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Incorporation of barium in titanium oxide and lanthanum oxide

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Abstract

Two series of samples, noted TiBaX and LaBaX (where X=at.% of Ba), have been prepared in neutral medium from TiO_2, La_2O_3, and $\gamma BaCO_3$. These samples were calcined under air at 450 and 1150 °C then characterized by X-ray diffraction (XRD), thermoreduction under H_2 and scanning electron microscopy (SEM). After hydrolysis the conversion of La_2O_3 in to $La(OH)_3$ is complete while TiO_2 is only partially hydrated. Obtained results show that after calcination at: (1) 450 °C, barium is not inserted into the structure of TiO_2 while light interaction occurs between the barium and lanthanum; (2) 1150 °C, it forms mixed oxides $BaTiO_3$ and $BaTi_4O_9$ for TiBaX and $BaLa_2O_4$ for LaBaX. The microscopy showed that these phases are better crystallized.

Keywords: TiO_2; La_2O_3; Barium; Calcination; TPR; Structure

1. Introduction

The examples of utilization of TiO_2 and La_2O_3 are numerous:

- In electronics luminescent materials [1], ceramic dielectrics [2] for integrated circuits for microwave, isolators, filters, ceramics, superconductors [3], etc...
- In catalysis reactions of oxidative coupling of methane (COM) [4–6], oxidation, hydrogenation, and hydrogenolysis of hydrocarbons, automotive post-combustion, [7–11], etc... The reducibility of rare earth oxides (CeO_2, etc...) was advanced to explain the decrease in performance of modified rare earth catalysts. Nevertheless, most of these studies have been determined by the structural aspect, the conductive properties, and by the chemical behaviour.

Doping of rare earth oxides by group IIA elements increases the activity and selectivity during the COM [12–14]; this efficiency is attributed to a decrease of density and a high basicity of these catalysts [15]. La_2O_3 doped by calcium presents an important protonic conductivity in a wet atmosphere between 600 and 1200 °C [16]. The coprecipitation of three different oxides (BaO, Ln_2O_3, TiO_2) gives a unique phase in the $BaO–Ln_2O_3–TiO_2$ system [17,18].

In this paper, we report the effect of barium on the structures of TiO_2 and La_2O_3.

2. Experimental

2.1. Preparation of samples

TiO_2 and La_2O_3 used in this study, from Merck, purely 99.9% in mass, their surface areas are about 10.3 and 5.3 m^2 g^{-1}, respectively. $BaCO_3$ (from BDH Chemicals) is at 99%; their surface is 2.3 m^2 g^{-1} environ. TiO_2 and La_2O_3 were hydrolyzed in an excess of distilled, deionized (D.D) water for 16 h at 80 °C [19]. $BaCO_3$ was added to these solutions, the mixture was homogenized at the same temperature

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Table 1
Samples list

Barium (at.%)	0	5	10	15	20
TiO_2	TiBa0	TiBa5	TiBa10	TiBa15	TiBa20
La_2O_3	LaBa0	LaBa5	LaBa10	LaBa15	LaBa20

during 5 h. The products obtained were filtered and dried overnight in air at 120 °C, they are noted TiBaX and LaBaX (X=at.% of Ba). This procedure of pretreatment results insures larger surface area and smaller particle size than original starting material. Calcinations were led under airflow of (3 l/h), in dynamic reactor: with heating rate of 10°/min and isothermal at 450 and 1150 °C during 3 h (Table 1).

2.2. Characterization

X-ray diffraction (XRD) patterns were collected by using a Philips PW1800 diffractometer operated at (40 kV, 30 mA), using CuK_α radiation $K_{\alpha1}$ (1.54056 Å) and $K_{\alpha2}$ (1.54439 Å), the ratio of intensities being in order of 0.5. The phase identification was performed using the Joint Committee on Powder Diffraction Standards (JCPDS) database.

