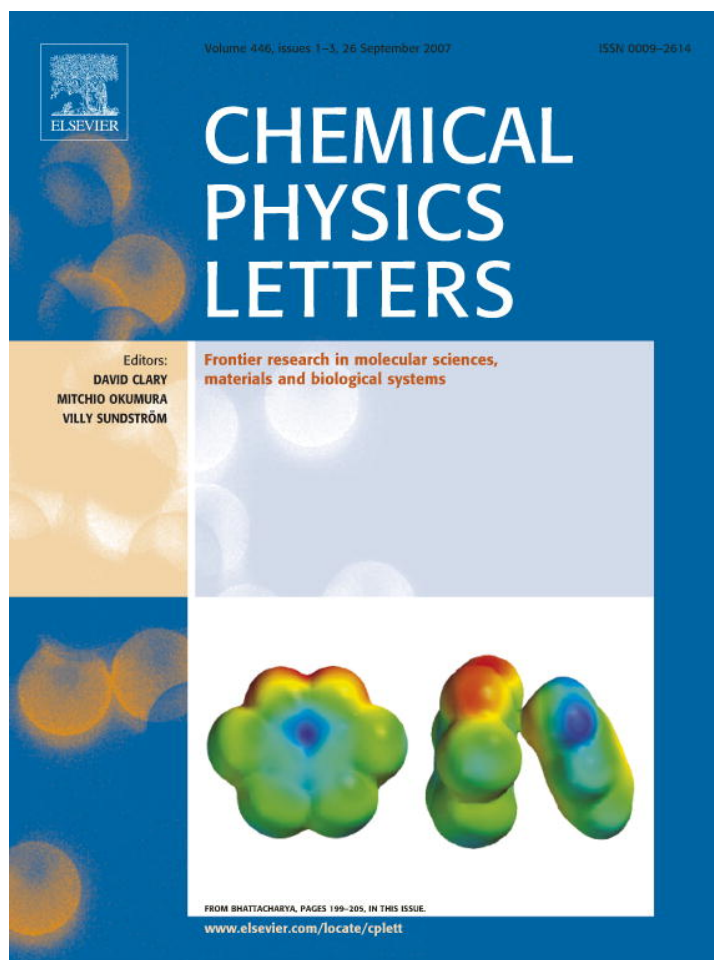


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Pure niobia as catalyst for the oxidation of organic contaminants: Mechanism study via ESI-MS and theoretical calculations

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Abstract

In this work, synthetic and natural niobium oxide (niobia), were used to promote the oxidation of methylene blue dye. The samples were characterized by XRD, XPS and FTIR measurements. The presence of reactive species on the surface of the samples strongly increases the oxidation rate of the methylene blue dye. The reaction mechanism was studied by ESI-MS analyses. Moreover, kinetic data and XPS spectroscopy suggest that the oxidation of the organic dye involves oxidizing species mainly generated after previous treatment with H₂O₂. The results also showed that the oxidation takes place by a homolytic mechanism via radical intermediates.

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1. Introduction

It has been reported that niobium is interesting and important for some catalytic reactions, and then the research and development of niobium compounds in catalytic applications have increased in recent years [1]. However, the use of pure niobium oxides as a catalyst for the oxidation of contaminants in aqueous medium is scarce in bibliography. It has been reported a study with niobium oxides as a catalyst for hydroxylation, but combined with an inorganic cation at high temperature [2]. In general, research focuses on the study of the catalytic performance of Nb₂O₅ impregnated with metal oxides [3]. The particular properties of the niobium, such as, redox properties, photosensitivity, acidity and catalytic behaviour [4], constitute the motivation to understand and use niobium for catalytic purposes.

In the present work it has been studied the reactivity of the species generated on the niobium oxide samples. Some

experiments have been carried out to study the effects of natural and synthetic Nb₂O₅ on the degradation of organic dye in the presence of hydrogen peroxide. The reaction mechanism of the heterogeneous dye/niobia/H₂O₂ system, has been studied on-line by ESI-MS and theoretical calculations.

