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Article

Effect of Tungsten Doping on Catalytic Properties of Niobium Oxide

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Um novo material à base de nióbia (Nb_2O_5) foi sintetizado e quimicamente modificado para oxidar compostos orgânicos em meio aquoso, na presença de H_2O_2. A nióbia foi modificada por dopagem com tungstênio e também tratamento com H_2O_2 com o intuito de potencializar suas propriedades oxidativas. A investigação dos produtos gerados pela oxidação do azul de metileno, usando a técnica de espectroscopia de massas com ionização por eletrospray (ESI-MS), mostrou que o corante foi sucessivamente oxidado produzindo diferentes compostos intermediários. A sucessiva hidroxilação durante o processo oxidativo indica a alta reatividade dos radicais hidroxilas que são gerados, envolvendo H_2O_2 sobre a superfície do grão de nióbia dopada com W. Estes resultados sugerem fortemente que o H_2O_2 pode regenerar *in situ* o grupo peróxido, permanecendo ativo no sistema.

A novel material based on niobia (Nb_2O_5) was synthesized to oxidize an organic compound in aqueous medium in the presence of H_2O_2 after chemical modifications. Niobia was modified by doping with tungsten and also treating with H_2O_2 in order to maximize the oxidative properties of this oxide. The analysis of the products from methylene blue dye oxidation with electrospray ionization mass spectrometry (ESI-MS) showed that the dye was successively oxidized to different intermediate compounds. The successive hydroxylation during this oxidation strongly suggests that highly reactive hydroxyl radicals are generated involving H_2O_2 on the W-doped niobia grain surface. These results strongly suggest that the H_2O_2 can regenerate *in situ* the peroxo group remaining active the system.

Keywords: niobia, tungsten, catalytic oxidation, organic contaminant

Introduction

Currently, the pollution of water resources is a serious problem in various developed countries. Among several productive sectors responsible for the degradation of aquatic environmental quality, the textile industries stand out, because they generate a great volume of wastewater with a high organic load and biochemical oxygen demand, low dissolved oxygen concentrations, strong coloration and low biodegradability. These wastewaters also possess great propensity to alter biological cycles, due to their toxicity and carcinogenic and mutagenic potential.[1]

The conventional techniques applied to the treatment of textile wastewater, such as coagulation/flocculation, membrane separation and adsorptive processes (using activated carbon for instance), simply concentrate or transfer the pollutant from one phase to another, creating a secondary pollutant, which degradation still remain a problem to be solved. Biological treatment is not the solution for this problem, due to the low biodegradability or toxicity of various dyes.[2,3] For that reason, the development of new technologies is necessary to have more efficient and cost effective degradation of organic molecules, such as the textile dyes.

In that context, in recent years systems based on Nb_2O_5 have been receiving special attention, due to their

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high catalytic activity in several important chemical processes, such as: dehydration, hydration, hydrolysis, condensation, dehydrogenation, alkylation, photochemical, electrochemical, polymerization and organic compound oxidation reactions.[4-7] Another interesting aspect is that their natural occurrence and relatively high abundance in the earth's crust (approximately 20 mg kg^{-1}) make their use as a low cost material.[8] Furthermore, niobium and other transition metals, such as, Mo, W, V, Ta, when in contact with hydrogen peroxide (H_2O_2), form active species called peroxo group.[9] These species have been attracting special attention due to their chemical coordination, biological importance (antitumor activity), as well as their role as catalyst in various reactions.[10] Moreover, they are potentials oxygen donors to the organic substrate in aqueous medium. These groups can act as stoichiometric oxidizers or as catalysts in the presence of oxidizing agents, such as H_2O_2, used to regenerate those species *in situ*.[11]

In that direction, the objective of this work is to present the application of a synthetic niobium oxide (pure Nb) and one modified by the doping with tungsten (NbW), on the oxidation of methylene blue dye in the presence of H_2O_2. In addition, the surface of the NbW catalyst was previously treated with H_2O_2 (hereafter NbW//H_2O_2) for the generation of surface oxygenated groups, in order to improve the catalytic activity for pollutant oxidation.

Experimental

Synthesis and modification of niobia

The niobium oxide (pure Nb) was prepared by dropping slowly 20 mL of NaOH (1 mol L^{-1}) in a 500 mL Teflon becker containing 100 mL of a $NH_4[NbO(C_2O_4)_2(H_2O)](H_2O)_n$ solution (17.9 g) (CBMM- Brazilian Metallurgy and Mining Company, Araxá-MG) at 70 °C under vigorous stirring. Soon afterwards it was vacuum-filtered and washed with distilled water until pH 7. The material was oven-dried at 90 °C for 12 h and soon afterwards calcined at 600 °C for 3 h. For the doped material, the previous procedure was followed, however, with the addition of the salt $Na_2WO_4{\cdot}2H_2O$ (1.6 g), in order to obtain 5% W in mass.

