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SnO_2 nanoparticles functionalized in amorphous silica and glass

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ABSTRACT

Two different routes to obtain SnO_2 nanoparticles, undoped and doped with rare earth metals (Eu or Pr), are described herein. The first route was based on the polymeric precursor method that led to the obtainment of SnO_2 nanoparticles dispersed in amorphous silica. The second route was simply the impregnation with $SnCl_4$ aqueous solution of SiO_2–CaO glass microparticles functionalized with hydroxyl ($^-$OH) groups. The materials were characterized by N_2 physisorption, XRD, EDS and TEM analyses. We also present the results of catalytic experiments involving the nanocrystalline composites in ethanol steam reforming. The catalytic properties of the undoped composites with SnO_2 supported on SiO_2–CaO glass differ from their doped analogues, however, they were both selective towards ethylene formation, in contrast to the doped composite obtained by the polymeric precursor method.

1. Introduction

Several technological and scientific phenomena in materials science are directly related to particle size. In some cases, such as for catalysts, it is desirable to produce materials with nanometer-scale structures to obtain specific properties. A recent method to obtain several stable metal nanoparticles is based on the use of an amorphous matrix and the functionalizing of nanoparticles in different solid supports [1–3].

In this study SnO_2 particles chemically functionalized in silica-derived material and chemically modified glass (based on SiO_2–CaO) were synthesized and chemically modified by rare earth metal doping. Different routes of synthesis and dopants were used in order to compare the structural characteristics and catalytic performance of analogous materials. We also present the preliminary results of their application in the catalytic steam reforming of ethanol. Tin oxide nanoparticles have been previously investigated in our laboratory. This oxide has been used in a large range of technological applications, including sensors and catalysts. We recently showed that the modification of the nanometric-scale structure and the composition of particles can lead to interesting selectivity changes for the methanol decomposition and aldolization reaction between acetone and methanol [3,4].

2. Experimental

2.1. SnO_2 nanoparticles synthesized by polymeric precursor route

The chemical process used for the preparation of the SnO_2–SiO_2 doped and undoped nanoparticles, see Fig. 1, consisted of the initial formation of a metal-citrate by mixing citric acid (CA) (Aldrich) [3,5], the metal precursor $SnCl_2$ $2H_2O$ (Aldrich), a tetramethyl orthosilicate (Merck) solution and as the dopant a 5 mol% aqueous solution of Eu_2O_3 (Aldrich) in relation to Sn. The CA:metal mol ratio was 3:1 in water. The subsequent step is polymerization, by the addition of ethylene glycol (EG). These mixtures were homogenized for 15 min at room temperature and the polymerization was initialized by adding EG in a mass ratio of 40:60 in relation to the citric acid. The final SnO_2 nanocomposites were obtained by a two-step pyrolysis of the polymeric intermediate at 250 °C for 2 h, and a second heat treatment at temperatures higher than 500 °C performed in an air atmosphere.

2.2. Synthesis of SnO_2 nanoparticles by milling SiO_2–CaO functionalized glass

Initially, common glass sheets (Pro-Cito) consisting mainly of SiO_2 (50–60%) and CaO (27–35%) were milled in a Quimis ball mill for a period of 20 h. The milled material was sieved and only the particles smaller than 300 μm were used for the synthesis. The next stage consisted of pre-washing the glass microparticles with water and isopropyl alcohol (Synth), followed by a treatment with 0.25 mol L^{-1} NaOH using ultra-sound for 12 h. The aim of this treatment was to

