JOURNAL OF
Materials
CHEMISTRY

Synthesis and characterization of a new ruthenium containing LDH: [Zn–Al–$RuCl_5H_2O^{2-}$]

Jérôme Inacio,[a] Christine Taviot-Guého,*[a] Sandrine Morlat-Thérias,[b] Marie-Elisabeth de Roy[a] and Jean-Pierre Besse[a]

[a]Laboratoire des Matériaux Inorganiques, 63177 AUBIERE Cedex, France.
E-mail: gueho@chimtp.univ-bpclermont.fr
[b]Laboratoire de Photochimie Moléculaire et Macromoléculaire, 63177 AUBIERE Cedex, France

Received 1st June 2000, Accepted 8th November 2000
First published as an Advance Article on the web 5th January 2001

A new ruthenium containing LDH has been synthesized by exchanging chloride anions in [Zn–Al–Cl] with the aquapentachlororuthenate(III) complex: $[RuCl_5H_2O]^{2-}$. This intercalation has been investigated by various analytical methods such as powder X-ray diffraction, chemical analysis, FT-IR, thermogravimetric analysis and cyclic voltammetry. The exchange, carried out in acidic media, led to a decrease in the Zn/Al molar ratio suggesting a dissolution–reconstruction process or the formation of defective hydroxyl sheets. The interlayer free spacing and the presence of water molecules make it impossible to determine the orientation of the complex anion. The electrochemical study confirms the oxidation state as +3 for the ruthenium ions and demonstrates the difficulty in reducing them once intercalated.

Introduction

Layered double hydroxides (LDHs), also known as anionic clays, are lamellar mixed hydroxides with interlayer spaces containing exchangeable anions.[1,2] They are represented by the general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[A^{m-}_{x/m}\cdot nH_2O]^{x-}$ abbreviated hereafter as $[M^{II}–M^{III}–A]$ where M^{II}, M^{III} are divalent and trivalent elements and A^{m-} the gallery anion. The wide range of preparation methods and compositions make it possible to obtain materials with specific properties. Currently there is intense interest in finding uses for these materials in catalysis and as adsorbents.[3]

In this paper, we report the synthesis and the physicochemical characterization of a new ruthenium containing LDH prepared by exchanging chloride anions in [Zn–Al–Cl] with the aquapentachlororuthenate(III) complex $[RuCl_5H_2O]^{2-}$. The thermal behavior of this material and the reduction process of ruthenium located inside a layered double hydroxide matrix are also investigated.

LDHs intercalated with metal complex anions have drawn interest as catalysts and as materials for modified electrodes.[4,5] Here, we are interested in the synthesis of ruthenium supported catalysts. The insertion of noble metals inside the structure of precursors overcomes the problem of dishomogeneity and low stability often found for noble metal-based catalysts prepared by impregnation methods. Recently, ruthenium and rhodium ions were introduced into the brucite layer by isomorphic substitution of the cations at the octahedral sites.[6,7] In the field of environmental catalysis, such materials have shown excellent catalytic activities for the oxidation of alcohols in the presence of molecular oxygen and for N_2O decomposition.[8] Ru-based catalysts are also applied to the detoxification of chlorophenols in water.[9]

Experimental

Synthesis

The method of synthesis used was anion exchange. LDHs with different layer cations were tested but only with [Zn–Al–Cl] as the precursor was the exchange complete; total dissolution of [Mg–Al–Cl], [Cu–Cr–Cl], [Cu–Al–Cl] and [Zn–Cr–Cl] matrices was observed.

All syntheses were performed under a nitrogen atmosphere at room temperature using freshly boiled deionized water.

[Zn–Al–Cl] precursor, with a Zn/Al molar ratio of 3, was prepared by the coprecipitation method[10] at a constant pH of 8.5 ± 0.1, by reacting an aqueous solution of $AlCl_3$ ($0.25\ mol\ L^{-1}$)/$ZnCl_2$ ($0.75\ mol\ L^{-1}$) with a $2\ mol\ L^{-1}$ NaOH solution. The precipitate was aged in the mother solution for 24 h, then recovered by three centrifugation cycles in water and dried under dynamic vacuum.