The synthetic niobia doped with tungsten (NbW) was submitted to hydrogen peroxide treatment in order to generate more active surface sites according to recent works.[12,13] This treatment was made adding 300 mg of niobia, 4 mL of H_2O_2 (30% V/V) and 80 mL of distilled H_2O, leaving them in contact for 30 min. Soon afterwards the material was vacuum-filtered, washed with distilled H_2O and oven-dried for 12 h at 90 °C. A simplified scheme of the niobia modification by doping with W and the H_2O_2 treatment is illustrated in the Figure 1. The treatment of Nb^{5+} soluble salts with H_2O_2 makes the solution yellowish due to the formation of peroxo-niobium groups.[9,14] The color change was observed, same dealing with solid material as can be seen in the photograph of Figure 2.

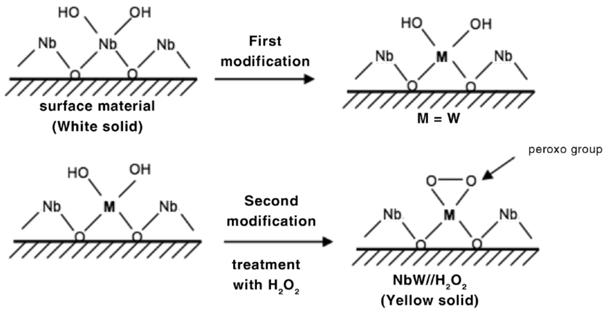

Figure 1. Simplified scheme of the niobium oxide modification by doping with W and the H_2O_2 treatment.

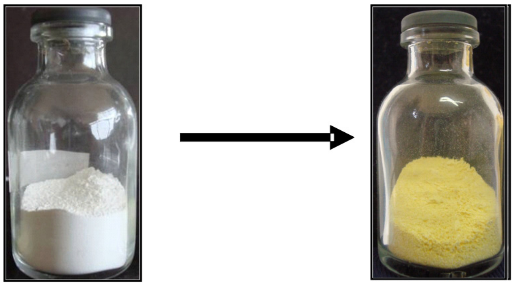

Figure 2. Photograph of white (before H_2O_2 treatment) and yellow catalysts (after H_2O_2 treatment) (see online version).

Materials characterization

XRD measurements of the samples were carried out with a SIEMENS D-5000, powder diffractometer at 40-50 mA, equipped with a variable slit, a diffracted beam monochromator, and a scintillation counter. The diffractograms were recorded in the 2θ range (10-80°) with a speed of 0.5° min^{-1} using Cu Kα radiation (1.5418 Å). TPR experiments were performed in a CHEMBET 3000 equipment with 20 mg_{sample} under 80 mL min^{-1} H_2 (5%)/N_2 with heating rate of 10 °C min^{-1}. Spectra were recorded in a Digilab (Excalibur, FTS 3000) FTIR spectrometer and processed with IRDM (IR data manager) software using the KBr pellet technique. Morphological analysis was also performed by scanning electron microscopy (SEM Leo Evo model 40XVP).

Catalytic tests: organic dye oxidation

UV-Vis spectroscopy studies

Oxidation tests were conducted with a model organic molecule, methylene blue dye (MB), in aqueous medium using pure Nb, NbW and NbW treated with H_2O_2, called NbW//H_2O_2.

The oxidation tests were carried out at 25 °C, using 9.9 mL of a solution containing the MB dye (50 mg L^{-1}) and 10 mg of catalyst, in the presence of H_2O_2 50% V/V (0.1 mL). The discoloration kinetics of the MB dye was monitored by UV-Vis spectroscopy (Shimadzu-UV-1601 PC) at 665 nm, the characteristic wavelength of MB dye.

ESI-MS studies

The possible oxidation products were analyzed by electrospray ionization mass spectrometry. For that, an ion trap electrospray ionization mass spectrometer, (Agilent-1100) was used. The samples were inserted in the equipment by infusion, at a flow rate of 15 µL min^{-1}, with charge control in the quadrupole (ICC) adjusted to 30,000 and positive mode. The drying gas (N_2) temperature was 325 ºC, flow rate 5 L min^{-1}, ion extraction potential –3.500 V.

Results and Discussion

Materials characterization

In order to characterize the catalysts after doping with tungsten and treating with H_2O_2, infrared spectra (Figure 3) of the materials were obtained.