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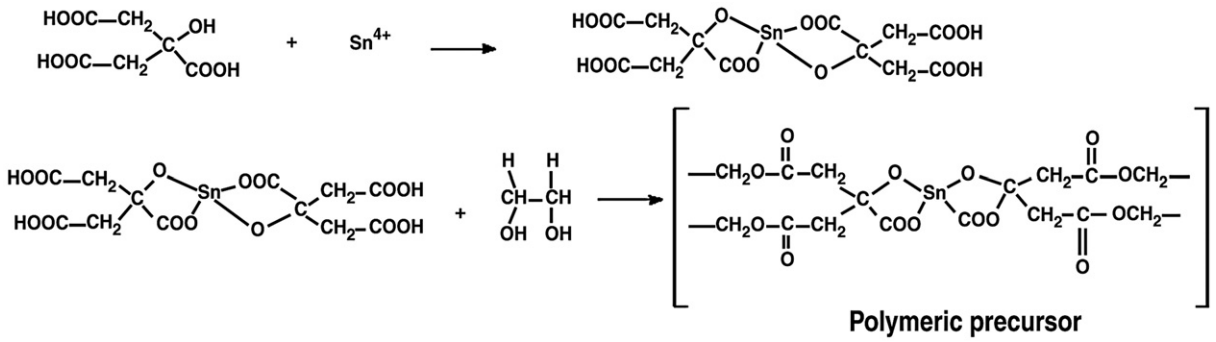

Fig. 1. Reaction of the formation of the polymeric precursor using Sn^{4+} ions.

create functional $^{-}$OH groups on the glass surface since reports in the literature [6,7] suggest that Sn^{4+} ions (in solution) are adsorbed on the modified glass surface. The material was then dried for later addition of a 0.1 mol L^{-1} aqueous solution of $SnCl_4$ $5H_2O$. In order to obtain the doped nanoparticles, 1 mass% of Pr (praseodymium nitrate, Aldrich) was used in relation to the mass of Sn. Finally, the samples were dried at 200 °C for 3 h and calcined in air at temperatures higher than 500 °C for 2 h. A diagrammatic representation of the procedure used in the synthesis is given in Fig. 2.

2.3. Characterization

The structural analysis of SnO_2 nanoparticles was carried out by X-ray diffraction (XRD; Siemens, model D-5000). The structure and morphology of the samples were studied by transmission electron microscopy (TEM; Jeol, model 3010, operated at 300 kV) equipped with X-ray energy dispersive spectroscopy (EDS). In order to analyze samples by electron microscopy, a dispersion of the material was carried out in an alcohol medium and a few drops were dropped onto carbon-coated Cu grids. The specific surface area of the nanocomposites was determined using an Autosorb-1C analyzer (Quantachrome Instruments). The chemical concentration of all tin samples, after heat treatment, was determined by Energy Dispersive X-ray Fluorescence Spectrometer (Shimadzu EDX 720).

Catalytic performance tests were conducted at atmospheric pressure with a quartz fixed-bed reactor fitted into a programmable oven, at a temperature of 500 °C. The water:ethanol mixture (molar ratio 3:1) was pumped into a heated chamber, with a temperature of approximately 200 °C, and vaporized. The water–ethanol gas (N_2) stream (30 mL/min) was then fed to the reactor containing 100 mg of the catalyst. The experiments were performed under diluted conditions (80% N_2). The reactants and the composition of the reactor effluent were analyzed with a gas chromatograph (Shimadzu GC 8A), equipped with a thermal conductivity detector, a Porapak-Q and 5A molecular sieve columns with Ar as the carrier gas. Reaction data were recorded for 4 h.

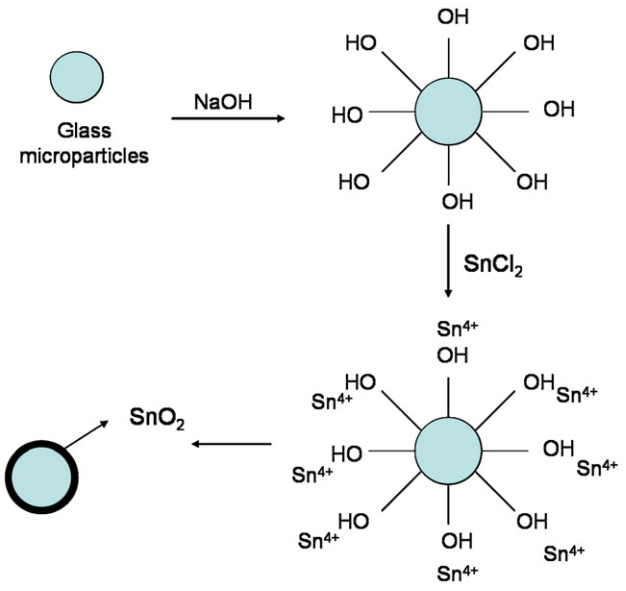

Fig. 2. Diagrammatic representation of the procedure used for the synthesis of the glass microparticles containing the SnO_2 nanostructures.