2. Experimental

2.1. Materials and characterization

Three different materials has been used: (i) a natural niobia supplied by CBMM – Companhia Brasileira de Metalurgia e Mineração (CBMM niobia); (ii) a synthetic niobium oxide (synthetic niobia) and (iii) this same synthetic sample previously treated with H₂O₂ (synthetic niobia//H₂O₂). Synthetic niobia was prepared from NH₄[NbO(C₂O₄)₂(H₂O)] (H₂O)_n and NaOH (50 mL, 1 mol L⁻¹) by co-precipitation followed by thermal treatment at 60 °C for 72 h [5].

XRD measurements of the samples have been carried out with a SIEMENS D-5000, powder diffractometer at 40–50 mA, equipped with a variable slit, a diffracted beam

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monochromator, and a scintillation counter. The diffractograms have been recorded in the range 2θ (10 – 80°) with a speed of $0.5^\circ \text{ min}^{-1}$ using Cu $K\alpha$ radiation (1.5418 \AA).

The recorded spectra obtained from the FT-IR spectrometer (Digilab Excalibur, FTS 3000) have been processed with the IRDM (IR data manager) program. The specimens were pressed into small discs using a spectroscopically pure KBr matrix.

XPS has been performed by using Mg $K\alpha$ radiation ($h\nu = 1253.6 \text{ eV}$) and VG hemispherical electron-energy analyser using a pass energy of 20 eV . The pressure of the chamber during the measurement was around 10^{-9} Torr. The binding energies were corrected for the charging effect by assuming a constant binding energy for the adventitious C1s peak of 284.6 eV .

The oxidation of 50 mg L^{-1} methylene blue dye with H_2O_2 (0.3 mol L^{-1}) at pH 6.0 has been performed by using a total volume of 10 mL and 10 mg of the oxide catalyst. The reactions have been monitored by UV–vis measurements (Shimadzu-UV-1601 PC) in a recirculating controlled temperature bath kept at $25 \pm 1^\circ \text{ C}$.

2.2. Studies by ESI-MS

The analysis of the solution composition after the reaction has been accomplished by introducing aliquots of the solution into the ESI source (Agilent MS-ion trap mass spectrometer) with a syringe pump at a flow rate of 5 mL min^{-1} . The spectra were obtained as an average of 50 scans of 0.2 s each. Typical ESI conditions were as follows: capillary temperature of 1508° C ; carrier gas (N_2) at a flow rate of 20 units (ca. 4 L min^{-1}); spray voltage of 4 kV ; capillary voltage of 25 V ; tube lens offset voltage of 25 V .

2.3. Computational methods

The calculations have been achieved by the GAUSSIAN98 package [6]. Each involved transition, intermediate and precursor states were calculated and fully optimized by DFT. The energy profile at the selected DFT geometries along the reaction pathway has been computed at B3LYP theory level using the 6-31+G(d,p) basis set. This computational procedure has been previously employed on similar systems successfully [7]. Furthermore, after each optimization the nature of stationary point was established by calculating and diagonalizing the Hessian matrix (force constant matrix). The solvent effect was evaluated using the polarized continuum model (PCM), initially proposed by Barone et al. [8].

3. Results and discussion

3.1. Methylene blue dye oxidation

It has been observed that there was not significant discoloration of the methylene blue solution in contact with the H_2O_2 solution in absence of niobia. In the presence

of the synthetic niobia catalyst a slight discoloration is observed at the beginning, followed by a significant discoloration (Fig. 1a) after 90 min of reaction. Total discoloration took place after 150 min. This sample, after a previous treatment with hydrogen peroxide (synthetic niobia// H_2O_2), showed a strong discoloration at 90 min, indicating that the treatment with H_2O_2 improves the catalytic activity in the oxidation of the dye.

The natural sample, CBMM niobia, showed a high removal of the dye after 60 min of reaction, but with the leaching of the niobium from the Nb_2O_5 . After the oxidation reaction, we removed the solid niobia by filtration followed of centrifugation and then the niobium concentration was analysed using plasma emission spectroscopy. From those data, we did not observe any leaching from the synthetic niobia. On the other hand, in the case of CBMM niobia, the soluble niobium was determined with the discoloration of the methylene blue dye solution.