Anion exchange with $[RuCl_5H_2O]^{2-}$ was carried out as follows: 20 mg of [Zn–Al–Cl] precursor was dispersed in 50 ml of water (pH = 5.0) and added to 50 ml of a $10^{-3}\ mol\ L^{-1}$ solution of $K_2RuCl_5H_2O$ (pH = 3.8); the mixture was stirred for 4 h. During the exchange, the pH remained around 4. The resulting dark green material was washed and dried in a similar way to the precursor.

According to the literature,[11] $K_2RuCl_5H_2O$ gives an acidic aqueous solution which slowly decomposes at room temperature in air and in basic media. First, the color changes from red to yellow-brown which is ascribed to the exchange of chloride ligands by water molecules giving rise to $[RuCl_2(H_2O)_4]^+$ species. Then, oxidation takes place resulting in a black solid $Ru(OH)_3$. Note that under our conditions, no color change of the supernatant solution was observed which remained reddish throughout the exchange process.

Characterization

Elemental analyses were performed at the Centre d'Analyses de Vernaison, CNRS, France. The powder X-ray diffraction (PXRD) patterns were recorded on a Siemens D501 diffractometer using Cu-Kα radiation (step: 0.08° 2θ; count time: 4 s). Infrared transmission spectra were recorded on a Perkin Elmer 2000 FT spectrometer using the KBr pellet technique (1 wt.% sample in KBr). Thermogravimetric analyses (TGA) were performed on a Setaram TG/DTA92 instrument. The samples were heated at a scan rate of $5\ °C\ min^{-1}$ under an Ar

DOI: 10.1039/b004375n

atmosphere. The evolved gases were analyzed in parallel to the thermal analyses using a Balzers mass spectrometer MS-Cube MSC 200. Specific surface areas were derived from nitrogen adsorption isotherms measured on a Fisons SP 1920 instrument at liquid nitrogen temperature, after degassing the samples at 80 °C for 6 h. Cyclic voltammetric studies were performed with glassy carbon electrodes either on a bare electrode (denoted GC) or on an LDH modified electrode (denoted GC/LDH). Aliquots of 10 μL of 1 g L^{-1} of a LDH suspension in water were deposited by syringe on an electrode rotating at 35 revolutions per minute to allow the formation of a homogeneous film during drying (30 min). Electrochemical experiments were performed with a three-electrode cell and an EG&G PAR model 273 potentiostat. The three-electrode cell was equipped with a working electrode, a platinum counter-electrode and a saturated calomel reference electrode (SCE). During all experiments, it was maintained under an inert atmosphere (Ar) at room temperature.

Results and discussion

The chemical formulae of the compounds were calculated by combining the results of the chemical and thermogravimetric analyses (Table 1). The decrease in the Zn/Al atomic ratio upon intercalation of $[RuCl_5H_2O]^{2-}$ anions indicates a partial dissolution of Zn^{2+} ions from the hydroxide layers, which is explained tentatively below. Both materials exhibit diffraction patterns characteristic of a layered structure (Fig. 1). However, the exchanged material, $[Zn–Al–RuCl_5H_2O]$, is much less crystalline than the precursor; this is likely to be caused by structural disorder or small particle size. The crystallographic parameters are calculated for a hexagonal cell on the basis of a rhombohedral *R*-3*m* symmetry. For [Zn–Al–Cl], they were refined by a least-squares procedure while for $[Zn–Al–RuCl_5H_2O]$, due to the poorness of the structural information, only approximate values could be determined using the 110 and 003 reflections. The increase in the interlamellar distance for the exchanged compound, 10.14 Å, in comparison with that determined for the precursor, 7.79 Å, and the fact that the 006 reflection is of greater intensity than the 003 reflection are consistent with the presence of $[RuCl_5H_2O]^{2-}$ species in the interlayer space. As already noticed, the Zn/Al atomic ratio decreases drastically during the exchange process, from 3.12 to 1.44, which induces a visible shift of the 110 peak. The corresponding values of the lattice parameters *a*, 3.08 Å and 3.06 Å respectively, agree well with previous studies on the variation of the lattice parameter *a* as a function of the Zn/Al ratio[12] which eliminates the possibility of Ru incorporation. Owing to the acidic conditions required by $[RuCl_5H_2O]^{2-}$ anions, a partial dissolution of the divalent ions of the brucite-like layers or a dissolution–reconstruction process might explain this lowering of the Zn/Al ratio. Note that the obtention of defective sheets, after exchange reaction carried out in rather acidic media, has already been reported for the synthesis of pillared clays with Keggin ions.[13]