3. Results and discussion

3.1. SnO_2 nanoparticles synthesized by polymeric precursor route

Fig. 3a illustrates the typical XRD patterns of Eu-doped SnO_2/SiO_2 samples, at different heat-treatment temperatures. In these patterns the peaks can be ascribed to the tetragonal cassiterite phase of crystalline SnO_2 [3]. No diffraction peaks related to the secondary phase of silica and Eu were observed in the doped sample. A similar behavior was also observed for the undoped samples (not shown). This suggests that the SnO_2 nanoparticles are dispersed in the amorphous silica. Fig. 3b and c shows the high resolution transmission electron microscopy (HRTEM) images of Eu-doped SnO_2/SiO_2, annealed at 900 and 1000 °C, respectively, which show in some regions of the material a mean particle size of less than 9 nm. Fig. 3b clearly shows several amorphous regions of silica between the SnO_2 nanocrystalline particles. It is believed that these amorphous regions have an important role in the control of the particle size of SnO_2 nanostructures [6,7], and thus, apparently, the coalescent effect is decreased. Additional analysis by EDS coupled to TEM was carried out to probe the composition of the SnO_2 material functionalized with Si, as shown in Fig. 3d. The peaks of Sn, O and Si were clearly observed. In this analysis Eu was not detected, since the concentration of this component in the sample is too low. However, the final Eu, Si and Sn contents in the Eu-doped SnO_2/SiO_2 samples were 0.7, 22.0 and 77.3 wt.%, respectively, as determined by Energy Dispersive X-ray Fluorescence Spectrometer.

Leite et al. [8] suggested that rare earth dopants can be used to control particle size and protect SnO_2 against particle growth at high temperatures. The formation of a second phase, composed of the dopant element, which is segregated at the particle surface (metastable solid solution), may be monitored by XRD with the appearance