The catalytic activity showed by the synthetic niobia can be due to the surface groups, known as niobium peroxo complexes [9,10], formed by the presence of H_2O_2 . These peroxo species are potentially oxygen donors to organic substrates in the liquid phase [11]. Moreover, Bayot et al. [12] reported that these species can act as catalysts in the presence of oxidizing agents, like H_2O_2 , which is used to regenerate *in situ* the formation of the niobium peroxo species (Fig. 1b). The removal capacity is only improved after

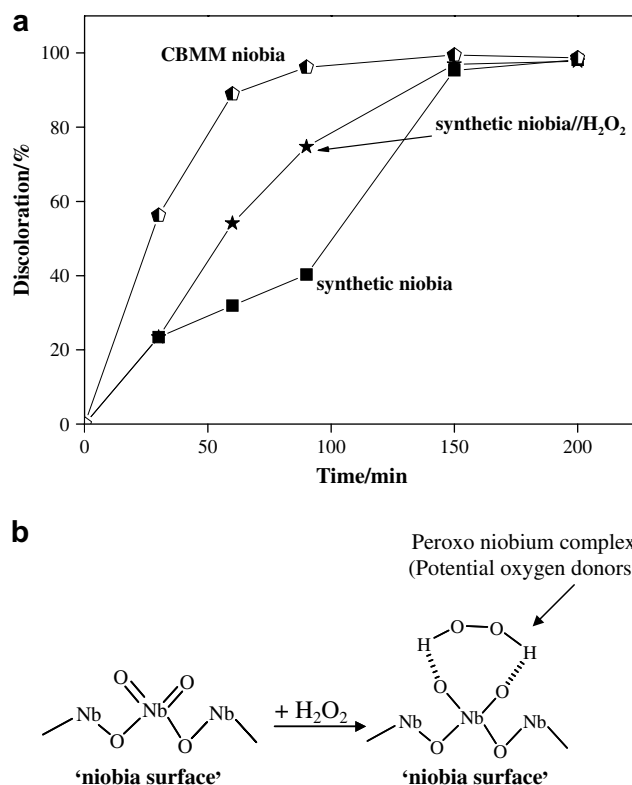


Fig. 1. Discoloration of methylene blue dye with niobia and hydrogen peroxide monitored by UV–visible spectrometry (a) and scheme of the formation of peroxo niobium complex on niobia surface (b).

90 min of reaction because this is the required time to form peroxy complexes on the catalysts surface. These considerations can also be used to explain why the activity of the synthetic niobia previously treated with H_2O_2 is higher than the untreated synthetic niobia.

3.2. Identification of intermediates species via on-line ESI-MS monitoring

The identification of reaction intermediates was performed on-line by the ESI-MS equipment during the oxidation of the methylene blue dye (Fig. 2). It is interesting to observe that the signal corresponding to $m/z = 284$ was mainly detected up to 90 min of reaction for the synthetic niobia, suggesting a slight removal of the methylene blue dye by adsorption. After 150 min of reaction strong signals corresponding to $m/z = 300$; 316 and 332 are detected, due to successive hydroxylation of the dye structure.

The catalytic activity of a synthetic niobia sample previously treated with H_2O_2 was tested. This previous treatment leads to much higher catalytic activity for the synthetic niobia. Actually, from Fig. 2b, the increasing number of reaction intermediates can clearly be observed after 45 min of reaction. Moreover, at 150 min of reaction the total removal of color was observed, as well as the appearance of signals corresponding to $m/z = 160$ and 320.

Based on the previously published articles [13,14] and the results from Fig. 2 we could propose that the reaction initiated with the activation of H_2O_2 by niobia was followed by the transference of the $\cdot\text{OH}$ radical to the organic dye, producing different fragment compounds as showed

by the intense signals. The proposed mechanism was based on the activation of H_2O_2 via a Haber Weiss mechanism to form a radical $\cdot\text{OH}$ as suggested by ESI-MS data. It has been previously reported that it is difficult to differentiate among a heterolytic, Mars-van Krevelen-type mechanism, and competing homolytic pathways via radical intermediates [15–17].

To date, no other similar studies with niobium samples dedicated to the research of methylene blue degradation via a heterogeneous mechanism has been reported. We strongly consider that this work could be helpful to shed some more light on the use of niobia as a catalyst for the oxidation of contaminants in aqueous medium.

