

PHOTODEGRADATION OF METHYLENE BLUE UNDER A NEW $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ NANOSTRUCTURED MATERIAL

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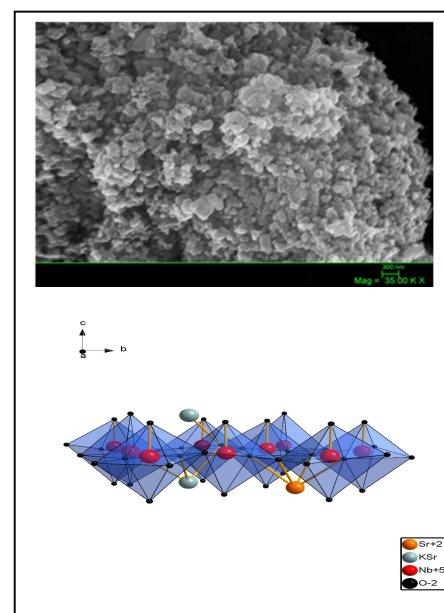
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ABSTRACT

The photocatalytic activity of a $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ nanostructured material was studied using methylene blue as test molecule. The influence of the calcination's time was also studied. Characterization was performed by FTIR, XRD and SEM. The diffraction line profile and the refinement of the structural parameters of $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ were obtained from the XRD patterns by the Rietveld method. The sample calcined by 6h seems to be the more photoactive. It has been attributed to the presence of niobium bond with apical oxygen in the $[\text{NbO}_6]$ octahedron as suggest the XRD analysis. This apical oxygen is very reactive and can leads to the formation of superoxoradical anions ($\text{O}_2^{\circ-}$). The niobate-based materials show low photoactivity, however it can be suggested that they can be potentially used for selective photocatalysts processes.



INTRODUCTION

Ferroelectric oxides with the tetragonal tungsten bronze (TTB)-type structure have been the forefront of both research and industrial applications. TTB-type structure can be considered a derivative of the classical perovskite structure and can be described by the chemical formula $(A1)_2(A2)_4C_4\text{Nb}_{10}\text{O}_{30}$ where A1, A2, and C denote different sites in the crystal structure. A wide variety of cation substitutions have been possible due to the presence of several interstices in the (TTB)-type structure [1]. This methodology permits to modulate physical properties of these materials such as electro-optic, nonlinear, elasto-optic, pyroelectric and electrical properties [2]. In recent years, our group have published several catalytic [3] and photocatalytic applications of Nb-based

materials [3,4]. In this sense, the objective of the present work is to study the photocatalytic activity of a $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ nanostructured material was studied using methylene blue as test molecule as a function of the calcination's time.

METHODOLOGY

$\text{KSr}_2\text{Nb}_5\text{O}_{15}$ nanostructured powder was prepared by the mechanical mixture of oxides via high-energy ball milling (HEBM) [3-5]. The starting reagents were $\text{Nb}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$, K_2CO_3 and SrCO_3 . Samples were prepared by using a HEBM type Attritor (Netzsch) with a milling chamber of zirconium (600 ml). The mixture of the starting materials was carried out in isopropyl alcohol using stabilized zirconia balls. The mixture was agitated with a Molinex-type agitator shaft with eccentric radial disks that accelerated the grinding media, which gave an extra radial impulse during each rotation of the shaft with a motor of 1/3 hp. The milling was performed with a rate of 1200 rpm for 5 h. After milling, the material was dried with forced air flow at 373 K. Powders were obtained after calcination at 1100°C for 4, 6, 10 and 12h, in a tube furnace under an integral oxygen atmosphere. An oxygen flow of 300 mL/min was maintained during a complete thermal cycle. Samples were denoted in a single manner as KSrNb-t , being t the time of calcination at 1100°C. Characterization was performed by FTIR, XRD and SEM. Conditions for the photocatalytic tests have been reported in a previous work [6].

RESULTS AND DISCUSSION

Fig. 1A shows the kinetics of MB adsorption in the dark and Fig. 1B shows the kinetics of MB photodegradation (Fig. 1B). A summary of the kinetic results such as the MB adsorbed (n_{ads}) and the first-order apparent rate-constants (k_{app}) is included in Table 1.

