



Functional nanostructured catalysts based on the niobates to the dry methane reforming and ethylene homologation reactions

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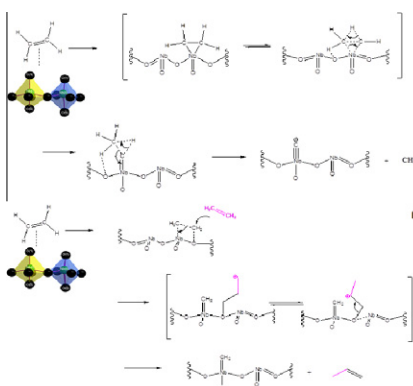
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HIGHLIGHTS

- Dry methane reforming and ethylene homologation reaction.
- Catalytic and selectivity properties of niobate-based nanostructured materials.
- Reaction mechanism to the propylene formation from ethylene.

GRAPHICAL ABSTRACT



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ABSTRACT

Catalytic activity and selectivity of niobate-based nanostructured materials were investigated. Dry methane reforming (DMR) and ethylene homologation reaction (EHR) were selected as test reactions. $\text{KSr}_2\text{Nb}_5\text{O}_{15}$, $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ and $\text{NaSr}_2(\text{NiNb}_4)\text{O}_{15-\delta}$ niobate powders were prepared by the high energy ball milling method and calcined in a reductor atmosphere. N_2 adsorption isotherms, X-ray diffraction and infrared spectroscopy characterization was performed. Hydrogen pretreated niobates showed from low to moderate catalytic initial activity in DMR's test, nevertheless the materials were deactivated rapidly and the kinetic parameters associated to deactivation were estimated. Otherwise, non-treated catalysts showed a high initial activity in EHR's test and $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ catalyst requires 24 h to the total deactivation with a high selectivity to form propylene. A reaction mechanism to the propylene formation is discussed.

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1. Introduction

An increasing research has been addressed to ferroelectric oxides in the search by new materials and properties for technological applications [1]. Niobates with a tetragonal tungsten bronze (TTB)-type structure are of great scientific, technical, and industrial

interest as materials for laser modulation, frequency multiplicity, and the generation of second harmonics for applications in pyroelectric detectors and piezo electric transducers [2,3]. Furthermore, due to the fact that the Nb-based materials have redox, strong acidic and photosensitivity properties they have been broadly studied in the last years at several catalytic and photocatalytic applications [4–16]. Niobate-based oxide materials show activity in different catalytic processes such as oxidative dehydrogenation of alkanes [17], oxidative coupling of methane [18], oxidation and ammoxidation of olefins [19], removal of nitrogen oxides in preventing air pollution [20], CO hydrogenation toward high hydrocarbons [21,22],

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hydrotreating reactions [23,24], organic synthesis by solid-acid assisted-catalysis [16,25–27] and photocatalysis [11–15,28,29]. However, very few studies concerning niobate-based catalysts have been reported in very important processes related with fuel production such as hydrocarbon reforming, catalytic cracking and homologation reactions [16]. Conventional Nb-based catalysts are acid and therefore readily deactivated by the high coke deposits commonly formed in these processes. To our knowledge, this is the first report on the nanostructured niobate oxide as catalysts for dry methane reforming (DMR) and ethylene homologation reaction (EHR). DMR was selected as a model catalytic test [30,31] because the importance of this reaction in the production of synthesis gas or syngas ($\text{CO} + \text{H}_2$). Syngas is the feed for the Fischer–Tropsch synthesis [32], methanol [33] and dimethyl ether [34]. EHR was also selected as a catalytic test because the high acidic character of niobium oxide materials can be used as a driven-force for the catalytic cracking of ethylene [35–37] as the first reaction step in EHR. In this sense, $\text{KSr}_2\text{Nb}_5\text{O}_{15}$, $\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ and $\text{NaSr}_2(\text{NiNb}_4)\text{O}_{15-\delta}$ powders were prepared and the DMR and EHR reactions under mild experimental conditions were performed.

2. Experimental

2.1. Synthesis

All reagents employed were analytical grade. $\text{KSr}_2\text{Nb}_5\text{O}_{15}$ single phase powder was prepared [1] by the high energy ball milling method from a mechanical mixture of oxides. Mechanical mixture of oxides/carbonates leads to an ultra-fine and homogeneous fine powders, exhibiting high crystallinity and single phase characteristics. The starting reagents were tetrahydrated niobium oxide ($\text{Nb}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$), potassium carbonate (K_2CO_3) and strontium carbonate (SrCO_3). The preparation was carried out using a HEBM-type Attritor (Netzsch) with a 600-mL zirconium milling chamber that was cooled with circulating water throughout the process. The mixing of starting materials was performed in isopropyl alcohol using stabilized zirconia balls of 1.2-mm diameter. A powder-to-ball weight ratio of 1:16 was used. The mixture was agitated with a Molinex-type agitator shaft with radial eccentric disks that accelerated the grinding media; the agitator shaft gives an extra radial impulse during each rotation of the shaft with a 1/3-hp motor. The milling speed was performed with a rate of 1200 rpm by 6 h. After milling of reagents, the material was dry in a glove box under forced air flow at 100 °C and then deagglomerated in an agate mortar at a 350-mesh. Single phase powders were obtained after calcination at 1100 °C during 10 h in a tube furnace with integral oxygen atmosphere. 300 mL min^{-1} O_2 flow was maintained during a complete thermal cycle, heating cycle and cooling cycle. The absence of the oxygen atmosphere can lead to a biphasic material or in others situations to mixtures of materials with different symmetry [1,3].

