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Short communication

Active potassium niobates and titanoniobates as catalysts for organic sulfide remediation

Clara Saux [a,*], Candelaria Leal Marchena [a], Robinson Dinamarca [b], Gina Pecchi [b], Liliana Pierella [a]

[a] Centro de Investigación y Tecnología Química (CITeQ), UTN — CONICET, Maestro Marcelo Lopez esq. Cruz Roja Argentina, 5016 Córdoba, Argentina
[b] Department of Physical Chemistry, University of Concepción, Concepción, Chile

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ABSTRACT

Pure ($KNbO_3$) and titanium-substituted ($KTi_{0.1}Nb_{0.9}O_3$ and $KTi_{0.2}Nb_{0.8}O_3$) potassium niobates with perovskite crystalline structures were prepared, characterized and tested as catalysts in the selective oxidation of 2-(methylthio)benzothiazole to its corresponding sulfoxide and sulfone. These catalysts, which have not previously been reported for organic sulfide remediation, are the most active catalysts among those discovered to date for this type of oxidation reaction. Hydrogen peroxide was employed as the oxidant, and the reaction parameters were tested in order to find milder reaction conditions.

1. Introduction

The heteroatomic benzothiazole ring is present in diverse and important organic compounds that are used as pesticides, biocorrosion inhibitors, chemotherapeutic compounds, etc. [1] with a high production volume. However, the largest use of benzothiazoles is as vulcanization accelerators in rubber production, as they catalyze the formation of sulfide linkages between unsaturated elastomeric polymers [2]. Several benzothiazoles have been detected in surface water, industrial wastewater and the receiving water from the runoff of impervious urban surfaces [3]. Considering their acute aquatic toxicities determined in various test systems [4] and low rates of biodegradability, it is necessary to find ways to abate them. An alternative for generating more biodegradable compounds from benzothizaoles is to oxidize them to their corresponding sulfoxides and sulfones [5]. Catalytic wet peroxide oxidation (CWPO) is an ecologically attractive catalytic approach aimed at the deep oxidation of weakly biodegradable toxic organic compounds in wastewater [6]. Considering that aqueous hydrogen peroxide is inexpensive and produces only water as by-product, it has been used as an attractive and environmental friendly oxidant [7]. Heterogeneous catalysts based on low-valence transition metals have shown good results and have been widely studied for the CWPO of organic pollutants because their oxidation efficiencies are relatively high compared with homogeneous catalysis under the same operating conditions [8]. Moreover, solid catalysts can be recuperated by means of a simple separation step and reused. In this sense, the employment of mixed oxides appears as a promising alternative. Perovskite-type oxide have gained attention as catalysts due to their well-known thermal stabilities in a broad range of oxygen partial pressures and their resistance to catalytic poisons [9]. In particular, potassium niobate has been widely reported for photocatalysis [10] and soot oxidation [11]. In the present article, the catalytic activities of pure ($KNbO_3$) and substituted ($KTi_{0.1}Nb_{0.9}O_3$ and $KTi_{0.2}Nb_{0.8}O_3$) potassium niobate perovskite-type oxides used as catalysts for an organic sulfide remediation reaction using 2-(methylthio)benzothiazole as the model substrate are reported for the first time.

2. Experimental

$KNbO_3$, $KTi_{0.1}Nb_{0.9}O_3$ and $KTi_{0.2}Nb_{0.8}O_3$ powders were prepared adding KNO_3 and $Ti(OC_4H_9)_4$ to a NbF_5 solution [12]. The viscous gels were dried and then thermally treated in air in an electric furnace at 600 °C for 10 h [13]. Specific areas were calculated from nitrogen adsorption isotherms, on a Micromeritics ASAP 2010 at 77 K. X-ray powder diffraction (XRD) patterns were obtained with nickel-filtered $CuK\alpha_1$ radiation using a Rigaku diffractometer. TPR experiments were performed in a TPR/TPD 2900 Micromeritics system by passing a 5% H_2/Ar flow. For the O_2-TPD experiments, the samples were preheated in an O_2 flow for 1 h at 700 °C, cooled down to room temperature in the same atmosphere, and then switched to a helium flow with the oxygen desorption monitored using a TCD. The catalytic selective oxidation of 2-(methylthio)benzothiazole with H_2O_2 as the oxidizing agent was carried out in a glass reactor (25 cm^3) with magnetic stirring,

* Corresponding author.
E-mail address: csaux@frc.utn.edu.ar (C. Saux).

