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Catalysis Today 78 (2003) 439–447

CATALYSIS TODAY

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Water-soluble niobium peroxo complexes as precursors for the preparation of Nb-based oxide catalysts

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Abstract

In the frame of research aimed at developing new synthetic procedures of multimetallic Nb-based catalysts, peroxo complexes of niobium(V) of general formula $A^{I}_{3}[Nb(O_2)_4]$ and $A^{I}_{3}[Nb(O_2)_x(H_yL)]\cdot nH_2O$ (A^I: NH_4^+, $CN_3H_6^+$ (gu); L: oxalate, tartrate, citrate) have been prepared and characterized on the basis of elemental and thermal analysis, FTIR and ^{13}C-NMR spectra. The crystal structure of $(gu)_3[Nb(O_2)_4]$ and $(gu)_3[Nb(O_2)_2(C_2O_4)_2]\cdot 2H_2O$ have been determined. The application of the obtained Nb complexes as precursors for the preparation of silica-supported Nb–Mo–O catalysts has been demonstrated. Combining Nb peroxo-carboxylato compounds with analogous Mo(VI) compounds in a silica-impregnation method carried out in aqueous medium leads to the formation of the supported $Nb_2Mo_3O_{14}$ phase.

Keywords: Nb-based catalysts; Peroxo complexes; Precursors—Nb–Mo oxide

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1. Introduction

Oxidative dehydrogenation (ODH) of light alkanes is an energetically attractive route for the production of alkenes and particularly propene. Among the different catalysts proposed in the literature for this process, mixed oxide catalysts containing vanadium are the most frequently studied and are often reported to be catalytically active and selective for propane ODH. Niobium belongs to the same group but it is much more inert in its chemistry and less easily reduced than vanadium. According to many studies, niobia-based catalysts are efficient for the selective oxidative conversion of lower alkanes (C_3, C_4) [1] and for instance, pure niobium pentoxide itself is a very selective catalyst for propane ODH even though its catalytic activity is only moderate [2]. In recent years, it has been shown that associating niobium pentoxide with elements such as vanadium, molybdenum or antimony can considerably improve the catalytic activity while maintaining a high selectivity [2,3]. More particularly, phases like $Nb_2Mo_3O_{14}$ and $NbSbO_4$ were mentioned as active for ethane ODH and propane ammoxidation, respectively [4,5]. In some recent work, the interest of the sol–gel prepared $NbVO_5$ phase for that reaction was also suggested [6]. Because of the very limited availability of soluble niobium compounds, the preparation of such Nb-based catalysts is not straightforward. New research work on suitable Nb precursors seems therefore to be particularly appreciated to broaden the panel of available catalysts, and to improve their physico-chemical properties

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PII: S0920-5861(02)00325-5

(phase homogeneity, dispersion on support, surface characteristics).

Our aim is to develop new coordination chemistry routes allowing to synthesize multimetallic Nb-based catalysts in which niobium is associated with other elements like vanadium, bismuth, antimony or molybdenum. The idea is to use, for the various elements to be incorporated in the catalysts, molecular precursors which are ideally compatible which each other, mainly from the point of view of solubility and thermal degradation scheme. This was previously shown to be a valuable approach for the synthesis of multicomponent silica-supported oxide catalysts [7].

As far as niobium is concerned, the most currently used precursors for the preparation of Nb-based catalysts are niobic acid, the pentachloride $NbCl_5$, the ammonium trisoxalato complex $(NH_4)_3[NbO(C_2O_4)_3]\cdot H_2O$ and Nb alkoxides [8–10]. Next to them, the peroxo compounds have recently attracted considerable attention as catalysts for oxidation with hydrogen peroxide in the liquid phase. For example, peroxoniobium(V) complexes have been reported to catalyse the homogeneous oxidation of benzyl alcohol by H_2O_2 [11]. In a context of solid catalysts preparation, these compounds seem to be adequate candidates because of their high solubility in water [12] which makes them suitable for the preparation of supported oxide catalysts by wet impregnation. Such complexes have already been used for the preparation of Fe–Nb bulk sulphide catalysts, starting from an aqueous solution of $(NH_4)_3[Nb(O_2)_2(C_2O_4)_2]$ and $Fe(NO_3)_3$ [13].