3.3. Reaction mechanism

The calculation of the Gibbs free energy for the stability of the intermediates was performed by the method implemented in the GAUSSIAN98 package [6]. The resulting energies values are shown in Table 1. Previous works [13,18] put in evidence that intense fragment corresponding to $m/z = 300$ (Fig. 2) result from the hydroxylation in the aromatic ring. According to data listed in Table 1, it can be observed that the hydroxyl group at C2 position is about $+3.30$ and $+6.65$ kcal mol $^{-1}$ more stable than the alternative C3 and C5, respectively. Further calculations revealed that the hydroxylation occurs at C4, which explains the resulting intense fragment corresponding to $m/z = 316$. Thus, compounds II and III (Fig. 3) are supposed to be stable and the reaction path may still involve other hydroxylations. From these results, the third hydroxylation would

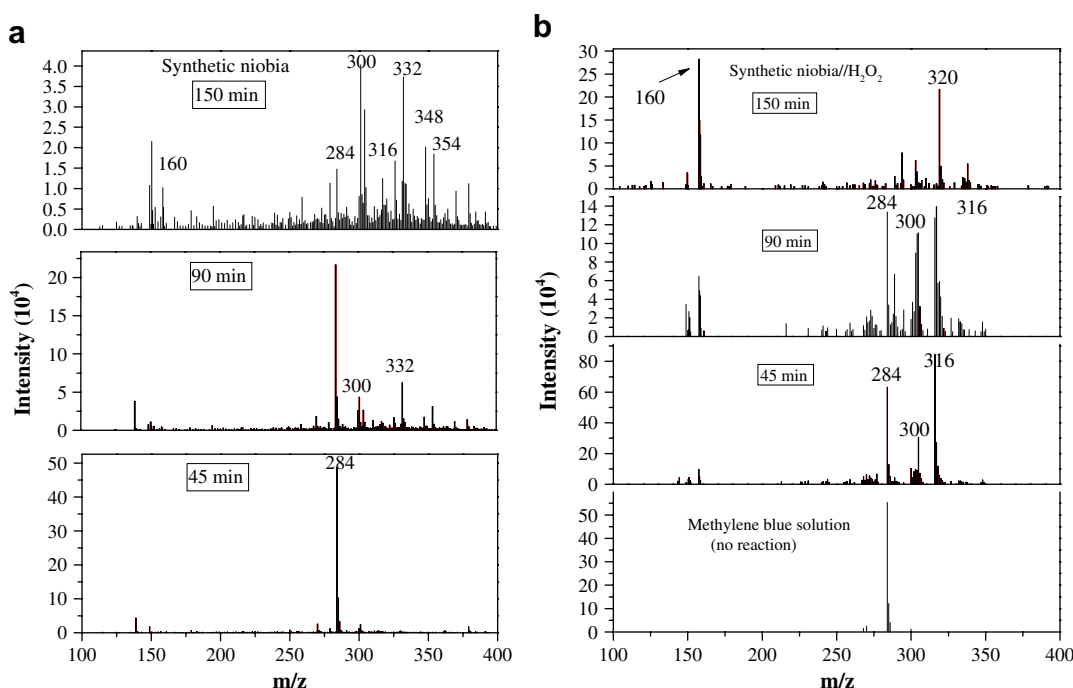


Fig. 2. ESI mass spectra in the positive ion mode for monitoring the oxidation of methylene blue dye in water by the synthetic niobia (a) and synthetic niobia/ H_2O_2 (b) in presence of H_2O_2 at different reactions times.

