Photodegradation of phenol red on a Ni-doped niobate/carbon composite

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Abstract

The photocatalytic activity of a new nanostructured Ni-doped niobate $KSr_2(Ni_{0.75}Nb_{4.25})O_{15-\delta}$ was studied using the phenol red dye as a test molecule and the influence of amorphous carbon deposits upon the photoactivity of the niobate-based materials was also verified. $KSr_2(Ni_{0.75}Nb_{4.25})O_{15-\delta}$ powder was prepared by a high energy ball milling method and the $C-KSr_2(Ni_{0.75}Nb_{4.25})O_{15-\delta}$ composite by the partial pyrolysis of the niobate dispersed in a polyester matrix. Materials were characterized by FTIR spectroscopy and X-ray diffraction (XRD). The diffraction line profile and the refinement of the structural parameters of $KSr_2(Ni_{0.75}Nb_{4.25})O_{15-\delta}$ were derived by the Rietveld method. Both samples showed similar phenol red photodegradation under steady-state kinetic conditions. However, amorphous carbon seems to beneficially affect the reaction mechanism which followed first order kinetics. In terms of $KSr_2(Ni_{0.75}Nb_{4.25})O_{15-\delta}$ concentration a clear enhancement in the photoactivity of the niobate in the presence of amorphous carbon by a factor 4.7 was found suggesting a synergy effect between both solids. We conclude that $C-KSr_2(Ni_{0.75}Nb_{4.25})O_{15-\delta}$ composite can be employed for the photocatalytic degradation of diluted pollutants.
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1. Introduction

Ferroelectric oxides with the tetragonal tungsten bronze (TTB)-type structure have been the forefront of both research and industrial applications. Ferroelectric TTB-type structure can be considered a derivative of the classical perovskite structure and can be described by the chemical formula $(A1)_2(A2)_4C_4Nb_{10}O_{30}$ where A1, A2, and C denote different sites in the crystal structure. All A1 cavities have cuboctahedral coordination, the A2 cavities have a pentacapped pentagonal prismatic coordination, and C cavities exhibit a tricappedtrigonal prismatic coordination. A wide variety of cation substitutions have been possible due to the presence of several interstices in the TTB-type structure [1–3]. The cation size and the replacement fraction of the cations at different sites in the TTB-type structure might modulate physical properties of these materials such as electro-optic, nonlinear, elasto-optic, pyroelectric and electrical properties [4]. In this sense, the engineering of non-stoichiometry compounds by doping via a non-isovalent substitution cation is an easier alternative. In recent years, several catalytic and photocatalytic applications have been broadly studied in Nb-based materials due to their redox, strong acidic and photosensitivity properties [5,6]. For example, oxide materials based on the niobate have showed activity and high selectivity in different catalytic processes such as oxidative dehydrogenation of alkanes [7], oxidative coupling of methane [8], dry methane reforming (DMR) [9], ethylene homologation reaction (EHR) [9] and photocatalysis [6,10]. Although TiO_2 oxide is widely used as photocatalytic material, currently niobate-based materials such as KNb_3O_8, $K_6Nb_{10.8}O_{30}$, $K_4Ce_2Nb_{10}O_{30}$, $NiNb_2O_6$, $K_4Nb_6O_{17}$, and $NiO–KTiNbO_5$ have been widely studied because of their excellent photocatalytic properties [11,12]. Niobate-based materials have presented high photocatalytic activity also in the field of water decomposition [13]. Up to

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now, the photocatalytic activity of $KSr_2Nb_5O_{15}$ has been reported in the photodegradation of organic pollutants in an aqueous phase [14]. However, the potential application in heterogenous photocatalysis of the non-stoichiometric niobate with tetragonal tungsten bronze (TTB)-type structure with formula close to $KSr_2(Ni_{0.75}Nb_{4.25})O_{15-\delta}$ dispersed in an amorphous carbon matrix is reported here for the first time.

2. Experimental

2.1. Synthesis

Single phase and crystalline powder of $KSr_2(Ni_{0.75}Nb_{4.25})O_{15-\delta}$ non-stoichiometric were prepared using the mechanical mixture of oxides via the high-energy ball milling method (HEBM) [15–17]. The preparation was done using a high-energy milling type Attritor (Netzsch). The starting high purity reagents were $Nb_2O_5 \cdot 4H_2O$, K_2CO_3, $SrCO_3$ and Ni_2O_3. The mixture of the starting materials was carried out in isopropylic alcohol using stabilized zirconia balls of 1.2 mm in diameter. A powder to ball weight ratio of 1:16 was used. The mixture was stirred with a Molinex-type agitator shaft with eccentric radial disks that accelerated the grinding media, which gives 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 of reagents, the material was dried in a glove box with forced air flow at 373 K. Single phase powders were obtained after calcination at 1373 K for 10 h. The precursor was calcined in a tube furnace under an integral oxygen atmosphere. An oxygen flow of 300 mL/min was maintained during a complete thermal cycle. Powder was de-agglomerated in an agate mortar with a 350-mesh minimum. At this process the particles showed to be fragile.