The reducibility of materials was studied by temperature-programmed reduction (TPR) under hydrogen (H_2/Ar), flow H_2 0.15 cc/min+Ar 20 cc/min, from room temperature to 1300 K with a rate of 5 °C/min. The analysis was conducted in a chromatograph equipped with molecular sieve 5A and thermal conductor detector (TCD, 110 mA). The mass of materials samples was about 250 mg.

Scanning electron micrographs were obtained with Philips SEM 505 microscope operating at 25 kV and magnification values of ×5000–10 000. This instrument is equipped with an energy dispersive X-ray microanalyzer, EDAX 9100, which permitted analytical electron microscopy measurements. The samples were sputter coated with gold.

3. Results and discussion

3.1. Analysis by XRD and micrography SEM of samples

3.1.1. Samples calcined at 450 °C

The XRD patterns of TiBaX calcined under air at 450 °C show that there are no interactions between barium and oxide of titanium. The spectra of TiBaX (Fig. 1A) indicate the witherite ($\gamma BaCO_3$) and the anatase.

The XRD patterns of LaBaX calcined at 450 °C are reported on the Fig. 1B. The analysis of these spectra shows that these samples contain $La_2O_2CO_3$, $La(OH)_3$, and $\gamma BaCO_3$ (witherite). The sample LaBa15 contains, respectively, 4.2%, 86.9%, and 8.8% of these compounds. One notes a light displacement of peaks XRD for $La(OH)_3$ and $BaCO_3$, which indicates a beginning of interaction between these two compounds.

3.1.2. Samples calcined at 1150 °C

After calcination at 1150 °C, XRD patterns (Fig. 2A) of samples TiBaX show three phases: oxide of titanium in the rutile form and two mixed oxides barium-titanate whose formula are $BaTiO_3$ and $BaTi_4O_9$. Those are well crystallized, the first has a tetragonal structure (P4mm, $a=b$=3.985 Å and c=4.037 Å), classical perovskite type, and the second an orthorhombic structure (Pnmm, a=6.290 Å, b=14.529 Å,

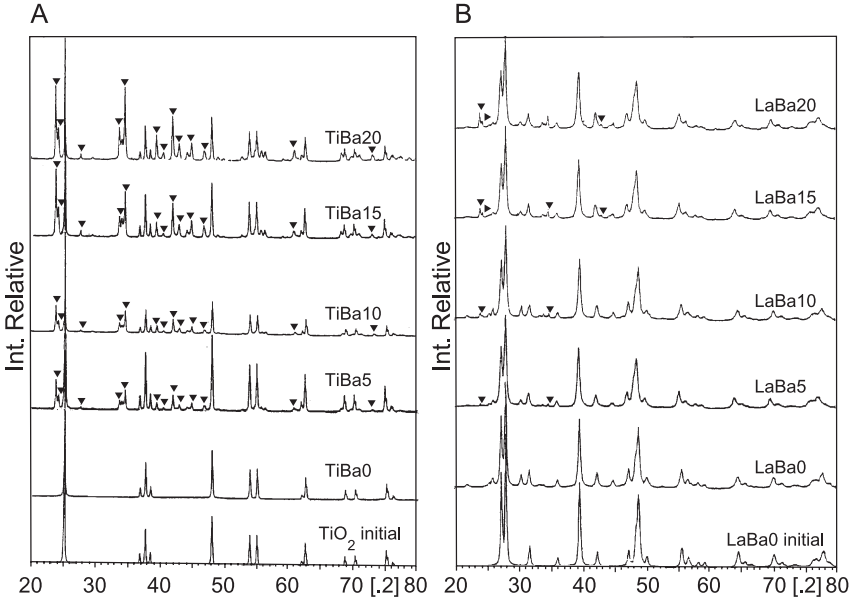

Fig. 1. XRD patterns of TiBaX (A) and LaBaX (B) samples calcined at 450 °C: (A) Spectra of TiO_2 anatase and $BaCO_3$ witherite (raies ▼); (B) Spectra of $La(OH)_3$ and $BaCO_3$ witherite (raies ▼).