Table 1
Gibbs free energy of **II** and **III** intermediates using B3LYP/6-31+G(d,p)

Intermediate	Hydroxyl position	ΔG (kcal mol ⁻¹)
II	2	0.00
	3	+3.30
	5	+6.04
III	2, 2'	0.00
	2, 5'	+34.69
	3, 2'	+11.73
	3, 3'	+14.26
	3, 5'	+3.25
	5, 5'	+21.22

more likely occur at 5 position. This is a critical step, as it would simultaneously lead to the formation of hydroquinone or hydroquinone-like intermediates generated by the $\cdot\text{OH}$ attack. This is an unstable key-intermediate that points out the quick and high probability of rupture of both chemical bonds C1–C2 and C5–C6 (Fig. 3). This could justify the formation of **V** ($m/z = 130$). Nevertheless the presence of $\cdot\text{OH}$ in the reaction medium the oxidation of **V** probably occurs, which consequently generates the **VI** stable specie, with $m/z = 160$. These calculations show a good agreement with the experimental data (Fig. 2). Surprisingly, the fragmentation pathway is quite similar to the one described in our previous study [13]. This could strongly suggest that the reaction with niobia catalyst initializes by the activation of H_2O_2 to produce an $\cdot\text{OH}$ radical.

3.4. Characterization of niobia samples

Synthetic niobia and synthetic niobia/ H_2O_2 were characterized by XPS analyses (Fig. 4). The spectrum from the synthetic niobia showed only a peak at 529.9 eV related to the oxygen anions (O^{2-}) bound to the niobium in the lattice [19]. From the synthetic niobia/ H_2O_2 , the main peak at 529.9 eV is accompanied by a peak at 532.1 eV attributed to the formation of hydroxyl groups on the niobia surface.

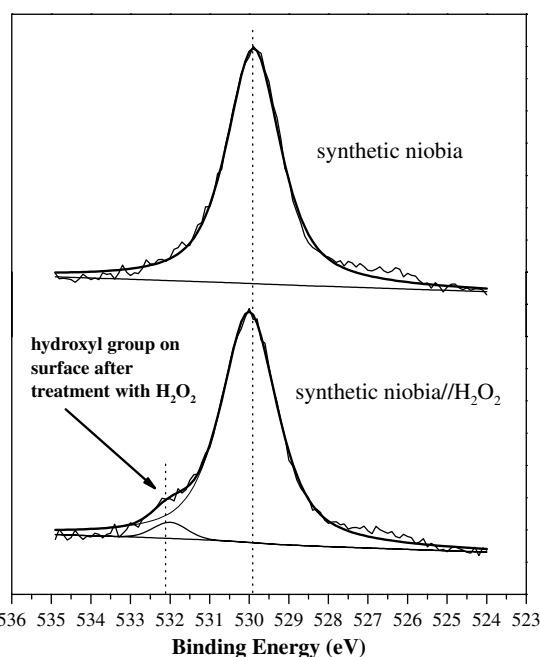


Fig. 4. XPS profiles of O 1s region of synthetic niobias.

face. The better catalytic activity of the material after the previous treatment with H_2O_2 may be due to these hydroxyl groups.

XRD patterns shown in Fig. 5a for the samples indicate that the materials are amorphous. These results are in very good agreement with other experimental studies [19]. The presence of hydroxyl groups was confirmed by FTIR spectroscopy (Fig. 5b). Both samples showed a broad band centered at 645 cm^{-1} and a shoulder at 895 cm^{-1} , which can be attributed to the amorphous niobia. The band at 1629 cm^{-1} for the synthetic niobia is due to the bending vibrations of the H_2O molecules. The broad band at 3404 cm^{-1} can be attributed to the OH-stretching vibration of H_2O molecules and a typical signal at 3143 cm^{-1} , due to the bulk hydroxyl stretch [5]. Moreover, the band at