A band at 3412 cm^{-1} assigned to the OH stretching of Nb–OH and a typical signal at 3140 cm^{-1}, due to the bulk hydroxyl stretching. A broad band at 1637 cm^{-1} related to adsorbed water on the Nb_2O_5 surface, a band at 870 cm^{-1} assigned to Nb–O or W–O stretchings, and bands between 500 and 950 cm^{-1} corresponding to Nb–O–Nb and W–O–W angular vibrations also can be observed.[15] A band at approximately 537 cm^{-1} was also observed, related to the presence of O–O type asymmetrical stretching bonded to the metal ($Nb(O_2)$) and even at 820-870 cm^{-1} referring just to the O–O stretching (peroxo).[9] Qualitatively, a decrease in the signal from superficial OH vibration can be observed due to the previous treatment with hydrogen peroxide. Reflectance spectra were obtained in the attempt to more efficiently identify the surface groups (Figure 3b). Bands can be observed regarding to stretching of internal hydroxyls at 3202 cm^{-1}, now also observed in the samples doped with W, and superficial at 3488 cm^{-1}. In fact, those bands were more evident in the diffuse reflectance spectra, compared to those of transmittance in Figure 3a. An intense band is observed at 1696 cm^{-1} regarding the angular deformation of O–H of H_2O adsorbed or bonded to the surface, for the samples pure Nb and NbW. However, the niobia doped with W previously treated with H_2O_2 (NbW//H_2O_2) displays an abrupt fall of that band intensity. That result can indicate that the previous treatment with H_2O_2 reacts with the original OH surface groups. In addition, the bands in 1417 and 1275 cm^{-1} are assigned to the residual organic component ($NH_4(NbO(C_2O_4)_2(H_2O))\ (H_2O)_n$) of neat niobia precursor.[15]

The morphology of the materials was studied by scanning electronic microscopy. The micrographs of the materials are presented in Figure 4.

The micrographs of the samples pure Nb (Figure 4a) and NbW (Figure 4b) clearly show a modification in the morphological characteristics after the doping with W. Pure Nb presents irregular sized crystals, while the NbW sample presents smaller crystals and with greater regularity. Those results are in agreement with the alterations obtained in oxides after the doping with different metals.[16] It can also be observed that the pre-treatment with H_2O_2 of the W doped niobium provokes a drastic modification in the morphology (Figure 4c). The materials present crystallite sizes between 10-30 µm and 400 µm, approximately, for NbW and NbW//H_2O_2, respectively. The SEM results suggest the occurrence of a nucleation process as related by Finney and Finke.[17]

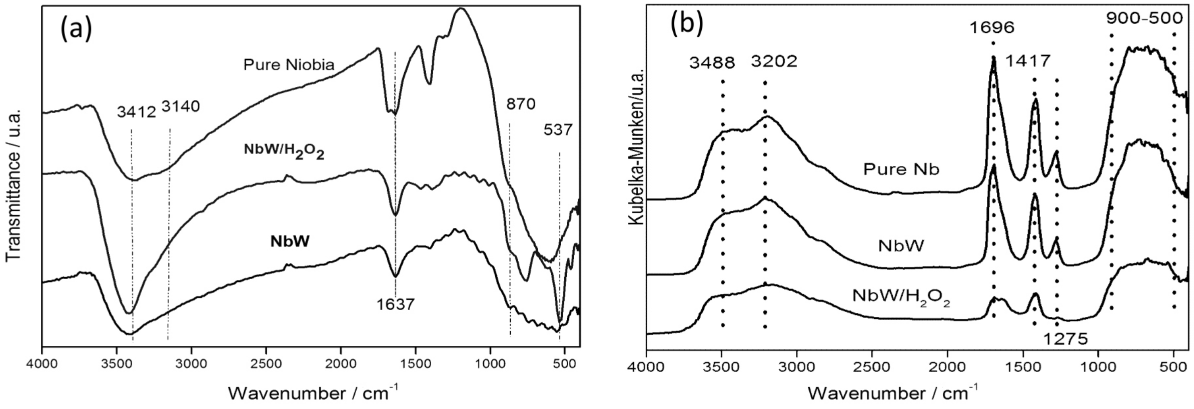

Figure 3. FTIR spectra of the synthetic niobia sample using (a) transmittance and (b) reflectance spectroscopy.