Using Miyata's reported sheet thickness of 4.8 Å, an interlayer free spacing of 5.74 Å is obtained for $[Zn–Al–RuCl_5H_2O]$. This value is higher than any end-to-end distances of pseudo-octahedral $[RuCl_5H_2O]^{2-}$: the longest distances are along the C_4 axis Cl–Ru–O 4.43 Å and in the equatorial plane Cl–Ru–Cl 4.66/4.78 Å.[11] The presence of water molecules is likely to enlarge the basal spacing thus making it impossible to ascertain the actual orientation of the interlayer anion.

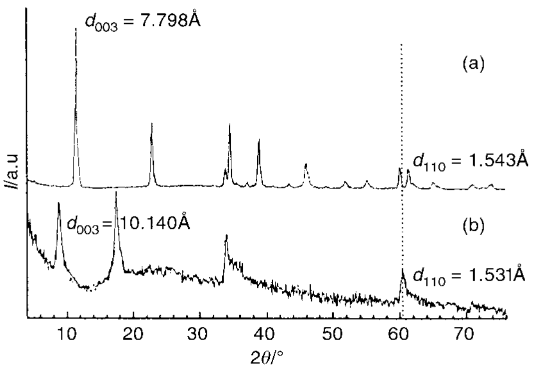

Fig. 1 PXRD patterns of (a) [Zn–Al–Cl] and (b) $[Zn–Al–RuCl_5H_2O]$.

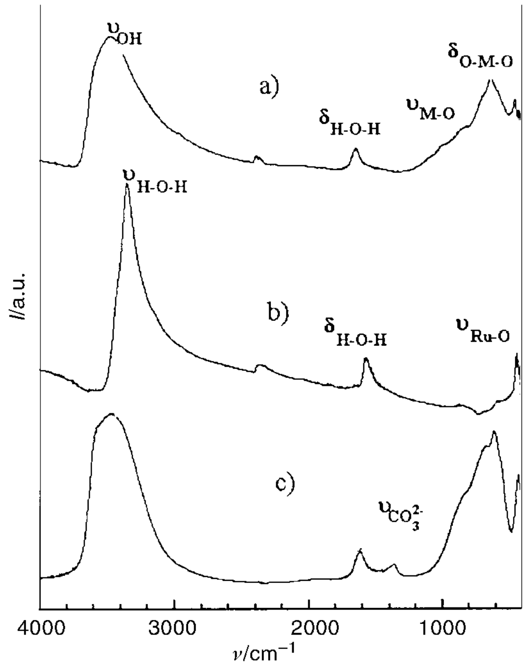

Fig. 2 IR spectra of (a) [Zn–Al–Cl], (b) $[K_2RuCl_5H_2O]$ and (c) $[Zn–Al–RuCl_5H_2O]$.