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immersed in a thermostated bath and equipped with a reflux condenser. The catalytic tests were performed from room temperature to 60 °C evaluating different reaction conditions such as the mass of catalyst and different molar ratios of sulfide/H_2O_2 (R). Several solvents with different dielectric constants were tested. Prior to analysis, the catalyst was separated out by filtration. Organic compounds were quantitatively analyzed by gas chromatography (Perkin Elmer Clarus 500) with a HP1 capillary column and a FID as well as qualitatively by GC–MS (Shimadzu QP 5050 GC-17 A) using a HP-5 (25 m × 0.2 mm i.d) capillary column.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Specific area

The specific BET areas of the catalysts are summarized in Table 1. Even though lower surface areas are reported for the perovskite-type oxides prepared by citrate or sol–gel methods [14], the obtained values in the range 3 to 6 $m^2\ g^{-1}$ are in the range reported for alkaline niobate perovskites [13,15].

3.1.2. X-ray diffraction (XRD)

The diffraction patterns of the catalysts are shown in Fig. 1. Sharp diffraction peaks indicative of mixed crystal phases can be observed for the different titanium contents [16]. A careful analysis of the XRD patterns in comparison with the K–Nb–F–O components in the database indicates that for pure potassium niobate powder, the $KNbO_3$ orthorhombic structure (32–822) [17] is obtained [13]. Ushikubo reported that niobium oxide can easily react with many other oxides to form mixed oxide phases with complex structure active [18], therefore it is not surprising that the large number of additional reflections attributed to segregated phases. With regard to potassium titanoniobates, the $KNbO_3$ perovskite phase is also obtained along with new segregated phases identified by the diffraction peaks as an orthorhombic $KTiNbO_5$ (71–1747). Some impurities that corresponds to KNb_2O_5F (36–0808) have been previously reported for $SrTi_{1-x}Nb_xO_3$ [16]. Moreover, a shift in the reflections of the $KNbO_3$ perovskite phase towards higher 2 theta angles is detectable (inset Fig. 1). This behavior indicates a decrease in the interplanar distance, i.e. a lattice contraction of the crystalline structure [17], due to the smaller radius of Ti^{4+} (0.062 nm) than Nb^{5+} (0.064 nm).

3.1.3. Temperature programmed reduction (TPR)

The TPR profiles (Appendix 1) do not show any reduction peaks up to 700 °C, indicative of high thermal stability in reductor atmosphere and similar to the stoichiometric and non-reducible $LaFeO_3$ [19]. Although no previous reports of the thermal behavior of niobate perovskite-type oxides in hydrogen were found, the obtained results are related to the large stabilities of the oxidation states of the B cations (Nb^{5+} and Ti^{4+}). Moreover, previous reports of decreases in the extent of reduction of $SrCo_{0.8}Fe_{0.2}O_3$ perovskite upon Nb doping [20] support this hypothesis.

3.1.4. Oxygen desorption profiles (O_2-DTP)

The oxygen desorption profiles shown in Fig. 2 indicate physically weakly held adsorbed oxygen at ~80 °C, chemically adsorbed oxygen that desorbs between 200 °C and 500 °C and lattice oxygen or oxygen species occupying inner vacancies that desorb at temperatures up to 600 °C [18]. Increases in both, chemical and lattice oxygen's, in the peak starting at 500 °C not finished at 700 °C can be seen. As this later peak is associated with oxygen species occupying the inner vacancies created by non-stoichiometry's [21], the increase in the oxygen desorbed as Ti^{4+} content increase can be related to an increases in the redox properties of the perovskite. Because DTP–MS experiments confirm that the evolved gas and the He flow only contain oxygen, the deconvolution of the oxygen desorption curves using a Lorentzian shape allows the calculation of the desorbed oxygen in the corresponding temperature ranges. The amounts of desorbed O_2 in Table 1 are comparable to other substituted perovskites [22]. Lattice oxygen is expected to be of less importance compared to chemisorbed oxygen in the selective oxidation of 2-(methylthio)benzothiazole reaction that occurs at low temperatures.

Finally, the characterization results reveal that tetravalent Ti^{IV} on Nb^{V} can be successfully incorporated into the octahedral B-site of the perovskite lattice (XRD), leading to a large extent of oxygen vacancies (O_2-DTP).

Table 1
Characterization results of $KTi_xNb_{1-x}O_3$ (x = 0.0, 0.1, 0.2) niobates.