The peroxo complexes of niobium already described in the literature concerned essentially the homoleptic tetraperoxoniobates of general formula $M^I_3[Nb(O_2)_4]$ (M^I: Na^+, K^+ (or $K_{1/3}Mg_{1/3})^+$, Rb^+, Cs^+, $NH_4{}^+$ and $CN_3H_6{}^+$) [14–16] and heteroleptic peroxo-carboxylato compounds such as $K_3[Nb(O_2)_3(L)]\cdot nH_2O$ (L: tartrate, citrate, glycolate, malate and dipicolinate) [12] and $(NH_4)_3[Nb(O_2)_2(C_2O_4)_2]\cdot H_2O$ [17]. Only few of them have been characterized structurally [14,15,17]. Unfortunately, most of these compounds contain alkali metals which are difficult to remove from the solid phase when they are used as oxide precursors.

In the present work, we dedicated a particular attention to peroxo-carboxylato compounds of general formula $A^I_3[Nb(O_2)_x(H_yL)]\cdot nH_2O$ (L: oxalate, tartrate, citrate) containing non-metallic counter-ions A^I like ammonium ($NH_4{}^+$) or guanidinium ($CN_3H_6{}^+$ or gu^+), which will leave no residue in the catalyst after calcination. This paper will describe fundamental research carried out on these Nb complexes, including structural analysis of some of them, and their application to the preparation of the silica-supported $Nb_2Mo_3O_{14}$ phase, by combining them with the analogous Mo-based precursors.

2. Experimental

2.1. Reagents

Oxalic acid dihydrate, $H_2ox\cdot 2H_2O$ (Merck), citric acid monohydrate, $H_4cit\cdot H_2O$ (Merck), DL-tartaric acid, H_4tart (ACROS Organics) and guanidinium carbonate, $(gu)_2CO_3$ (Aldrich) were commercial products used as received. Niobic acid, $Nb_2O_5\cdot nH_2O$ was supplied from CBMM (Brasil). Hydrogen peroxide, H_2O_2 (35 wt.%, ACROS), ammonium hydroxide, NH_4OH (25 wt.%), absolute ethanol and acetone were used without purification.

Silica (Merck, grade 10184, 291 m^2/g), Nb_2O_5 (Alfa Aesar, 99.9985%) and MoO_3 (Alfa Aesar, 99.95%) were used for the catalysts preparation without any pretreatment.

2.2. Synthesis of the niobium compounds

2.2.1. Preparation of $A^I_3[Nb(O_2)_4]$ (A^I: $NH_4{}^+$ and $CN_3H_6{}^+$)

Ammonium tetraperoxoniobate was prepared by treating a slurry of niobic acid (1 g) in distilled water (25 cm^3) with a 35 wt.% solution of H_2O_2 (25 cm^3) and ammonia (6 cm^3, 25 wt.% solution). The cloudy solution is agitated for a few hours. When the solid is totally dissolved, addition of acetone (100 cm^3) yields a white precipitate, which was filtered off, washed with acetone and air-dried.

The guanidinium derivative was prepared following the same way but replacing ammonia with $(gu)_2CO_3$ (1.75 g). The compound was obtained as a crystalline light-yellow solid. The slow evaporation at 5 °C of an aqueous concentrated solution yields small crystals (**1**) suitable for structure determination by single-crystal X-ray diffraction.

2.2.2. *Preparation of* $A^{I}_{3}[Nb(O_2)_2(ox)_2]\cdot nH_2O$ (A^{I}: NH_4^{+} *and* $CN_3H_6^{+}$)

$A^{I}_{3}[Nb(O_2)_4]$ (3.02 mmol) and $H_2ox\cdot 2H_2O$ (6.04 mmol) were dissolved in distilled water (10 cm^3) while stirring. The solution turns rapidly to a bright yellow colour. Addition of acetone (50 cm^3) yields a yellow microcrystalline solid, which was filtered off, washed with acetone and air-dried.

Small crystals of the guanidinium compound (**2**) were obtained by slow evaporation at room temperature of an aqueous concentrated solution.

2.2.3. *Preparation of* $(NH_4)_3[Nb(O_2)_3(H_2cit)]$

$(NH_4)_3[Nb(O_2)_4]$ (1.44 mmol) and $H_4cit\cdot H_2O$ (1.44 mmol) were dissolved in distilled water (10 cm^3) while stirring. The solution is treated with an excess of a 35 wt.% H_2O_2 solution (10 cm^3) and then evaporated up to a final volume of ca. 10 cm^3. Addition of ethanol (50 cm^3) yields a yellow oil which was decanted and stored at 5 °C in pure ethanol. After 24 h, a yellow highly hygroscopic solid was formed, filtered off under nitrogen, then washed with ethanol and dried under vacuum.