2.2. Pyrolysis method

C-containing $KSr_2(Ni_{0.75}Nb_{4.25})O_{15-\delta}$ composite was prepared by a partial pyrolysis method similar to the process developed by the Pechini method consisting in the formation of a polymeric resin produced by polyesterification between a metal chelate complex from hydroxycarboxylic acid and a polyhydroxyalcohol such as ethyleneglycol. Citric acid ($C_6H_8O_7 \cdot H_2O$), ethyleneglycol ($HOCH_2CH_2OH$), and $KSr_2(Ni_{0.75}Nb_{4.25})O_{15-\delta}$ were the starting reactants. The citric acid was dissolved in ethyleneglycol (mass ratio of 40:60) with continuous magnetic stirring at 70 °C to promote polymerization. After the polyesterification reaction, a polymeric gel was obtained. The polymer maintained in the beaker was submitted to a primary calcination in a box-type furnace. The composite was obtained by a one-step calcination heating cycle under static air atmosphere from room temperature up to 300 °C at constant heating rate of about 1 °C min^{-1}. The composite was deagglomerated in the agate mortar with a 350-mesh minimum and denoted C-$KSr_2(Ni_{0.75}Nb_{4.25})O_{15-\delta}$.

2.3. Photocatalytic tests

Photocatalytic activity of $KSr_2(Ni_{0.75}Nb_{4.25})O_{15-\delta}$ and C-$KSr_2(Ni_{0.75}Nb_{4.25})O_{15-\delta}$ composite was studied by following the kinetics of phenol red disappearance as the test molecule. A low-flow dynamic and open to air photocatalytic reactor was used (Fig. S1, Supplementary material). 1 L volume with 3.53×10^{-5} mol L^{-1} initial phenol red concentration in the presence of 100 mg or 200 mg weight for the niobate-based materials was used. A low power (15 W) UV lamp (285 nm) was used as an irradiation source. In order to well-establish the photocatalytic behavior of the present niobate-based materials, both the kinetic of phenol red degradation by direct photolysis in the absence of solids (Figs. S2 and S3, Supplementary material) and the kinetic of phenol red disappearance in the presence of the amorphous carbon matrix (Figs. S4 and S5, Supplementary material) were followed. The concentration of phenol red in aqueous solution was determined by the changes in absorbance at 480 nm with a Colorimeter. The disappearance of phenol red was reported in terms of the conversion (X) obtained by the following expression:

$$X = [(C_o - C_t)/C_o] \cdot 100 \approx [(A_o - A_t)/A_o] \cdot 100 \qquad (1)$$

where C_o is the initial concentration of phenol red dye, C_t is the concentration at the reaction time t, and A_o and A_t are the initial absorbance and the absorbance at reaction time t.

2.4. Characterization

Texture characterization of samples was performed by adsorption–desorption N_2 isotherms at 77 K. The full isotherms in the range of 4×10^{-3}–84 kPa were measured in Micromeritics ASAP-2020. Equivalent surface area, micropore volume, and pore diameters were obtained by Brunauer–Emmet–Teller (BET), Harkins–Jura (HJ) and Horvath–Kawazoe (HK) methods, respectively. HJ and HK methods were employed because they are better suited algorithms for TTB-type structures.

Structural characterization of the $KSr_2(Ni_{0.75}Nb_{4.25})O_{15-\delta}$ powders was carried out by X-ray diffraction (XRD). A Shimadzu (model XRD-6000) diffractometer with Cu-Kα_1 radiation ($\lambda = 1.54056$ Å) and a graphite monochromator was used. Measurements were carried out over an angular range of $5° \leq 2\theta \leq 80°$ with slower scanning rate equal to 0.5°/min and with a scanning step of 0.02° and 2.40 s as fixed counting time. Divergence, scattered and receiving radiation slits were 1°, 1° and 0.2 mm respectively. The structures were refined according to the Rietveld method [17–19] using the Fullprof program [20]. Refinement parameters and variables adopted were the background coefficients, profile coefficients, scale factor, lattice parameters, atomic coordination, occupancy factors and isothermal parameters for five species of atoms (K^+, Sr^{2+}, Ni^{2+}, Nb^{5+} and O^{2-}). The background level was fitted with a five-order polynomial function, and the peak shape, with a pseudo-Voigt function. The angular dependence of the peak full-width at half-maximum (H) was defined by the