Catalyst	S_{BET}, $m^2\ g^{-1}$	Detected XRD phases		Desorbed oxygen mmol $gcat^{-1}$
$KNbO_3$	3	$KNbO_3$		0.34
$KTi_{0.1}Nb_{0.9}O_3$	6	$KNbO_3$	$KNbTiO_5$	0.42
$KTi_{0.2}Nb_{0.8}O_3$	6	$KNbO_3$	$KTiNbO_5$	0.50

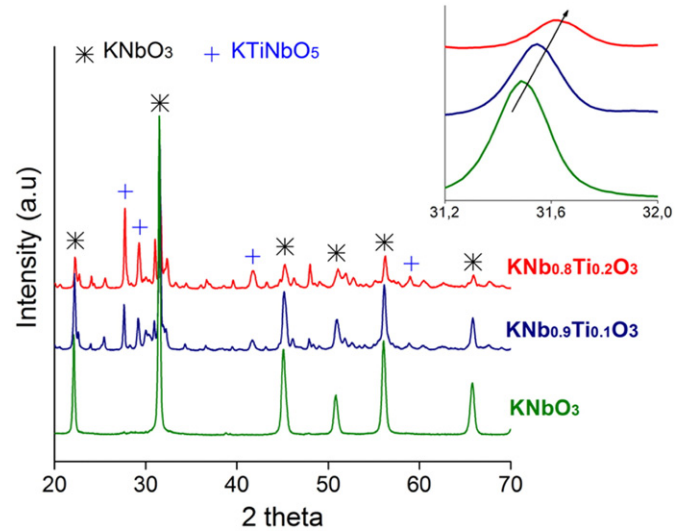


Fig. 1. X-ray diffraction patterns of $KNb_{1-x}Ti_xO_3$ (x = 0.0, 0.1, 0.2) niobates.

3.2. Catalytic activity

3.2.1. Effect of Ti substitution

The catalytic activities in the oxidation of 2-(methylthio)-benzothiazole (2MTBT) are shown in Table 2. The non-catalyzed

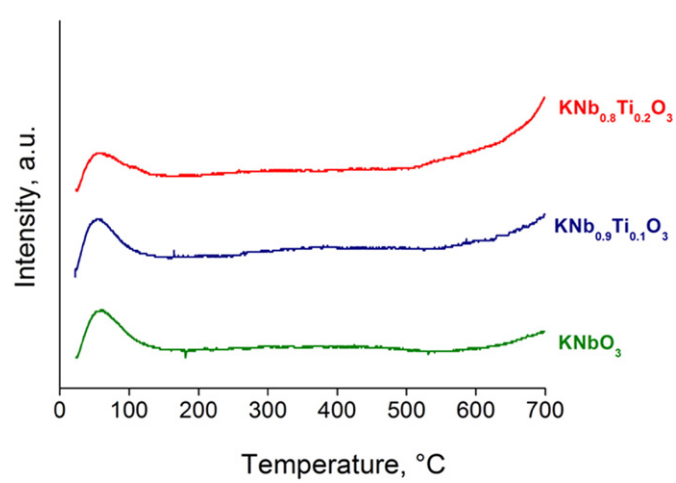


Fig. 2. Oxygen desorption profiles of $KNb_{1-x}Ti_xO_3$ (x = 0.0, 0.1, 0.2) niobates.

Table 2
Catalytic activities and selectivities of $KTi_xNb_{1-x}O_3$ (x = 0.0, 0.1, 0.2) on 2MTBT oxidation.

Entry	Catalyst	Conversion*	Selectivity*	
			Sulfoxide	Sulfone
1	$KNbO_3$	99.7	29.7	70.2
2	$KTi_{0.1}Nb_{0.9}O_3$	99.5	5.4	94.6
3	$KTi_{0.2}Nb_{0.8}O_3$	99.9	6.5	93.5
4	None	5.1	81.3	18.7

Reaction conditions: 40 °C, acetonitrile, R = 0.1, 0.1 g of catalyst, after 1 h.
* Mol.%.

reaction (entry 4, Table 2) results are also included. The large catalytic activities and selectivities of these potassium niobates in the 2MTBT conversion are noticeable, as the corresponding sulfoxide and sulfone are the only reaction products. Additionally, niobium oxides have been proposed to be catalysts for pollution abatement due to their large selective to hydrocarbons for oxidation reactions [18].