2.2.4. *Preparation of* $(NH_4)_3[Nb(O_2)_3(H_2tart)]\cdot 1.5H_2O$

$(NH_4)_3[Nb(O_2)_4]$ (1.44 mmol) and DL-H_4tart (1.44 mmol) were dissolved in distilled water (10 cm^3) while stirring. The solution is treated with an excess of a 35 wt.% H_2O_2 solution (10 cm^3) and then evaporated up to a final volume of ca. 10 cm^3. Addition of ethanol (50 cm^3) and storage at 5 °C yields a fine white solid, which was filtered off, washed with ethanol and air-dried.

2.3. *Preparation of Nb–Mo oxides*

2.3.1. *Ternary phase* $Nb_2Mo_3O_{14}$

The method used for the preparation of the $Nb_2Mo_3O_{14}$ phase was the ceramic route carried out under vacuum in order to prevent loss of MoO_3 by volatilization. A milled mixture of MoO_3 and Nb_2O_5 was heated at different temperatures for 3 h in an evacuated, sealed quartz tube.

2.3.2. *Silica-supported Nb–Mo–O catalysts*

The preparation routes investigated for the preparation of silica-supported Nb–Mo–O catalysts consisted in associating the synthesized peroxo-carboxylato niobium complexes with similar complexes of molybdenum, using an aqueous wet impregnation method (Fig. 1). The catalysts precursors were pre-calcined at 375 °C/20 h and then calcined in the same conditions as used for getting the pure phase.

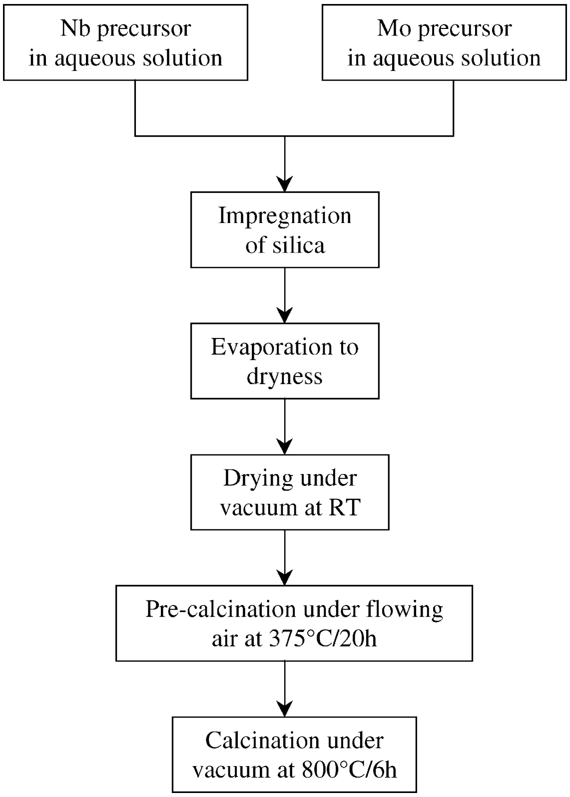

Fig. 1. Preparation scheme of silica-supported Nb–Mo–O catalysts.

The peroxo precursors were engaged in the molar ratio Nb/Mo = 2/3 corresponding to the stoichiometry of the pure phase $Nb_2Mo_3O_{14}$ ($(Nb + Mo)/SiO_2 = 20$ mol%).

2.4. *Characterization*

The obtained peroxo complexes were characterized on the basis of elemental analysis, infrared and ^{13}C-NMR spectroscopy. In view of their use as precursors for the oxide catalysts, their thermal behaviour was analysed by thermogravimetric analysis (TGA). C–H–N elemental analyses were carried out at the University College of London. IR spectra in the

4000–400 cm^{-1} range were recorded on a FTS-135 Bio-RAD spectrometer, using KBr pellets containing ca. 1 wt.% of the powder. TGA were performed in air at the heating rate of 10 °C/min using a Mettler Toledo TGA/SDTA851^e analyser. The ^{13}C-NMR spectra were recorded at 125 MHz in D_2O on a Bruker Avance 500 MHz spectrometer. The silica-supported catalysts were characterized by Raman spectroscopy, X-ray diffraction and surface area determination.