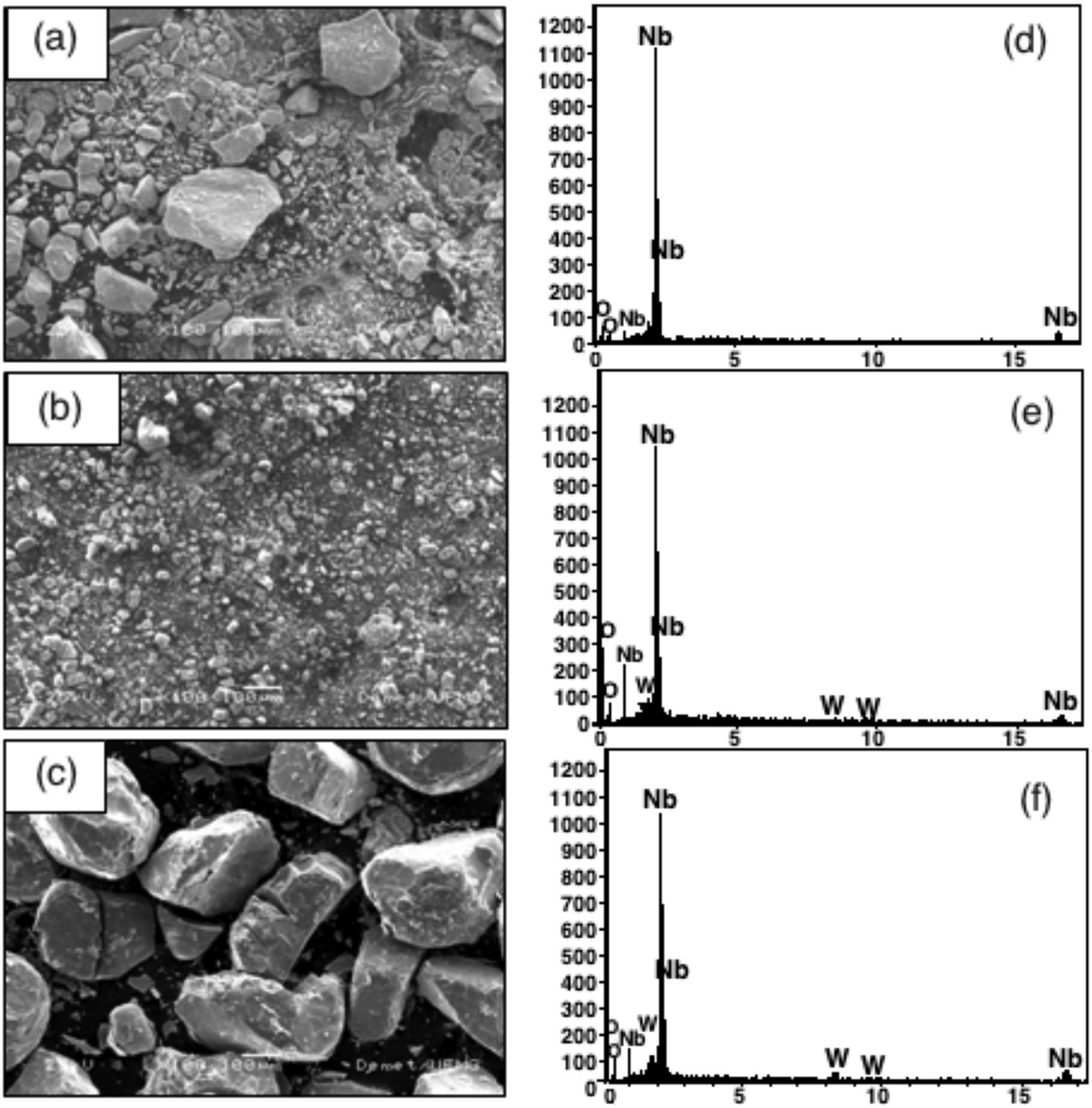

Figure 4. Scanning electron microscopy of the samples and EDS analysis for pure Nb(a) and (d), NbW (b) and (e), NbW//H_2O_2 (c) and (f).

The energy dispersive X-ray spectroscopy analysis (EDS) for pure Nb provided an approximate Nb level of 65% in mass. Regarding the sample containing tungsten (NbW) (Figure 4e), signals of that element with level of 2.1% in mass are observed. There was a significant decrease in the level of Nb (55% in mass) when compared to the pure Nb sample (Figure 4d). For the sample NbW//H_2O_2, the level of niobium obtained from the EDS analysis was 55% in mass (Figure 4f), however, the level of W went from 2.1% in NbW to 14.6% in mass for the sample NbW//H_2O_2. That result suggests that most internal W of the material is exposed to the surface with the treatment with H_2O_2, probably due to the dissolution of unstable niobium oxide crystallites.

The materials were also characterized by temperature programmed reduction (Figure 5a) and X-ray diffraction (Figure 5b) in order to identify the phases present and the influence of the tungsten presence.