Fig. 2 shows the infrared spectra of $K_2[RuCl_5H_2O]$, [Zn–Al–Cl] and $[Zn–Al–RuCl_5H_2O]$. For the salt, the broad band at *ca.* 3323 cm^{-1} is caused by the stretching vibration of water molecules ($\nu_{H–O–H}$), the corresponding bending vibration is at 1557 cm^{-1} ($\delta_{H–O–H}$) and the absorption at 430 cm^{-1} is due to an Ru–O stretching vibration ($\nu_{Ru–O}$).[14] As these bands coincide with those of the LDH matrix, the infrared spectrum of the exchanged material is virtually the same as the precursor: in addition to Ru–O bonds, the adsorption bands in the low wavenumber range are due to lattice modes; the broad adsorption close to 3400 cm^{-1} is assigned to the stretching of hydroxyl groups ($\nu_{O–H}$) and the medium band at 1620–1640 cm^{-1} to the deformation mode of water molecules existing in the interlayer including that of the complex ($\delta_{H–O–H}$). We also note the presence of a small amount of

Table 1 Chemical compositions and surface areas of [Zn–Al–Cl] and $[Zn–Al–RuCl_5H_2O]$

	Zn/Al molar ratio	Cl content/wt.%	Chemical formula[a]	Surface area/m^2 g^{-1}
[Zn–Al–Cl]	3	9.36	$Zn_{3.03}Al_{0.97}(OH)_8Cl_{1.19}\cdot 2.6H_2O$	30
$[Zn–Al–RuCl_5H_2O]$	1.44	25.33	$Zn_{2.35}Al_{1.65}(OH)_8Ru_{0.96}Cl_{4.80}(H_2O)_{0.96}\cdot 3.0H_2O$	54

[a] Calculated on the basis of the chemical analysis and the thermogravimetric analysis.

carbonate species, probably located on the surface of the material. This slight contamination is likely to occur during the washing/centrifuging cycles and has often been reported for LDHs owing to their basic character.[15] Besides, the chemical analysis indicates that the amount of $[RuCl_5H_2O]^{2-}$ anions exactly balances the positive charge of the main layers thus excluding the presence of carbonate anions in the interlamellar space.

The results of the thermal gravimetric analyses (TG and DTG) are shown in Fig. 3. The thermal decomposition mechanism of LDHs has been extensively studied.[16] [Zn–Al–Cl] decomposes in three steps: up to 200 °C, there is a loss of adsorbed and interlamellar water molecules; between 200 and 300 °C, dehydroxylation occurs; the third weight loss takes place at 450 °C and corresponds to the removal of chloride anions. Comparing the thermogravimetric curves before and after anion exchange reveals two clear differences: first, the weight loss below ≈300 °C is reduced in quantity for the exchanged materials and secondly, three distinctive steps are observed between ≈300–650 °C related to the presence of $[RuCl_5H_2O]^{2-}$ anions. In order to determine the nature of the species decomposing, we performed mass spectrometric analysis of the expelled gases. It appears that, while the dehydroxylation is principally completed at ≈300 °C in the precursor, it spreads out over a large temperature region ≈200–400 °C in the exchanged compound and partly overlaps the decomposition of interlayer $[RuCl_5H_2O]^{2-}$ anions. Indeed, mass spectrometric analysis indicates the release of water molecules only at *ca.* 330 °C (5 wt.%) and both HCl and Cl_2 gases (15 wt.%) between ≈350–450 °C. The last weight loss (15 wt.%) from ≈450 °C upwards corresponds exactly to the departure of three chloride ions. Hence, intercalated $[RuCl_5H_2O]^{2-}$ anions decompose in three steps: first, the removal of the water ligand at *ca.* 330 °C, then the departure of two chloride ligands between ≈350–450 °C and finally, the three remaining, strongly held, chloride ligands between ≈450–650 °C. The expected weight losses for a water molecule (2.5 wt.%) and two chloride ligands (10 wt.%) are lower than the experimental TG values obtained. The difference is due to concomitant dehydroxylation and interlayer anion decomposition that may be explained by a strengthening of the interaction between the brucite-like layer and the interlayer caused by more and/or stronger H bonds.