Raman spectra were recorded on a Renishaw spectrometer (type NIR 780TF Series Laser) at the wavelength of 785 nm. Powder XRD were carried out on a SIEMENS D-5000 diffractometer using the Cu Kα radiation. BET surface areas were measured with a Micromeritics ASAP 2000 analyser using nitrogen at 77 K.

2.5. *Structure determination for **1** and **2***

The crystallographic data are as follows:

(**1**) $C_3H_{18}N_9NbO_8$, Mr = 401.17, monoclinic, P*n*, $a = 8.603(3)$ Å, $b = 10.319(4)$ Å, $c = 8.895(3)$ Å, $\beta = 103.09(2)°$; $V = 769.1(5)$ Å^3, $D_x = 1.732$ g cm^{-3} for $Z = 2$. Mo Kα, $\lambda = 0.71069$ Å, $\mu = 0.835$ mm^{-1}, $R_1 = 0.029$ for 4189 observed reflections ($I \geq 2\sigma(I)$) and 0.030 for all 4361 data; wR$_2$ (all data) = 0.078. The intensities of the 16011 reflections (R int = 0.037) were collected from a crystal with dimensions 0.24 mm × 0.20 mm × 0.20 mm using a MAR345 image plate detector; θ ranges from 3.0 to 30°.

(**2**) $C_7H_{22}N_9NbO_{14}$, Mr = 549.24, monoclinic, P2$_1$/*n*, $a = 7.261(3)$ Å, $b = 26.735(9)$ Å, $c = 11.269(5)$ Å, $\beta = 104.08(2)°$; $V = 2122(1)$ Å^3, $D_x = 1.719$ g cm^{-3} for $Z = 4$. Mo Kα, $\lambda = 0.71069$ Å, $\mu = 0.651$ mm^{-1}, $R_1 = 0.047$ for 4497 observed reflections ($I \geq 2\sigma(I)$) and 0.050 for all 4772 data; wR$_2$ (all data) = 0.118. The intensities of the 44237 reflections (R int = 0.072) were collected from a crystal with dimensions 0.28 mm × 0.24 mm × 0.24 mm using a MAR345 image plate detector; θ ranges from 3.0 to 27.5°.

Both structures were solved by direct methods using SHELXS97 [18] and refined by full least-squares on F^2 with SHELXL97 [18]. All atoms, except those of the two water molecules in **2** which were located by Fourier difference, were calculated and included in the refinement with a common isotropic temperature factor.

3. Results and discussion

3.1. *Spectroscopic and chemical analysis of niobium compounds*

Table 1 lists, for each compound obtained, the results of the chemical analysis (C, H, N and H_2O) and the infrared bands assigned to some representative vibrational modes of the coordinated carboxylato and side-bonded peroxo ligands.

As far as the peroxo groups are concerned, the number of O–O stretching bands in the IR spectra of the peroxo-carboxylato complexes seems to be related to the number of peroxo groups present around the niobium atom. The spectra of the peroxo-oxalato compounds show two bands in the range 850–880 cm^{-1}, a

Table 1
Infrared and analytical data of Nb peroxo complexes[a]

Complex	Infrared data (cm^{-1})			Analytical data (%)[b]			
	ν_{as}(COO)	ν_s(COO)	ν(O–O)	C	H	N	H_2O[c]
$(NH_4)_3[Nb(O_2)_4]$	–	–	812m	0 (0)	4.13 (4.40)	15.01 (15.30)	–
$(gu)_3[Nb(O_2)_4]$	–	–	818m	0 (0)	4.81 (4.48)	31.44 (31.43)	–
$(NH_4)_3[Nb(O_2)_2(ox)_2]$	1725s, 1690s	1402m, 1390m	874m, 851m	11.96 (12.40)	3.80 (3.10)	10.58 (10.85)	–
$(gu)_3[Nb(O_2)_2(ox)_2]\cdot 2H_2O$	1716s, 1668s	1392m	867m, 853m	15.41 (15.30)	3.81 (4.01)	22.41 (22.95)	6.96 (6.56)
$(NH_4)_3[Nb(O_2)_3(H_2cit)]$	1614s	1400m	861m	17.54 (16.63)	4.32 (4.16)	8.49 (9.70)	–
$(NH_4)_3[Nb(O_2)_3(H_2tart)]\cdot 1.5H_2O$	1610s	1400m	849m	11.75 (11.48)	4.04 (4.55)	9.98 (10.05)	6.69 (6.46)

[a] s: strong, m: medium.

[b] Calculated values in parentheses.