The pure niobium oxide (pure Nb) presented two main reduction peaks centered at approximately 634 and 710 °C. Niobium oxide (Nb_2O_5) can undergo reduction to oxides with oxidation states of 4+ and 2+, according to the equations below:

$$Nb_2O_5 \xrightarrow{H_2} 2NbO_2 + H_2O \qquad (1)$$

$$2NbO_2 \xrightarrow{H_2} 2NbO + H_2O \qquad (2)$$

The literature relates that the formation of a dark blue solid (NbO_2) from Nb_2O_5 requires temperatures between 800-1300 °C.[4] For the W doped sample (NbW), the main

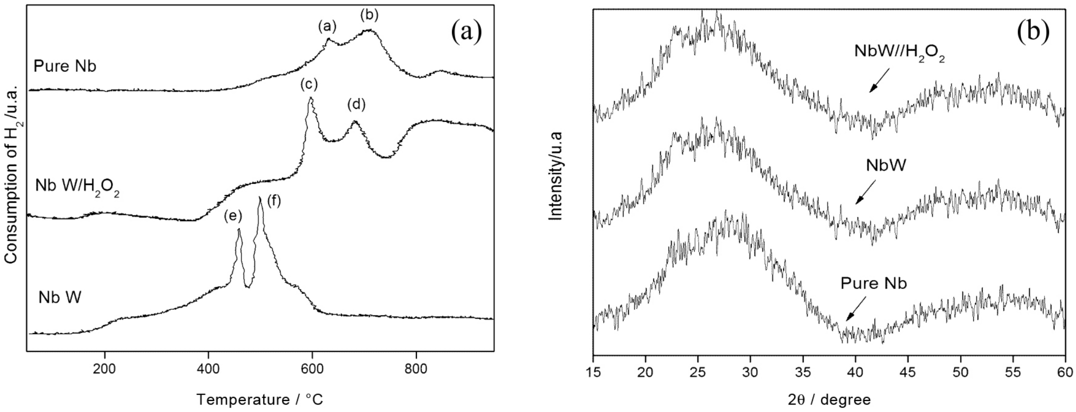

Figure 5. Temperature programmed reduction profiles and XRD analyses of the synthetics niobia.

reduction peaks occur at lower temperatures than those of the pure niobium oxide, centered at 458 and 499 °C, showing that the presence of W in the niobium structure facilitates the reduction with H_2. After the H_2O_2 treatment, the NbW//H_2O_2 sample presents a strong displacement to higher reduction temperatures of 575 and 683 °C. That result is in agreement with the SEM data (Figure 4), in which the crystallites size increased after the H_2O_2 treatment, explaining the observed displacement.

In X-ray diffractograms (Figure 5b), the absence of reflections is observed regarding niobium oxides or tungsten for the pure Nb, NbW samples and for NbW//H_2O_2, characterizing the presence of amorphous materials, which corroborates the data obtained by infrared spectroscopy.

Methylene blue dye oxidation in the presence of H_2O_2

The organic dye oxidation via heterogeneous catalysis was monitored by UV-Vis spectroscopy and the intermediates formation by electrospray ionization mass spectrometry (ESI/MS). ESI analysis was done to verify the effective oxidation of the dye, once the absence of color does not mean mineralization of the contaminant.

It can be observed in Figure 6a that using the pure Nb the removal occurs slowly up to 60 min of reaction, presenting about 20% of discoloration. However, after that time, an abrupt removal of the color occurs, reaching 80% after 90 min of reaction. This sample, after a previous treatment with hydrogen peroxide (pure Nb//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 catalytic activity showed by the synthetic niobia can be due to the surface groups, known as niobium peroxo complexes, formed by the presence of H_2O_2. These peroxo species are potentially oxygen donors to organic substrates in the liquid phase.[11] In order to understand that behavior and to identify possible reaction intermediates, ESI-MS studies were conducted after 60 and 90 min of reaction (Figure 6b). It can be clearly observed that after 60 min there is a decrease of the *m/z* = 284 signal related to cationic form of the dye. However, peaks are not observed regarding the formation of the reaction intermediates, suggesting removal by adsorption. After 90 min of reaction the *m/z* = 284 signal disappearance completely, however with the appearance of the dye oxidation intermediates with *m/z* = 304 and 369. At this reaction time, the *m/z* signals appearing at *m/z* = 130, 160, 241 and 268 are assumed to be related to dye oxidation intermediates, from fragmentations of the molecular structural ring that indicate the degradation of the organic compound may be brought to complete mineralization, as the total organic carbon analyses evidenced. It is evident, with these results, that the pure Nb needs some time (90 min) to become active and then promote a high removal of the MB dye. Similar studies were conducted for the NbW and NbW//H_2O_2 samples and presented in Figure 7.

