



## The molecular basis for the behavior of Niobia species in oxidation reaction probed by theoretical calculations and experimental techniques

T. C. Ramalho<sup>\*</sup>, L. C. A. de Oliveira, K. T. G. Carvalho, E. F. Souza and E. F. F. da Cunha

Department of Chemistry, Federal University of Lavras, Lavras-MG, 37200-000, Brazil. E-mail: [teo@ufla.br](mailto:teo@ufla.br)

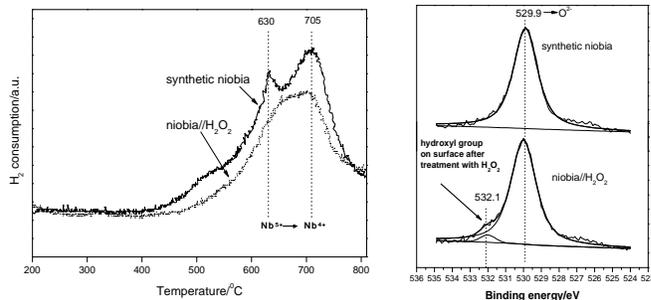
**Abstract** – This work describes the preparation and use of a new class of materials based on synthetic niobia as catalysts in the oxidation of organic compounds in aqueous medium. The chemical reactions were carried out in the presence of H<sub>2</sub>O<sub>2</sub>. The material was characterized with XPS and H<sub>2</sub>-TPR measurements. The methylene-blue dye was used in the decomposition study as a probe contaminant. The ESI-MS technique showed oxidation process observed through different intermediates. This suggests the use of niobia as an efficient catalyst in degradation reactions. Theoretical quantum DFT calculations were carried out in order to understand the degradation mechanism.

It has been reported that niobium is interesting and important for some catalytic reactions, and therefore 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 the bibliography. The particular properties of niobium, such as, redox properties, photosensitivity, acidity and catalytic behavior [2], constitute the motivation to understand and use niobium for catalytic purposes. Some important materials were been used as catalyst supports or promoters, but, we are interested in the utilization of niobia as a catalyst.

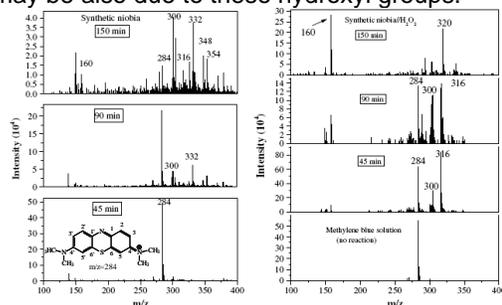
In this work, two different materials were utilized for the oxidation reaction in the presence of H<sub>2</sub>O<sub>2</sub>: (i) a synthetic niobia prepared in our laboratory (synthetic niobia) and (ii) this synthetic niobia previously treated with H<sub>2</sub>O<sub>2</sub> (30% v/v), called niobia//H<sub>2</sub>O<sub>2</sub>. Synthetic niobia was prepared from NH<sub>4</sub>[NbO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)](H<sub>2</sub>O)<sub>n</sub> (supplied by CBMM-Araxá-MG) and NaOH (50 mL, 1 mol L<sup>-1</sup>) by co-precipitation followed by thermal treatment at 60°C (72h). The material was characterized with XPS and H<sub>2</sub>-TPR (temperature programmed reduction) measurements.

The identification of reaction intermediates was performed on-line by the ESI-MS equipment during the oxidation of the methylene blue dye (Fig. 2). Strong signals corresponding to m/z = 300; 316 and 332 are detected only after 150 min of reaction for the synthetic niobia, due to successive hydroxylation of the dye structure. On the other hand, it is interesting to observe that these reaction intermediates were detected up to 90 min of reaction for the niobia//H<sub>2</sub>O<sub>2</sub>. The calculation of the Gibbs free energy for the stability of the intermediates was performed by the method implemented in the GAUSSIAN98 package. Previous works [3] put in evidence that intense fragment corresponding to m/z = 300 result from the hydroxylation in the aromatic ring. According to data obtained, it can be observed that the hydroxyl group at C2 position is about +3.30 and +6.65 kcal mol<sup>-1</sup> more stable than the alternative C3 and C5, respectively (Fig. 2).

These results show that materials are good catalysts for the oxidation of organic dyes in presence of the H<sub>2</sub>O<sub>2</sub>, and that the pre-treatment with H<sub>2</sub>O<sub>2</sub> (niobia//H<sub>2</sub>O<sub>2</sub>) improves the catalytic activity of the synthetic niobia. The better catalytic activity of the niobia//H<sub>2</sub>O<sub>2</sub> may be due to the highly reactive hydroxyl radical generated with the partial reduction of niobium observed at H<sub>2</sub>-TPR (Fig. 1a). Furthermore, the XPS O1s spectrum from niobia//H<sub>2</sub>O<sub>2</sub> show the main peak at 529.9 eV (related to O<sup>2-</sup>) is accompanied by a peak at 532.1 eV attributed to the formation of hydroxyl groups on the niobia surface (Fig. 1b). The better catalytic activity of the material after the previous treatment with H<sub>2</sub>O<sub>2</sub> may be also due to these hydroxyl groups.



**Figure 1:** H<sub>2</sub>-TPR profiles for the pure and H<sub>2</sub>O<sub>2</sub>-treated niobia (a) and XPS spectra (b).



**Figure 2:** ESI mass spectra in the positive ion mode for monitoring the oxidation by the AM by synthetic niobia (a) and niobia//H<sub>2</sub>O<sub>2</sub> (b).

[1] K. Tanabe. *Cat. Today* 78 1 (2003) 65 - 77.

[2] A.L. Petre, J.A. Perdigon-Melon, A. Gervasini and A. Auroux. *Catalysis Today* 78 1 (2003) 377- 386.

[3] L.C.A. Oliveira, M. Gonçalves, M.C. Guerreiro, T.C. Ramalho, J.D. Fabris, M.C. Pereira and K. Sapat. *Appl. Catal.* 316 (2007) 117.

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