



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 (KNbO₃) and titanium-substituted (KTi_{0.1}Nb_{0.9}O₃ and KTi_{0.2}Nb_{0.8}O₃) 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.

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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 benzothiazoles 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 oxides 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 (KNbO₃) and substituted (KTi_{0.1}Nb_{0.9}O₃ and KTi_{0.2}Nb_{0.8}O₃) 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

KNbO₃, KTi_{0.1}Nb_{0.9}O₃ and KTi_{0.2}Nb_{0.8}O₃ powders were prepared adding KNO₃ and Ti(OC₄H₉)₄ to a NbF₅ 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 CuKα₁ radiation using a Rigaku diffractometer. TPR experiments were performed in a TPR/TPD 2900 Micromeritics system by passing a 5% H₂/Ar flow. For the O₂-TPD experiments, the samples were preheated in an O₂ 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 H₂O₂ as the oxidizing agent was carried out in a glass reactor (25 cm³) with magnetic stirring,

* Corresponding author.

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

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/H₂O₂ (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 m² 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 KNbO₃ 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 KNbO₃ perovskite phase is also obtained along with new segregated phases identified by the diffraction peaks as an orthorhombic KTiNbO₅ (71–1747). Some impurities that corresponds to KNb₂O₅F (36–0808) have been previously reported for SrTi_{1-x}Nb_xO₃ [16]. Moreover, a shift in the reflections of the KNbO₃ 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 Ti⁴⁺ (0.062 nm) than Nb⁵⁺ (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 LaFeO₃ [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 (Nb⁵⁺ and Ti⁴⁺). Moreover, previous reports of decreases in the extent of reduction of SrCo_{0.8}Fe_{0.2}O₃ perovskite upon Nb doping [20] support this hypothesis.

3.1.4. Oxygen desorption profiles (O₂-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

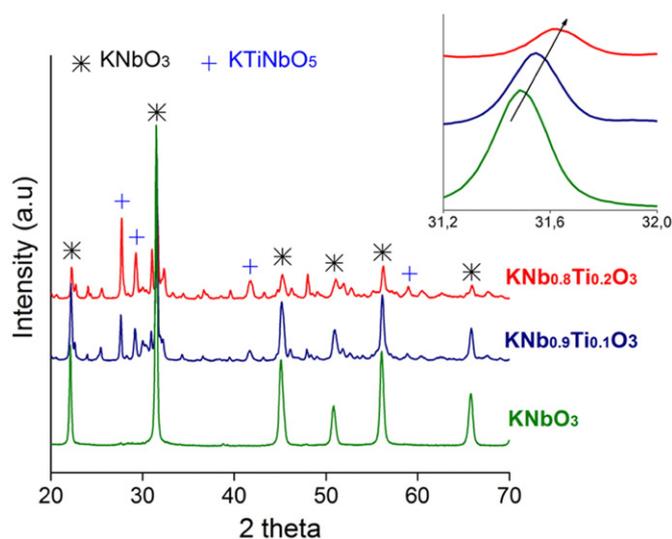


Fig. 1. X-ray diffraction patterns of KNb_{1-x}Ti_xO₃ (x = 0.0, 0.1, 0.2) niobates.

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 Ti⁴⁺ content increase can be related to an increase 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 O₂ 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 (O₂-DTP).

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

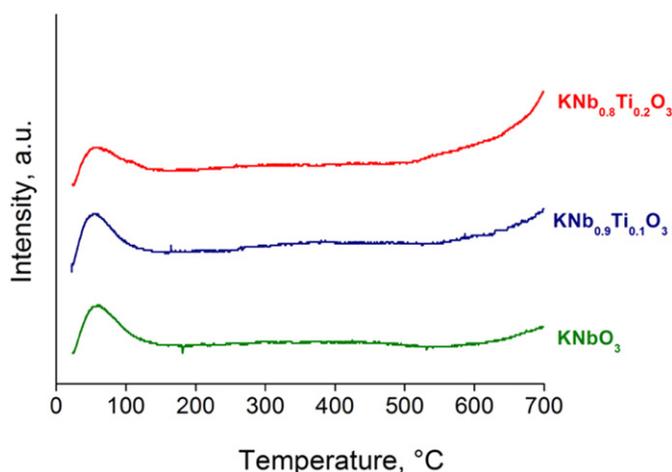


Fig. 2. Oxygen desorption profiles of KNb_{1-x}Ti_xO₃ (x = 0.0, 0.1, 0.2) niobates.

Table 1
Characterization results of KTi_xNb_{1-x}O₃ (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 KTiNbO ₅	0.42
KTi _{0.2} Nb _{0.8} O ₃	6	KNbO ₃ KTiNbO ₅	0.50

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