,2-cyclohexanediol was also formed together with cyclohexanone and cyclohexanol.

The activity of **1** was also tested for the oxidation of aliphatic alcohols. These reactions were carried out at 45°C for 20 h using 0.2 mmol of **1**, 132 mmol of H$_2$O$_2$ (15 ml of 30% H$_2$O$_2$) and 109 mmol (10 ml) of alcohol. The oxidation of 1-butanol and 2-butanol gave butyric acid and mehtyl ethyl ketone (MEK) respectively. *tert*-Butanol gave *tert*-butyl hydroperoxide, which is likely to be an acid-catalysed reaction as the cyclohexanol formation mentioned above. No other products were detected. However, alcohol conversions were very low: ca. 2% for 2-butanol and ca. 1% for 1-butanol and *tert*-butanol. Similarly, ethanol was converted to acetic acid and 2-propanol to acetone at very low conversions.

Additionally, the [Nb(O$_2$)$_4$]$^{3-}$ anion was immobilised on a quaternary ammonium polystyrene anion-exchange resin (0.22 mmol g^{-1} loading) and tested in the epoxidation of cyclohexene and oxidation of alcohols with H$_2$O$_2$. Supporting **1** on the resin strongly inhibited its activity for peroxide oxidation. The reaction of cyclohexene (30 mmol) in the system containing 0.25 g of the catalyst, 132 mmol H$_2$O$_2$ (15 ml of 30% H$_2$O$_2$) and 5 ml of acetonitrile at 50°C for 20 h gave cyclohexene oxide as the only product, but cyclohexene conversion was as low as 3%. The oxidation of 2-butanol under the same conditions gave only traces of MEK.

4. Conclusion

In this work, the sodium tetraperoxo niobate, Na$_3$[Nb(O$_2$)$_4$] · 13H$_2$O (**1**) has been prepared, structurally characterised and tested for the epoxidation of cyclohexene and oxidation of alcohols with hydrogen peroxide. The [Nb(O$_2$)$_4$]$^{3-}$ anion shows moderate catalytic activity but fairly good selectivity in the epoxidation of cyclohexene with 30% aqueous H$_2$O$_2$ in homogeneous solution. It also showed some catalytic activity for the homogeneous oxidation of alcohols (ethanol, isopropanol, 1- and 2-butanol) with H$_2$O$_2$. The [Nb(O$_2$)$_4$]$^{3-}$ anion immobilised on a quaternary ammonium polystyrene resin was much less active in the above reactions than the homogeneous catalyst. It should be noted, however, that the catalytic performance of [Nb(O$_2$)$_4$]$^{3-}$ may be improved by incorporating the peroxo anion in a strongly electrophilic matrix, e.g., in zeolites or polyoxometalates [8–10], which could be interesting for the future studies.

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