It is interesting to note that the thermal decomposition of $[RuCl_5H_2O]^{2-}$ is somewhat delayed when intercalated into LDH, shifted from 250 °C for the salt to 330 °C for [Zn–Al–$RuCl_5H_2O$]. Furthermore, although the temperatures are different, the three decomposition steps of the salt correspond exactly to the same losses as in the intercalate *i.e.* first the water molecule, then two chloride ions and finally, the three remaining chloride anions.

Fig. 4 shows the PXRD patterns of [Zn–Al–$RuCl_5H_2O$] calcined for 24 h in air at temperatures that thermogravimetric analysis indicates correspond to the formation of thermally stable phases. At 150 °C, all the peaks corresponding to LDH are retained with reduced intensities. From 250 °C upwards, the layered structure collapses through dehydroxylation leading to an amorphous pattern. At 150 °C in [Zn–Al–Cl], weak diffraction lines attributed to ZnO are recorded while its formation in [Zn–Al–$RuCl_5H_2O$] is only evidenced around 400 °C together with RuO_2. This cannot be considered as further evidence of the stabilization of the hydroxyl sheets for [Zn–Al–$RuCl_5H_2O$] since the Zn/Al molar ratio is very different from that in the precursor and also because of the poor signal-to-noise ratio of the PXRD patterns. At 800 °C, in addition to ZnO and RuO_2 phases, $ZnAl_2O_4$ spinel could also be present. With [Zn–Al–Cl], the spinel phase appears at lower temperature, around 700 °C.[17]

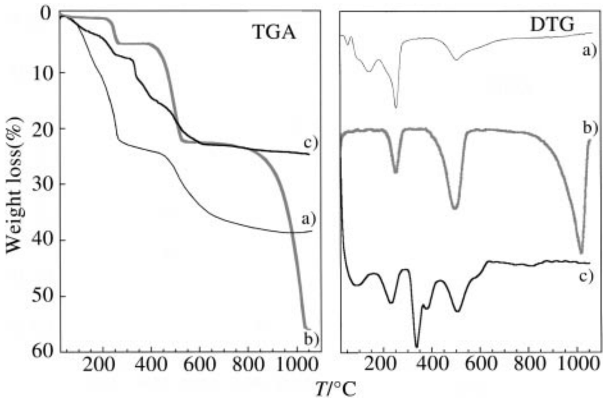

Fig. 3 Thermogravimetric (TG and DTG) curves of (a) [Zn–Al–Cl], (b) [$K_2RuCl_5H_2O$] and (c) [Zn–Al–$RuCl_5H_2O$].

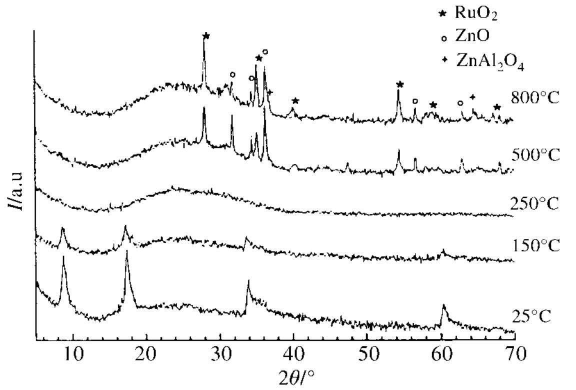

Fig. 4 PXRD patterns of [Zn–Al–$RuCl_5H_2O$] calcined at different temperatures in air.