Figure 7a displays that the removal of the dye (monitored by UV-Vis spectroscopy) for the sample pre-treated with H_2O_2 (NbW//H_2O_2) is significantly superior to the NbW sample, because the total dye removal occurs with only 30 min of reaction. In fact, ESI-MS studies, using the catalyst NbW//H_2O_2 (Figure 7b), show that after 30 min of reaction the signal regarding the MB dye disappears completely with the formation of several oxidation peaks and break of the dye structure. Those results clearly show the synergistic effect of the incorporation of W in the niobium oxide structure and the previous treatment with hydrogen peroxide on the removal capacity of organic compounds from the aqueous medium. After modifying the niobia through tungsten doping, treatment with H_2O_2 was carried out in order to increase the catalytic properties of the catalyzer by increasing the number of oxidizing groups throughout the entire surface of the material. A previous work showed that the catalytic activity by the

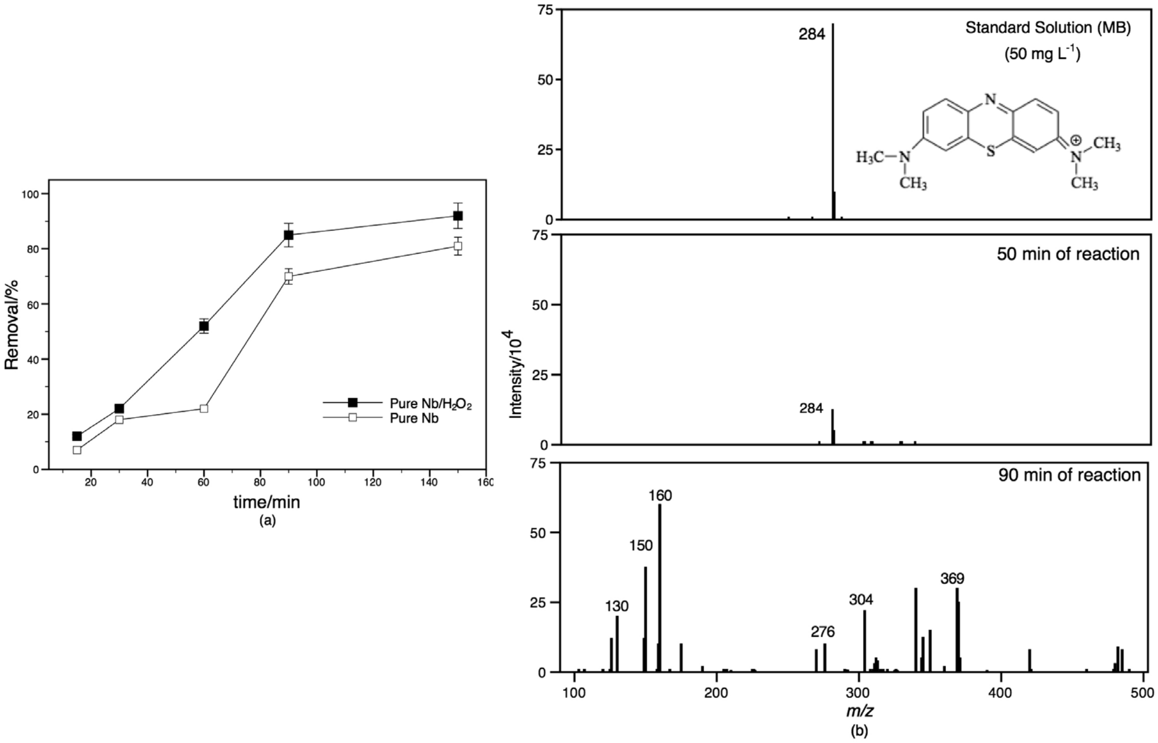

Figure 6. Discoloration measurements using methylene blue dye as model molecule in the presence of pure Nb (a) and ESI-MS analysis at different reactions times (b).