[c] Calculated from the TGA.

spectral shape which is assigned to a diperoxo species [19]. Next to this, the spectra of the peroxo-citrato and peroxo-tartrato compounds display only one peroxo band at 861 and 849 cm^{-1}, respectively, which is consistent with the results obtained by Dengel and Griffith [12] for the analogous potassium triperoxo compounds of general formula $K_3[Nb(O_2)_3(L)]\cdot nH_2O$.

The asymmetric stretching frequency of the carboxylato groups complexed to niobium appears, in the citrate and tartrate compounds, as a strong broad band near 1600 cm^{-1}. The coordination of the niobium atom by these carboxylato groups is evidenced by the broadening of this ν_{as}(COO) band and by its shift from a value of ca. 1700 cm^{-1} in the free carboxylic acid to ca. 1600 cm^{-1} in the complex. In the oxalato complexes, this is more complicated because of the numerous vibration modes of the oxalato group [19].

The niobium peroxo complexes were also investigated with ^{13}C-NMR spectroscopy. The relatively low stability of the tartrate complex in aqueous solution made these measurements and their interpretation quite difficult. The spectrum of $[Nb(O_2)_2(ox)_2]^{3-}$ displays two very close peaks at the values of 166.4 and 166.5 ppm, intermediate between the single carbon peaks occurring in free oxalic acid (161.4 ppm) and ammonium oxalate (173.1 ppm). This spectral shape suggests that complexation implies differentiation of the two carbon atoms in the oxalate ligand. The ^{13}C-NMR spectrum of $[Nb(O_2)_3(H_2cit)]^{3-}$ resonance occurs at the following values (δ in ppm): 42.9, 45.5, 82.8, 177.9, 178.5 and 187.3. The lines arising at 42.9 and 45.5 ppm correspond to the CH_2 groups of the ligand. These carbons which are identical in the free acid (one band at 43 ppm), are differentiated in the complex because of the coordination. Moreover, the band corresponding to the quaternary hydroxyl-bearing carbon in the complexed citrate has undergone a significant shift from a value of 73.0 ppm in the free acid to 82.8 ppm, suggesting implication of this carbon in the complexation with niobium. Finally, the three resonance bands at 177.9, 178.5 and 187.3 ppm correspond to the quaternary carbon atoms of the three carboxylate groups. In the free acid, these lines appear as two peaks at 173.2 and 176.6 ppm. These ^{13}C-NMR results suggest that the citrate ligand is bidentate, with binding atoms being oxygens from one carboxylato group and the hydroxyl group. Complexation with niobium should thus result in a five-membered chelate ring. This experimental observation is consistent with the observation of Dengel and Griffith [12] that only carboxylate ligands which allow the formation of this type of chelate ring leads to peroxo-carboxylato complexes of niobium. The ^{13}C-NMR spectrum of $[Nb(O_2)_3(H_2tart)]^{3-}$ is more complicated and shows two groups of resonance centered around 85 and 180 ppm, likely to arise from the hydroxyl-bearing and carboxylate carbon atoms, respectively (they are observed in the free acid at 72.0 and 177.1 ppm). The complexity of the resonances suggests that some decomposition of the compound in solution may have occurred. We suggest that the tartrate ligand is bidentate, with binding atoms being oxygens from one carboxylate and one hydroxyl group. Complexation should lead in that way to the formation of a five-membered chelate ring.

3.2. Thermal behaviour of niobium compounds

The compounds $(NH_4)_3[Nb(O_2)_4]$ and $(gu)_3[Nb(O_2)_4]$ show a poor thermal stability. The thermograms display a vigorous exothermal decomposition with a drastic weight loss at 80 and 130 °C, respectively. In the case of the ammonium derivative, this decomposition is quite violent and leads to an explosion. The stability of such peroxo compounds can be enhanced upon substitution of several peroxo groups by carboxylate ligands [12]. The thermal behaviour of the ammonium oxalate, citrate and tartrate complexes is relatively similar. After dehydration, the compounds undergo a three-step degradation up to a final decomposition temperature into Nb_2O_5 of ca. 600 °C. The thermogram of the guanidinium oxalato compound displays an additional step, probably due to the counter-ion itself. The TGA of the compound $(NH_4)_3[Nb(O_2)_2(ox)_2]$ is illustrated in Fig. 2.