In order to fully characterize [Zn–Al–$RuCl_5H_2O$], we looked at the reduction of intercalated ruthenium. In Figs. 5 and 6, we

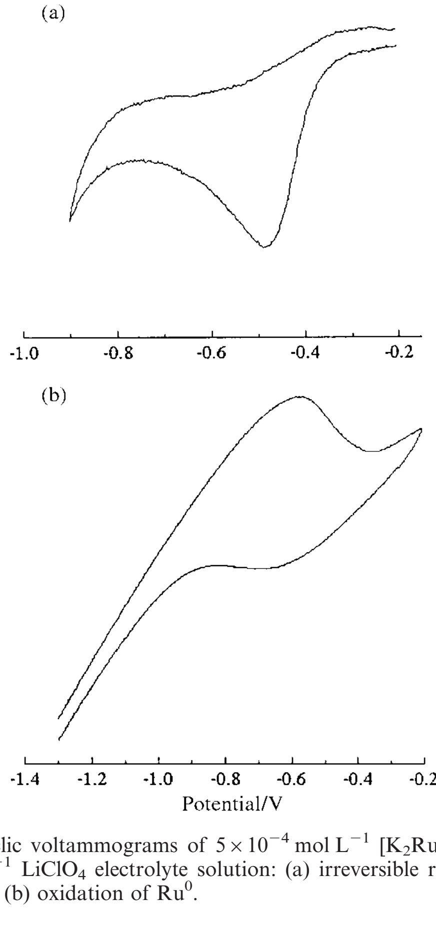

Fig. 5 Cyclic voltammograms of 5×10^{-4} mol L^{-1} [$K_2RuCl_5H_2O$] in 0.1 mol L^{-1} $LiClO_4$ electrolyte solution: (a) irreversible reduction of Ru^{3+} and (b) oxidation of Ru^0.

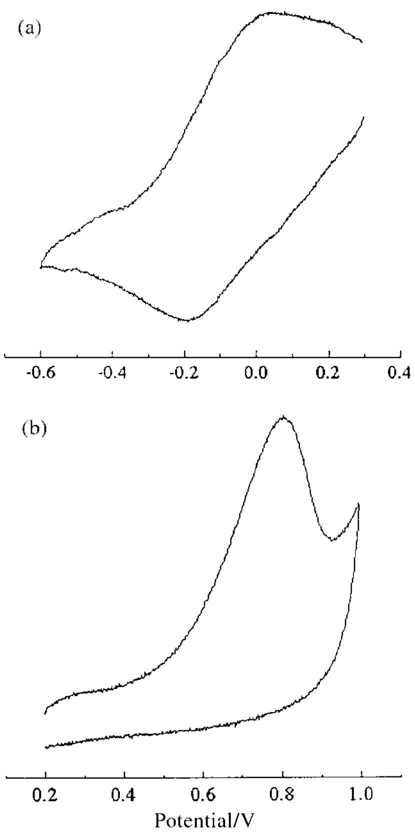

Fig. 6 Cyclic voltammograms of [Zn–Al–$RuCl_5H_2O$]-modified electrode: (a) reversible reduction of Ru^{3+} and (b) irreversible oxidation of Ru^{3+}.

compare the cyclic voltammetric plots obtained with $K_2[RuCl_5H_2O]$, in the first case, solubilized in aqueous solution using a glassy carbon electrode, and in the second case, when it is immobilized on LDH-modified electrodes. The literature shows different electrochemical behavior according to the nature of the ligand on the ruthenium complex.[18,19] At a glassy carbon electrode in electrolyte solution (0.1 M $LiClO_4$), the voltammogram of $K_2[RuCl_5H_2O]$ complex (Fig. 5(a)) exhibits an irreversible reduction wave at $E_{pc} = -0.48$ V corresponding to $Ru^{3+} + e^- \rightarrow Ru^{2+}$. When a more negative potential is applied (-1.3 V), we can see hydrogen bubbles and a metallic deposit on the electrode surface. Then, the voltammetric cycle (Fig. 5(b)) shows an oxidation wave at $E_{pa} = -0.57$ V which can be attributed to the oxidation of $Ru^0 \rightarrow Ru^{2+} + 2e^-$. The decrease in the cathodic peak intensity obtained for different voltammetric cycles with a GC/[Zn–Al–$RuCl_5H_2O$]-modified electrode (Fig. 6(a)) shows a quasi-reversible reduction of $Ru^{3+} + e^- Ru^{2+}$ (-0.2 V), even after proton reduction and no metallic deposit appears on the LDH film. Furthermore, the Ru^{3+} ions can be irreversibly oxidized to Ru^{4+} at $E_{pa} = 0.81$ V (Fig. 6(b)). Hence, when $[RuCl_5H_2O]^{2-}$ species are intercalated into LDH, the electrochemical response appears to be more stable and the reduction of Ru^{3+} ions occurs at less negative potential. While the $[RuCl_5H_2O]^{2-}$ complex in solution can be reduced by hydrogen to metallic ruthenium, when it is intercalated, the ruthenium ions are less accessible and no more Ru^0 can be generated. On the other hand, this electrochemical study confirms the oxidation state +3 of ruthenium ions in [Zn–Al–$RuCl_5H_2O$].