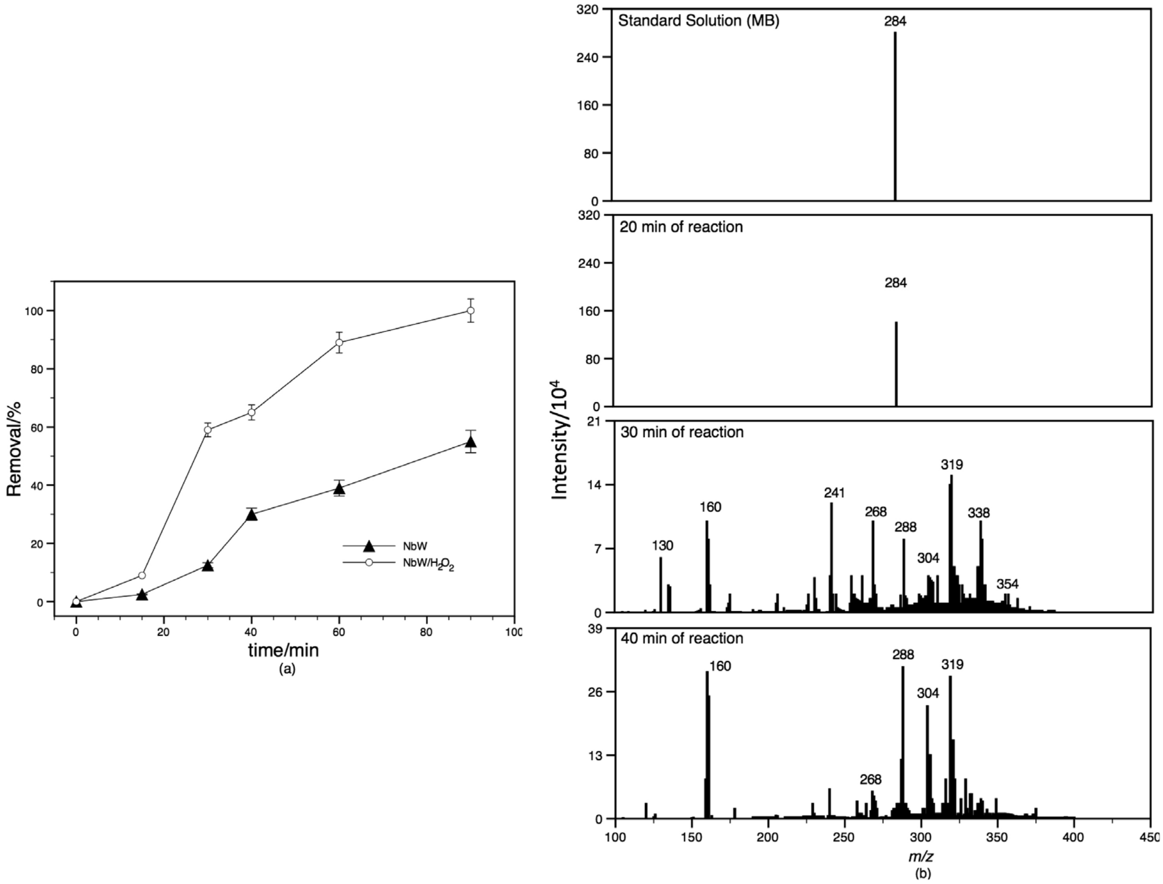

Figure 7. Discoloration measurements using methylene blue dye as model molecule in the presence of pure Nb and NbW//H_2O_2 (a) and ESI-MS at different reactions times using NbW//H_2O_2 (b).

synthetic niobia could be due to the surface groups, known as niobium peroxo complexes, formed by the treatment with H_2O_2.[13] The presence of tungsten in the catalyst seems to facilitate the generation of surface peroxo groups.

The real removal of the organic compound was evaluated for the most active catalyst, NbW//H_2O_2, by analysis of total organic carbon in solution. The results are presented in Figure 8 (a). Figure 8 (b) presents some structural proposals for the intermediates observed in the ESI-MS analyses. The NbW//H_2O_2 catalyst removed approximately 55% of the organic carbon, evidencing a high mineralization capacity of the organic compound when compared with other oxides in similar systems.[17]

It is important to highlight that some MB dye reaction intermediates observed by ESI-MS suggest the transfer of oxygenated groups from the catalyst surface to the organic molecule. As related in the literature, the peroxo species, formed in the presence of transition metals, such as Nb and W, and hydrogen peroxide, can donate such groups to the organic substrate in aqueous medium.[8-11] Therefore, after the dye oxidation, the presence of the oxidizer agent (H_2O_2) would regenerate those groups on the surface, as schematized in stages (i) and (ii) in Figure 9. That mechanism, known as Mars van Krevelen, was observed for reactions involving niobium compounds and it was showed in this work that the tungsten presence into the structure of niobia can intensify this effect.[18,19]