Figure 1. Kinetics of MB adsorption in the dark (A) and photodegradation (B) on $\text{KSr}_2\text{Nb}_5\text{O}_{15}$

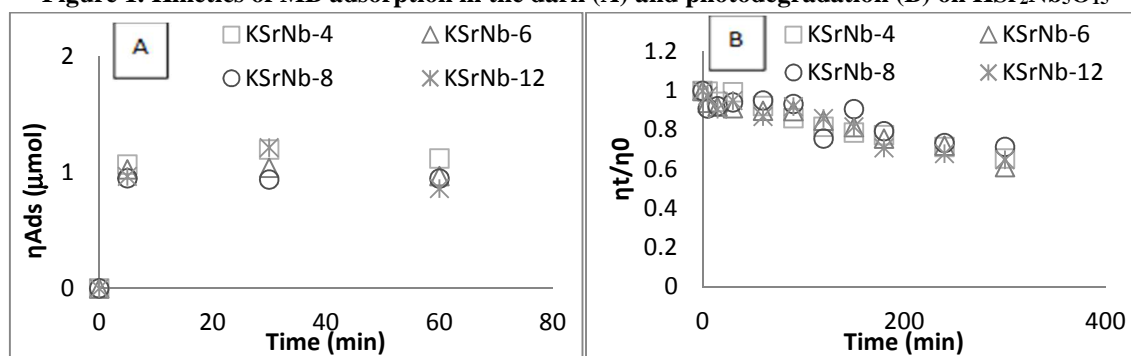


Fig. 1A shows that after 60 min, all samples seem to be in the equilibrium conditions of adsorption in the dark. Thus, we take this time as the minima required to achieve steady-state conditions of adsorption. Thus, the photocatalytic tests under UV-vis irradiation are driven after 60 min adsorption. Table 1 shows MB adsorption is monotonically lower for the long-term calcinating samples. In other words, the longer the calcination time the lower the MB adsorbed on $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ materials. This is because long-term's calcinated samples sinterize and therefore the crystal size of the particles is higher. This sintering effect was verified from the XRD analysis where the highest average crystallite size, around 32.5 nm for the powder calcined by 12h. Also,

the SEM images (not shown) confirmed this trend. Accordingly, the surface area of samples is expected to be lower in agreement with lower MB adsorption in the dark found for the samples calcined at higher times of calcinations.

Table 1. Summary of MB adsorbed in the dark (n_{ads}) and first-order apparent rate-constant (k_{app})

Sample	n_{ads} (μmol) ^a	k_{app} (min^{-1}) ^b $\times 10^{-3}$
KSrNb-4	1.123	1.42
KSrNb-6	0.972	1.64
KSrNb-8	0.950	1.22
KSrNb-12	0.863	1.30

^a MB adsorbed in the dark after 60 min (Fig. 1A). ^b k_{app} has been estimated from the linear regression [$\ln(n_0/n_t) = k_{app}t$] of the kinetic data from Fig. 1B.

Figure 1B seems to showed very similar kinetics trends in the photocatalytic degradation of MB. By contrast, a Vulcano-type trend between the photoactivity (measured by the k_{app}) and the calcination time was found. It can be seen from values in Table 1 that the first-order apparent rate-constant reached a máxima value of $1.64 \times 10^{-3} \text{ min}^{-1}$ for the $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ sample calcined by 6h. After this máxima the photoactivity decrease in the other two samples calcined by longer times. We have attributed this máxima photoactivity to an important presence of niobium bond with apical oxygen in the $[\text{NbO}_6]$ octahedron as suggest the XRD and FTIR analysis. This apical oxygen is very reactive and during irradiation, it can leads to the formation of superoxoradical anions ($\text{O}_2^{\circ-}$), responsible of the photodegradation of the MB. In this way, the increase of the average crystallite size as a function of thermal treatment time was correlated with the photoactivity, and therefore an optima aggregate development of the nanostructured niobate-based materials is required to achive a better photocatalytic behaviour. This phenomena was previously found by our group for the case of hybrid $\text{TiO}_2\text{-C}$ materials [7].

CONCLUSIONS

Niobate-based materials were prepared by an eco-friendly methodology. The structural and morphology of materials were characterized by XRD, FTIR and SEM, respectively, and from the photocatalytic tests performed of methylene blue photodegradation under UV-visible irradiation, it can be concluded that this new nanostructured materials can be potentially used for selective photocatalysts processes.

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