References

1 F. Trifiro and A. Vaccari, *Comprehensive Supramolecular Chemistry*, J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vogtle, eds., Pergamon, Oxford, 1996; vol. 7, p. 251.

2 A. de Roy, *Mol. Cryst. Liq. Cryst.*, 1998, **311**, 173.

3 (*a*) A. Vaccari, *Appl. Clay Sci.*, 1999, **14**, 161; (*b*) F. Malherbe, C. Depège, C. Forano, J. P. Besse, M. P. Atkins, B. Sharma and S. R. Wade, *Appl. Clay Sci.*, 1998, **13**, 451; (*c*) F. Malherbe, C. Forano, B. Sharma, M. P. Atkins and J. P. Besse, *Appl. Clay Sci.*, 1998, **13**, 381; (*d*) I. Rousselot, C. Taviot-Guého and J. P. Besse, *Int. J. Inorg. Mater.*, 1999, **1**, 165.

4 V. Rives and M. A. Ulibarri, *Coord. Chem. Rev.*, 1999, **181**, 61.

5 E. P. Giannelis, D. G. Nocera and T. J. Pinnavaia, *Inorg. Chem.*, 1987, **26**, 203.

6 F. Basile, L. Basini, G. Fornasari, M. Gazzano, F. Trifiro and A. Vaccari, *Chem. Commun.*, 1996, 2435.

7 T. Matsushita, K. Ebitani and K. Kaneda, *Chem. Commun.*, 1999, 265.

8 H. C. Zeng and X. Y. Pang, *Appl. Catal. B*, 1997, **13**, 113.

9 V. Felis, C. De Bellefon, P. Fouilloux and D. Schweich, *Appl. Catal. B*, 1999, **20**, 91.

10 S. Miyata, *Clays Clay Miner.*, 1975, **23**, 369.

11 E. A. Seddon and K. R. Seddon, *The Chemistry of Ruthenium*, R. J. H. Clark, ed., Elsevier, Amsterdam, 1984.

12 M. Khaldi, Materials Science Thesis, University of Clermont-Ferrand, France, 1995.

13 J. Wang, Y. Tian, R. C. Wang and A. Clearfield, *Chem. Mater.*, 1992, **4**, 1276.

14 N. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York, 1986.

15 T. Hibino, Y. Yamashita, K. Kosuge and A. Tsunashima, *Clays Clay Miner.*, 1995, **4**, 427.

16 T. Hibino, Y. Yamashita, K. Kosuge and A. Tsunashima, *Clays Clay Miner.*, 1995, **43**, 427.

17 V. Prevot, C. Forano, F. Abraham and J. P. Besse, *Inorg. Chem.*, 1998, **37**, 4293.

18 M. N. Collomb Dunand-Sauthier, A. Deronzier and M. Navarro, *Chem. Commun.*, 1996, 2165.

19 K. M. Kadish, V. A. Adamian, E. Van Caemelbecke, Z. Tan, P. Tagliesta, P. Bianco, T. Boschi, G. B. Yi, M. A. Khan and G. B. Richter-Addo, *Inorg. Chem.*, 1996, **35**, 1343.