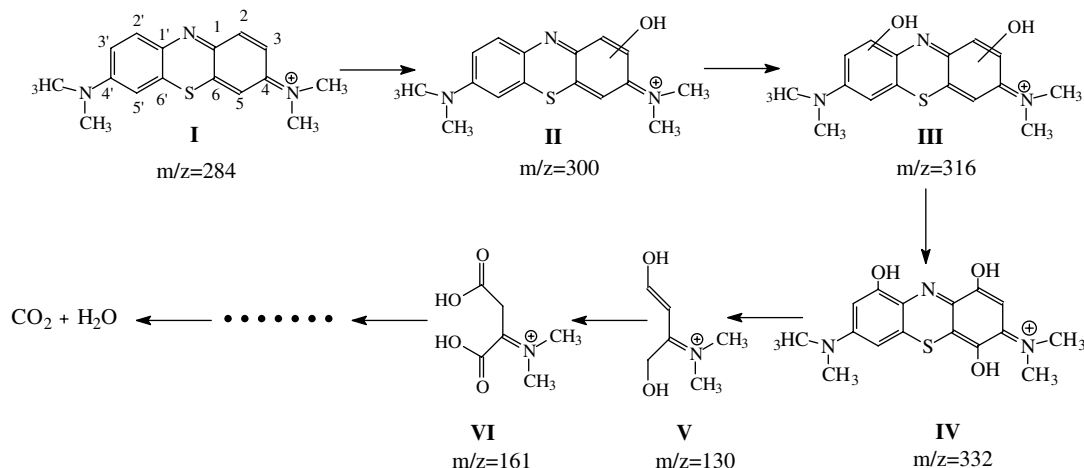


Fig. 3. Scheme with intermediates proposed for the oxidation of methylene blue dye ($m/z = 284$) by the niobia and H_2O_2 system.

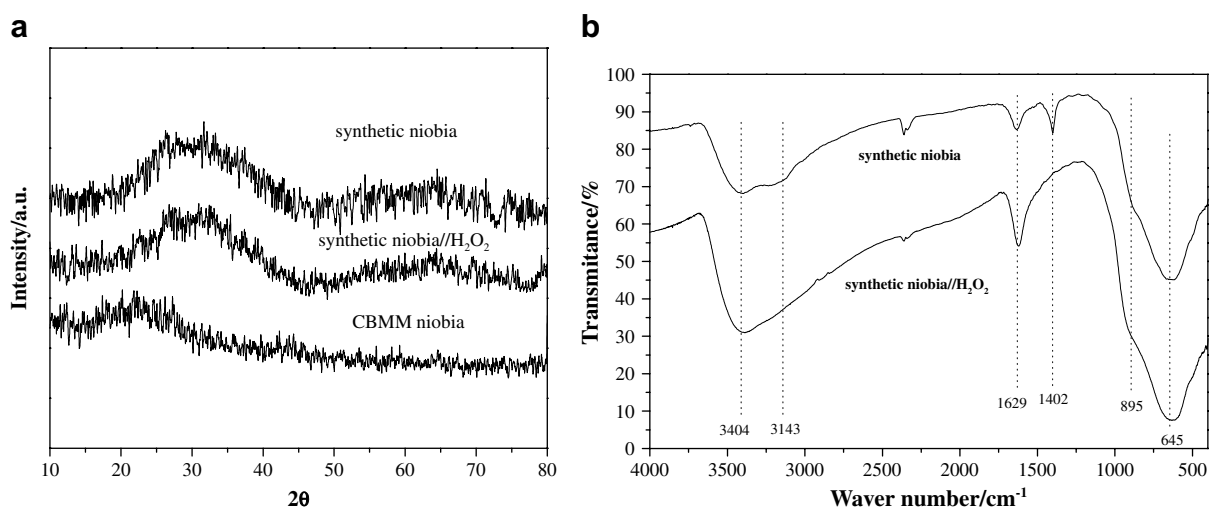


Fig. 5. XRD (a) and FTIR (b) analyses for synthetic niobias.

1402 cm^{-1} for the synthetic niobia could be attributed to the stretching vibrations of the oxalate precursor. It is also interesting to observe that the IR spectrum from the niobia previously treated with H_2O_2 shows a higher concentration of the superficial OH groups (3404 cm^{-1}) than the niobia without treatment.

4. Conclusion

Kinetic studies of the reaction monitored on-line by ESI-MS and the presence of intermediates suggest that the hydroxyl radical $\cdot\text{OH}$ promotes the organics oxidation. The understanding of the oxidation mechanisms is relevant for the treatment of organics in waste waters and essential to formulate novel, efficient and cost-effective processes. Despite of its great importance, the degradation mechanism using niobium oxides are yet unknown. Furthermore, poor detailed experimental and computational studies on the subject have been performed. However, these results, show that niobium is a good catalyst for the oxidation of organic compounds, and that the treatment of synthetic niobia with hydrogen peroxide before the reaction improves the catalytic activity, probably due to the reactive hydroxyl groups formed on the surface of the catalyst.

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