3.3. Crystal structure

In crystal **1**, as observed for $Na_3[Nb(O_2)_4]\cdot 13H_2O$ [14] and $KMg[Nb(O_2)_4]\cdot 7H_2O$, Nb is eightfold coordinated [15]. The four peroxide groups are bidentate and the coordination polyhedron is a dodecahedron. All the Nb–O distances are similar, ranging from 2.005(2) to 2.040(2) Å and the mean value of the O–O

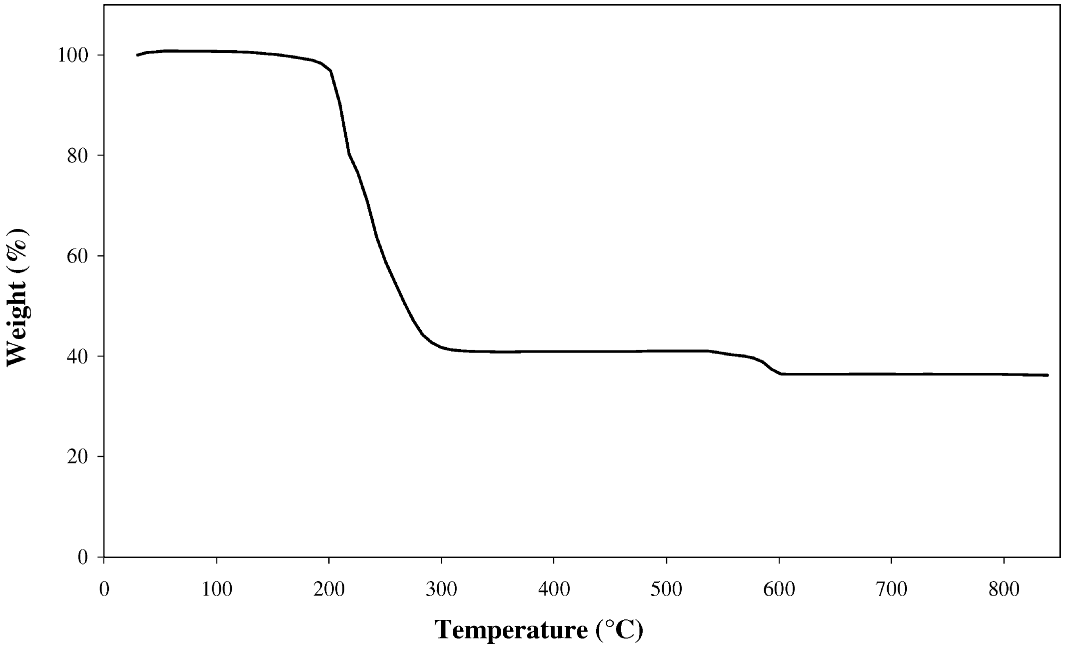

Fig. 2. TGA of the compound $(NH_4)_3[Nb(O_2)_2(ox)_2]$ in air (10 °C/min).

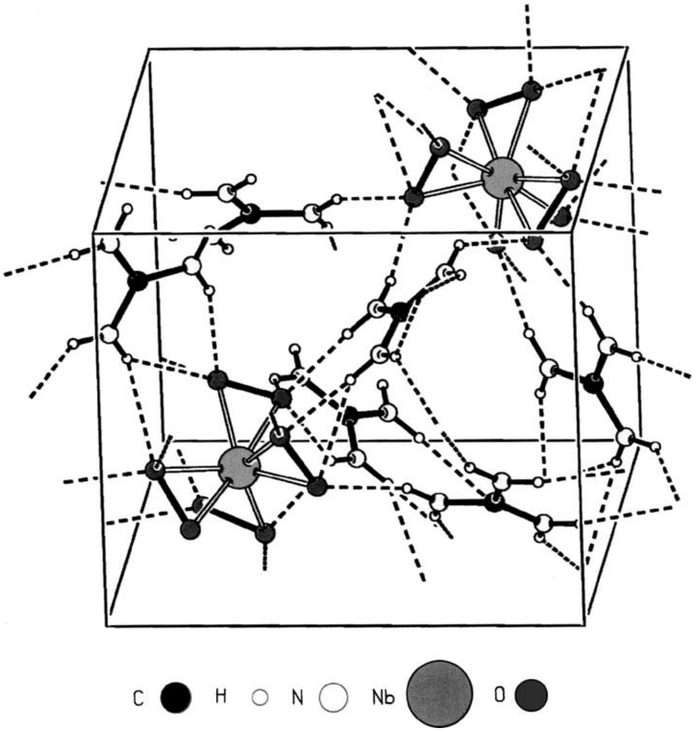

Fig. 3. Schematic view of the unit cell of $(gu)_3[Nb(O_2)_4]$ showing the hydrogen bond network.

bond length is 1.496(2) Å. The 18 hydrogen atoms of the cations are all involved in at least one hydrogen bond with one of the peroxo groups (Fig. 3).