It should be noted that the conversion levels (≥99.5%), are higher than those reported by many authors for this kind of reaction [23,24]. In general, in ABO_3 perovskite-type oxides, the catalytic activity is closely related to the nature and redox behavior of the B-site. Due to no changes in the redox properties of $KNbO_3$ upon Ti substitution, the catalytic activity behavior should be related to the formation of oxygen vacancies. For K-substituted lanthanum perovskites, the catalytic activity has been related to the formation of surface oxygen-containing complexes in nano-sized particles [25]. Moreover, for lanthanoid perovskites, Li et al. [26] reported that surface oxygen species are also active species, which migrate from the perovskite structure.

Fig. 3 shows the reaction evolution as function of reaction time. It is possible to observe that sulfoxide selectivity decreases while sulfone selectivity increases with time. This observation allows us to propose a two-step mechanism (Scheme 1).

In the first step, the sulfide is converted into sulfoxide and then the sulfoxide is oxidized into sulfone. A large increase in the selectivity to sulfone (entries 2 and 3, Table 2) upon titanium substitution into the $KNbO_3$ perovskite structure is detected. According to the obtained results, it is proposed that the substitution of such electronegativity cations gives rise to the enhancement of the activity to effectively decompose 2MTBT. These observations could be understood in terms of the weakening of transition metal–oxygen bond upon the Ti substitution responsible for a decrease in the activation energy of the second step of the oxidation pathway thus increasing the production of sulfone.

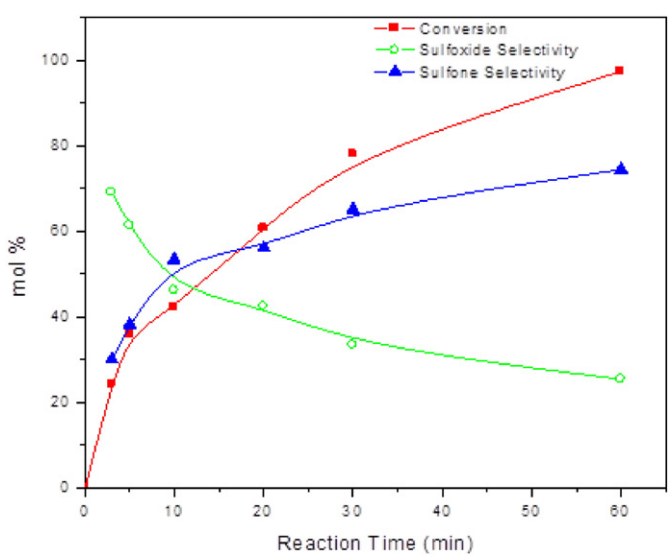
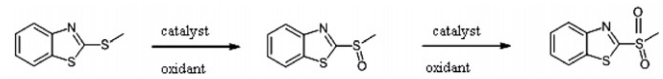


Fig. 3. Effect of reaction time on 2MTBT oxidation. Reaction conditions: room temperature; 0.1 g $KNbO_3$; acetonitrile; R = 0.1.



Scheme 1. Proposed 2MTBT oxidation pathway.

Moreover, the relationship between the chemical bonding nature of the Ti-substituted niobates with the oxygen vacancies should be an efficient tool for designing and developing new efficient and active catalysts to effectively decompose some organic molecules.

3.2.2. Effect of the nature of the solvent

Considering that the 2MTBT oxidation is a reaction that takes place in two liquid phases (aqueous and organic) and that the catalyst adds another phase (solid), the minimization of mass transfer problems is greatly necessary. A study on the effects of the nature of the solvent, using species with different polarities and proticities to optimize the so-called triple contact point where the catalyst, the oxidant and the reactant meet together, was proposed. The conversion levels and selectivities to sulfoxide and sulfone using acetone, acetonitrile, ethanol, methanol and 2-propanol were studied. When water and hexane were used as solvents, it was not possible to obtain a homogeneous liquid phase, and thus, 2MTBT conversion was extremely low. No changes in the conversion level (approx. 99.5 mol.% after the first reaction hour) using acetonitrile, ethanol, methanol and 2-propanol as the solvent were observed. In the case of acetone, a 63 mol.% conversion was obtained after 1 h of reaction time. Even when conversion values are not negligible, this behavior could be assigned to a more difficult contact between the hydrophilic catalyst surface and this aprotic solvent, which has the lowest dielectric constant (20.7 D). With regard to sulfone and sulfoxide selectivities, no significant differences were obtained, reaching approx. 40 and 60 mol.%, respectively. Moreover, higher initial reaction rates were obtained using 2-propanol, ethanol and methanol, indicating that protic solvents favored the triple contact due to the hydrophilic character of these alkaline niobates.