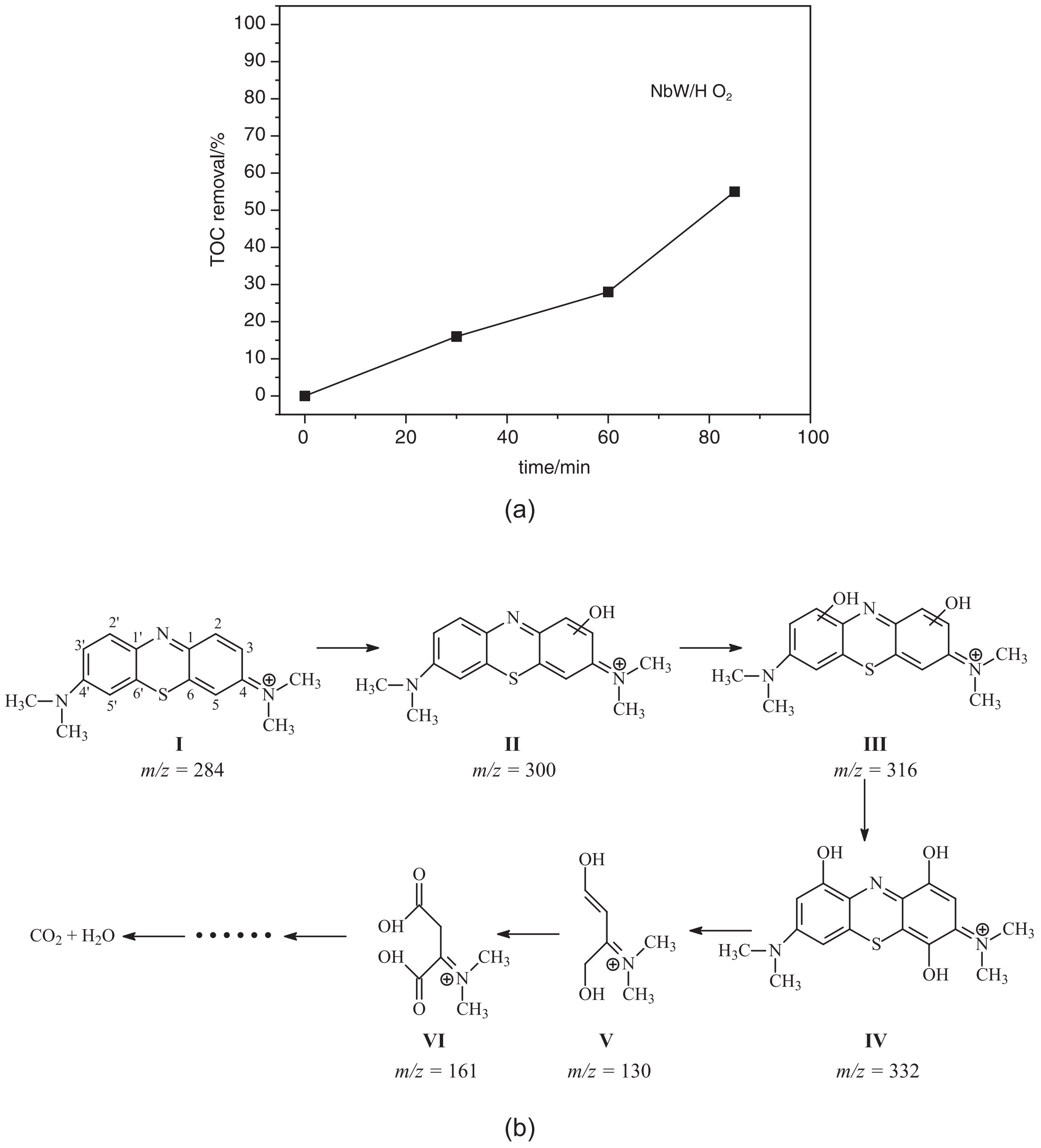

Figure 8. TOC analysis using NbW//H_2O_2 as catalyst (a) and a scheme with intermediates proposed for the oxidation of methylene blue dye (*m/z* = 284) by the catalysts.

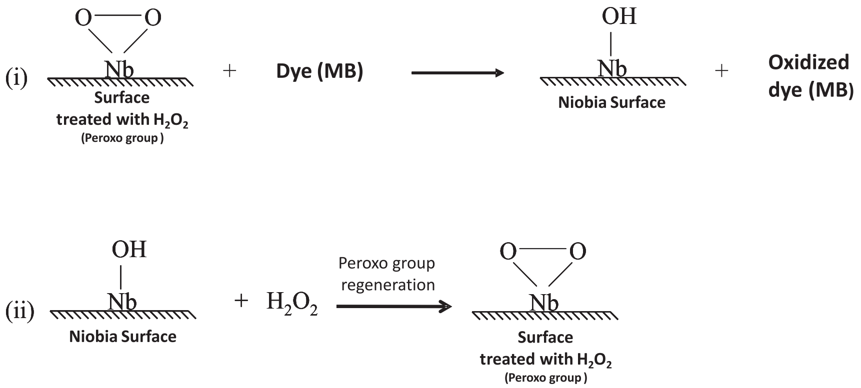

Figure 9. Scheme of the formation of peroxo niobium complex on niobia surface.

Conclusions

The innovative aspect of this work consists of the fact that the peroxo species, highly active, are formed on solid surfaces for application in heterogeneous catalysis. Furthermore, new niobium compound synthesis routes and modifications with W are proposed, promoting catalytic activity intensification of the catalysts.

The NbW sample, without previous treatment with H_2O_2, showed to be more efficient in the oxidation of the methylene blue dye, when compared to the pure niobia. NbW//H_2O_2 presented a slow removal up to 60 min of reaction that can be attributed to the necessity for the dye to accumulate on the niobia surface, when occurs the oxidation by the active sites (peroxo groups) on the catalyst surface.

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