In crystal **2**, the geometry of the anion $[Nb(O_2)_2(C_2O_4)_2]^{3-}$ is very similar to that reported by Mathern and Weiss [17] for the ammonium derivative. The coordination polyhedron is a dodecahedron and the two bidentate peroxide groups are in *cis* configuration. The mean values for Nb–O(peroxo) and Nb–O(oxalato) distances are respectively 1.978(2) and 2.128(2) and 1.482(3) Å for O–O bond length. As shown on the view of the unit cell (Fig. 4), all the guanidinium and water hydrogen atoms are involved in the hydrogen bond network.

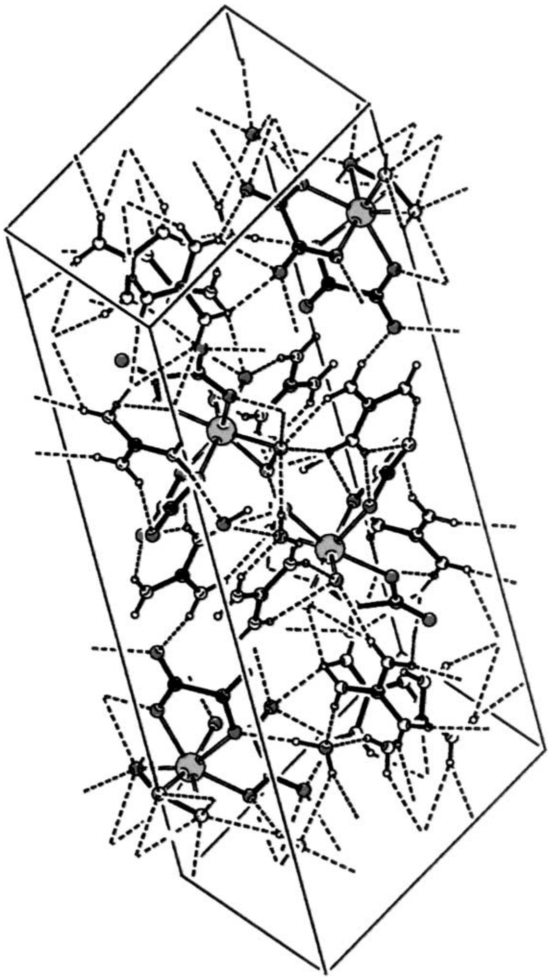

Fig. 4. Schematic view of the unit cell of $(gu)_3[Nb(O_2)_2(ox)_2]\cdot 2H_2O$ showing the hydrogen bond network (same symbols as in Fig. 3).

3.4. *Characterization of Nb–Mo oxides*

3.4.1. *Ternary phase $Nb_2Mo_3O_{14}$*

When using the ceramic method, formation of the dark green oxide $Nb_2Mo_3O_{14}$ was not observed at a temperature lower than 700 °C. At that temperature, the sample is still contaminated with the binary oxides, the ternary phase being obtained in pure form at 800 °C, with a very low specific surface area (0.91 m^2/g).

3.4.2. *Silica-supported Nb–Mo–O catalysts*

The different combinations of Nb and Mo precursors used for the preparation of silica-supported catalysts are listed in Table 2. The syntheses of the used peroxo-carboxylato compounds of molybdenum were adapted from those reported by Dengel et al. [20] for analogous potassium complexes. Crystal structures of most of them were determined and will be published elsewhere [21].

Fig. 5 allows to compare the XRD pattern of the silica-supported catalyst obtained from the peroxo-oxalato precursors with that of $Nb_2Mo_3O_{14}$ phase (JCPDS-file 18-840) and indicates the presence of this phase in almost pure form. Small amounts of the binary oxide MoO_3 (peak at $2\theta = 12.8°$) are actually detected. This spectrum displays also three unindexed peaks at 26.4, 30.4 and 38.9, which could be assigned to a phase resulting from a reaction between the Nb–Mo–O phases and the silica support.