3.2.3. Effect of the oxidant concentration

The effectiveness of H_2O_2 was probed because no conversion was achieved in its absence. The effect of the initial oxidant concentration was studied by changing the volume added while maintaining the other initial concentrations and reaction conditions constant. The obtained results shown in Fig. 4 indicate a progressive increase in the 2MTBT conversion level up to 2.0 ml of hydrogen peroxide. Further increases in the concentration of hydrogen peroxide do not modify the catalytic behavior. The increase by 5 mol.% of sulfone selectivity with an increase in the H_2O_2 volume from 2.0 to 3.0 ml is the expected behavior considering that in the presence of a larger amount of oxidant

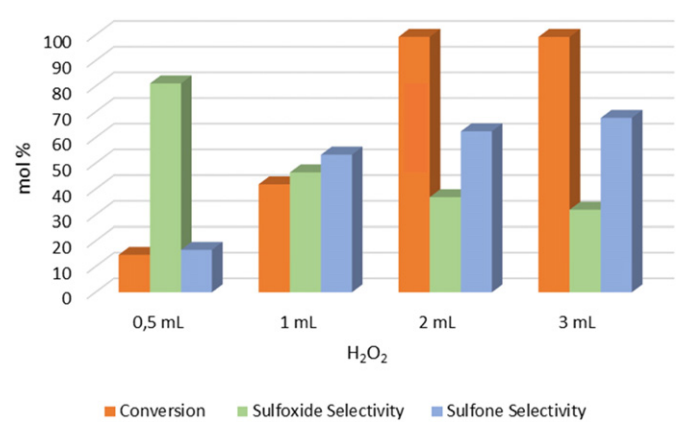


Fig. 4. 2MTBT conversion and sulfoxide and sulfone selectivities as function of H_2O_2 volume. Reaction conditions: room temperature; 0.05 g of $KNbO_3$; acetonitrile as solvent; after 1 h.

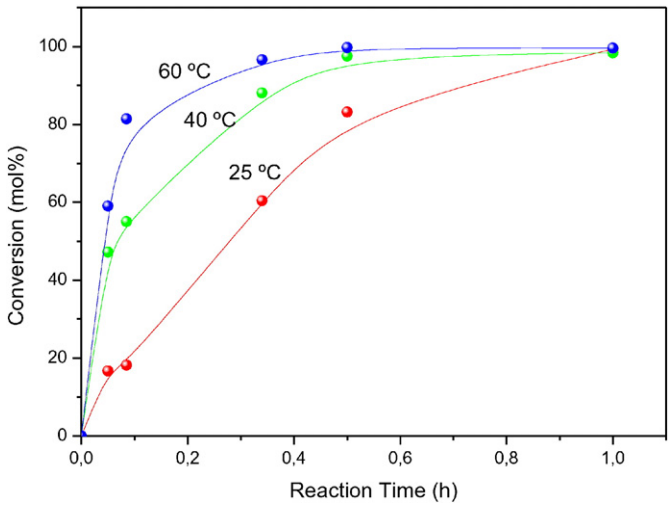


Fig. 5. Effect of the reaction temperature on 2MTBT conversion. Reaction conditions: 0.05 g of $KNbO_3$; R = 0.1; acetonitrile as solvent.

molecules, the second step of the proposed reaction pathway (Scheme 1) would be benefit.

3.2.4. Effect of the reaction temperature

The effect of the reaction temperature is presented in Fig. 5 for $KNbO_3$. Large differences in the conversion level and reaction time can be observed. Thus, complete conversion of 2MTBT at 60 °C is reached at 20 min of reaction time, but complete conversion requires 30 min at 40 °C and 1 h at 25 °C. Sulfoxide and sulfone selectivities were not affected with changes in the reaction temperature because their values remained almost unchanged at approximately 45 and 55 mol.%, respectively, after 1 h of reaction.

4. Conclusions

We report herein an efficient method for the selective oxidation of 2-(methylthio)benzothiazole to its corresponding sulfoxide and sulfone under mild reaction conditions employing potassium niobates and titanoniobates, that the activity depends on the degree of substitution, where the most active perovskite is the one with the highest substitution degree. These results indicate that the insertion of titanium ions into the perovskite lattice leads to a solid with structural and electronic defects and which provide sites with higher activity, the highest reported up until now for this type of contaminant.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2015.12.023.

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