$\text{Sr}_2\text{NaNb}_5\text{O}_{15}$ nanocrystalline powder was prepared from a mechanical mixture of oxides by the high energy ball milling method [3]. The starting reagents were tetrahydrated niobium oxide ($\text{Nb}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$), sodium carbonate (Na_2CO_3) and strontium carbonate (SrCO_3). After high energy milling of reagents the material was dry in a glove box under forced air flow at 100 °C. Single phase powders were obtained after calcinations at 1150 °C by 12 h under the same conditions described above.

$\text{NaSr}_2(\text{NiNb}_4)\text{O}_{15-\delta}$ nanocrystalline powder was also prepared from a mechanical mixture of oxides by the high energy ball milling method [1,3]. The starting reagents for preparing the precursor powder were tetrahydrated niobium oxide ($\text{Nb}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$), sodium carbonate (Na_2CO_3), strontium carbonate (SrCO_3) and nickel oxide (Ni_2O_3) in isopropyl alcohol. After the high energy milling of reagents, the material was dry in a glove box under forced air flow

at 100 °C. Single phase powders were obtained after calcination at 1150 °C by 10 h following the same conditions described above.

2.2. Characterization

Structural characterization of niobate-based nanostructured materials was carried out by X-ray diffraction (XRD). A diffractometer Siemens (modelo D-5000) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) and a graphite monochromator were used. Measurements were carried in the angular range $5^\circ \leq 2\theta \leq 80^\circ$ with a scanning step of 0.02° and a fixed counting time of 10 s. Divergence, scattered and receiving radiation slits were 1° , 1° and 0.2 mm, respectively. Refinement parameters are indicated in the discussion section.

Chemical bonds were analyzed by FTIR spectroscopy. The samples were diluted in KBr in a ratio of 1:100. Measurements were carried out with an instrument resolution of 1 cm^{-1} in the range of $1500\text{--}400 \text{ cm}^{-1}$ for 100 scans using a Fourier Transform spectrometer Digilab Excalibur (FTS 3100 HE series). This is the range where characteristic bands assigned to Nb–O bonds appear.

Texture characterization was performed by adsorption–desorption N_2 isotherms at 77 K. The full isotherms in the range of 4×10^{-3} to 84 kPa were measured in a 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 were employed because they are better suited algorithms for ITB-type structures.

2.3. Catalytic tests

2.3.1. Dry methane reforming

Dry methane reforming (DMR) was followed at mild experimental conditions (650 °C, 1 atm) in a continuous flow system with a bed-fix quartz reactor [30,31]. Samples were submitted to *in situ* pre-treatments [38–41] before activity test under H_2 flow (50 mL/min, 14.5 psi) from room temperature to 650 °C by 1 h with a heating rate of 10 °C/min. DMR conditions employed were 100 mg catalyst sample; 80 mL min^{-1} flow of both CH_4 and CO_2 (50 vol.%, 14.5 psi); reaction temperature 650 °C. Methane analysis was carried out in a Perkin Elmer Clarus 500 gas chromatography with FID detection. Catalytic activities were estimated by the following equation:

$$\text{Activity}_{(t)} = \frac{n_{\text{Conv.CH}_4(t)}}{\text{Mass}_{(\text{Catalyst})}} \quad (1)$$

being $n_{\text{Conv.CH}_4(t)}$ the methane conversion mols obtained from the following equation:

$$n_{\text{Conv.CH}_4(t)} = F_{\text{CH}_4} X_{\text{Conv.CH}_4(t)} \quad (2)$$

F_{CH_4} is the methane flow ($F_{\text{CH}_4} = 0.00327 \text{ mols/min}$) and $X_{\text{Conv.CH}_4(t)}$ is the proportion of methane converted. This fraction is obtained from the conversion:

$$X_{\text{Conv.CH}_4(t)} = 1 - \frac{n_{\text{CH}_4(t)}}{n_{\text{CH}_4(t=0)}} \quad (3)$$

with $n_{\text{CH}_4(t)}$ the methane mols at the reaction time t . n_{CH_4} where estimated with the calibration expression obtained by the internal standard method. Activity tests were done by triplicate and the reproducibility of results was better than 5%.

2.3.2. Ethylene homologation reaction from catalytic cracking

Ethylene homologation reaction (EHR) from the catalytic cracking was followed in a continuous flow system with a bed-fix quartz reactor. Samples were submitted to *in situ* pre-treatments [42] before activity test under He flow (50 mL/min, 14.5 psi) from room

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