The Raman spectrum of this Nb–Mo–O catalyst shows bands at the following values (cm^{-1}): 242m, 335w, 382w, 443w, 531w, 609m, 670m, 760s, 785s, 864m, 935m, 969m and is very similar to that obtained in $Nb_2Mo_3O_{14}$. This confirms the XRD results

Table 2
Combinations of Nb and Mo precursors used for the preparation of silica-supported Nb–Mo–O catalysts

Nb precursor	Mo precursor
$(NH_4)_3[Nb(O_2)_2(ox)_2]$	$(NH_4)_2[MoO(O_2)_2(ox)]$
$(NH_4)_3[Nb(O_2)_3(H_2cit)]$	$(NH_4)_2[MoO(O_2)_2(H_2cit)]$
$(NH_4)_3[Nb(O_2)_3(H_2tart)]\cdot 1.5H_2O$	$(NH_4)_2[MoO(O_2)_2(H_2tart)]\cdot 2H_2O$

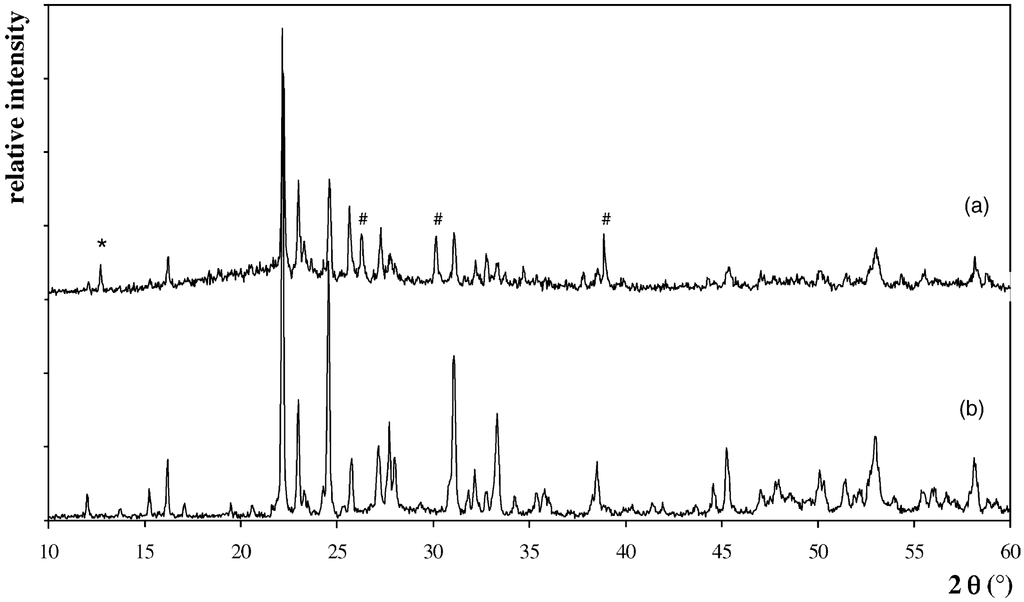

Fig. 5. X-ray diffraction pattern of (a) silica-supported Nb–Mo catalyst obtained from the peroxo-oxalato precursors (Nb/Mo = 2/3, (Nb + Mo)/Si = 10 mol%, T_{calc} = 800 °C) and (b) $Nb_2Mo_3O_{14}$ (T_{calc} = 800 °C) (★) MoO_3 and (#) unindexed peak.

although there is no evidence for Raman bands characteristic of MoO_3 (or Nb_2O_5). While the initial specific surface of the silica support was 291 m^2/g, this catalyst displays a BET surface of 4 m^2/g only, because of the drastic synthesis conditions used for the formation of the ternary active phase.

4. Conclusions

A series of peroxo and peroxo-carboxylato Nb(V) complexes has been synthesized and characterized. The crystal structures of two of them have been determined showing in both cases an eightfold coordination of Nb atoms displaying a dodecahedral geometry. Because of their high solubility in water (solution up to 1 M can be prepared), these compounds are shown to be useful precursors for mixed Nb–Mo oxide phases, when combining them with analogous peroxo-carboxylato complexes of Mo(VI). This procedure was successfully applied for the preparation of the $Nb_2Mo_3O_{14}$ phase supported on silica, although the severe experimental conditions required for the formation of the ternary phase result in samples with very low specific surface areas.

Acknowledgements

The authors thank the Belgian National Fund for Scientific Research (FNRS) for financial support, the CBMM company (Brasil) for supplying the niobic acid, Dr. B. Mathieu for carrying out the ^{13}C-NMR measurements and Prof. P.-P. Knops-Gerrits for access to the Raman equipment.

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