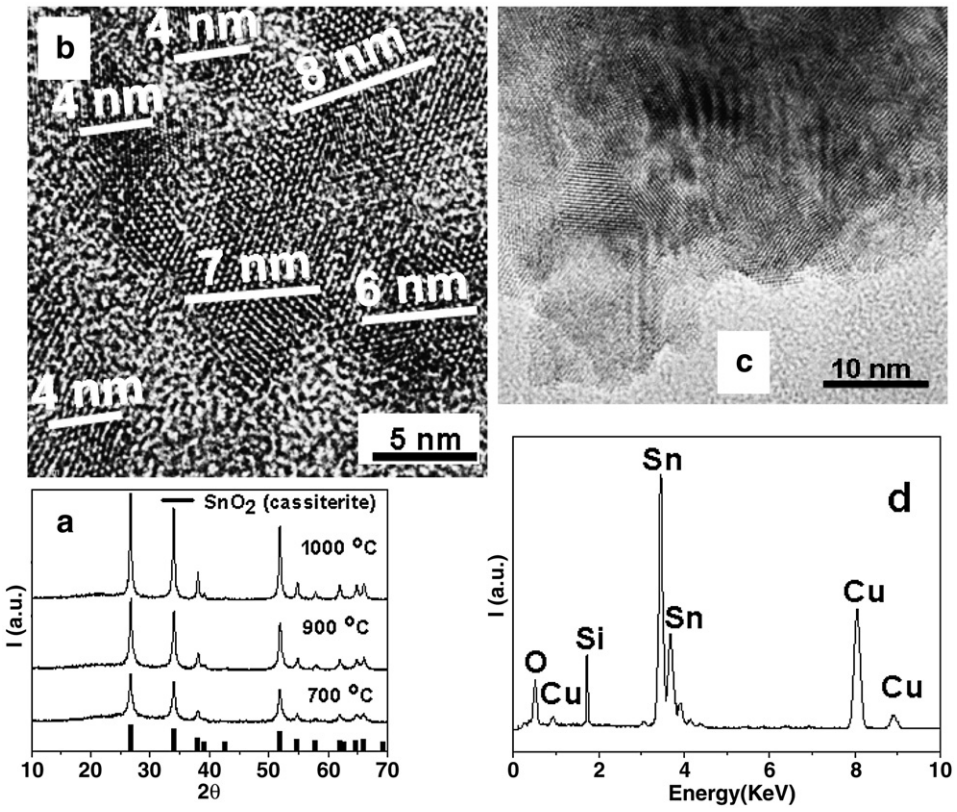

Fig. 3. a) XRD patterns of powdered Eu-doped SnO_2/SiO_2 samples; b) HRTEM images of powders annealed at 900 °C; c) HRTEM images of powders annealed at 1000 °C; d) EDS analysis of SnO_2 material functionalized with Si annealed at 900 °C.

of additional peaks (relating to the dopants) on the diffractogram with the increase in the treatment temperature of the material. This is consistent with findings reported in the literature [3,8]. However, the diffractogram peaks related to the SnO_2 phase did not show the formation of a solid solution, even for the sample heat-treated at 1000 °C. This suggests that the SnO_2 particles are strongly influenced by the presence of silica in the nanostructured system.

3.2. SnO_2 nanoparticles synthesized by milling SiO_2–CaO functionalized glass

Fig. 4a shows the XRD peaks of the crystalline phase as a function of the heat treatment of SnO_2 powders functionalized with micrometric particles of SiO_2–CaO glass. In Fig. 4a it can be observed that there is a slight narrowing of the diffraction peaks as a function of the increase in calcination temperature, which is related to the crystalline cassiterite phase of SnO_2. The XRD of the doped sample with 1 mass% of praseodymium showed no significant change as a consequence of the addition of dopant to the ceramic matrix.

Through an analysis of the SnO_2/SiO_2–CaO sample calcined at 700 °C, using the TEM technique, it was observed that the material used as a support had micrometric-sized particles. The TEM analysis of the edges of this material, as shown in Fig. 4b, had regions with a sufficiently fine thickness to allow a more detailed analysis of the surfaces, as well as the interaction of the glass particles with the SnO_2. Fig. 4c, obtained by HRTEM, clearly shows that one of these regions contains several SnO_2 nanoparticles with a narrow size range of 2–6 nm (diameter). This result verifies the efficiency of the chemical method employed in the functionalization of SnO_2 over the glass support. Additional analysis of these samples using TEM images of other regions, shown in Fig. 4d, reveals the presence of several nanoparticles, which are detailed in the HRTEM images in Fig. 4e (in dark circles). Reports in the literature [6,7] suggest that Sn^{4+} ions (in solution) are adsorbed on the modified glass, through electrostatic interactions of electronegative groups ($^{-}$OH) obtained in the activation of its surface, as can be observed in Fig. 2.

The final Si and Sn contents in the undoped SnO_2/SiO_2–CaO samples were 44 and 31 wt.%, respectively, determined by Energy Dispersive X-ray Fluorescence Spectrometer. The final Pr content of the dopants cannot be estimated through the technique used.

3.3. Catalytic applications

In order to investigate the catalytic activity of the samples, the steam reforming of ethanol was carried out. The catalytic behaviors of the different samples (SnO_2/SiO_2–CaO and Pr-doped SnO_2/SiO_2–CaO) were studied and compared (Fig. 5a and b, respectively). The catalytic behavior of the SnO_2/SiO_2 sample doped with Eu was also investigated (Fig. 6). The SnO_2/SiO_2–CaO and Pr-doped SnO_2/SiO_2–CaO catalysts showed similar activity in terms of ethanol conversion. In spite of the low specific surface areas (3 m^2/g for SnO_2/SiO_2–CaO and 2 m^2/g for Pr-doped SnO_2/SiO_2–CaO), the catalysts achieved reasonable ethanol conversion values at the beginning of the test, (around 40%). However, it is interesting to observe that the catalysts presented a distinct behavior in terms of product selectivities. From the results of Fig. 5, it can be seen that H_2, C_2H_4 and CH_3CHO were the products detected in the reaction effluent of the ethanol steam reforming process using the SnO_2/SiO_2–CaO catalyst. Ethylene was the major product formed, with lower amounts of hydrogen and acetaldehyde, indicating that ethanol

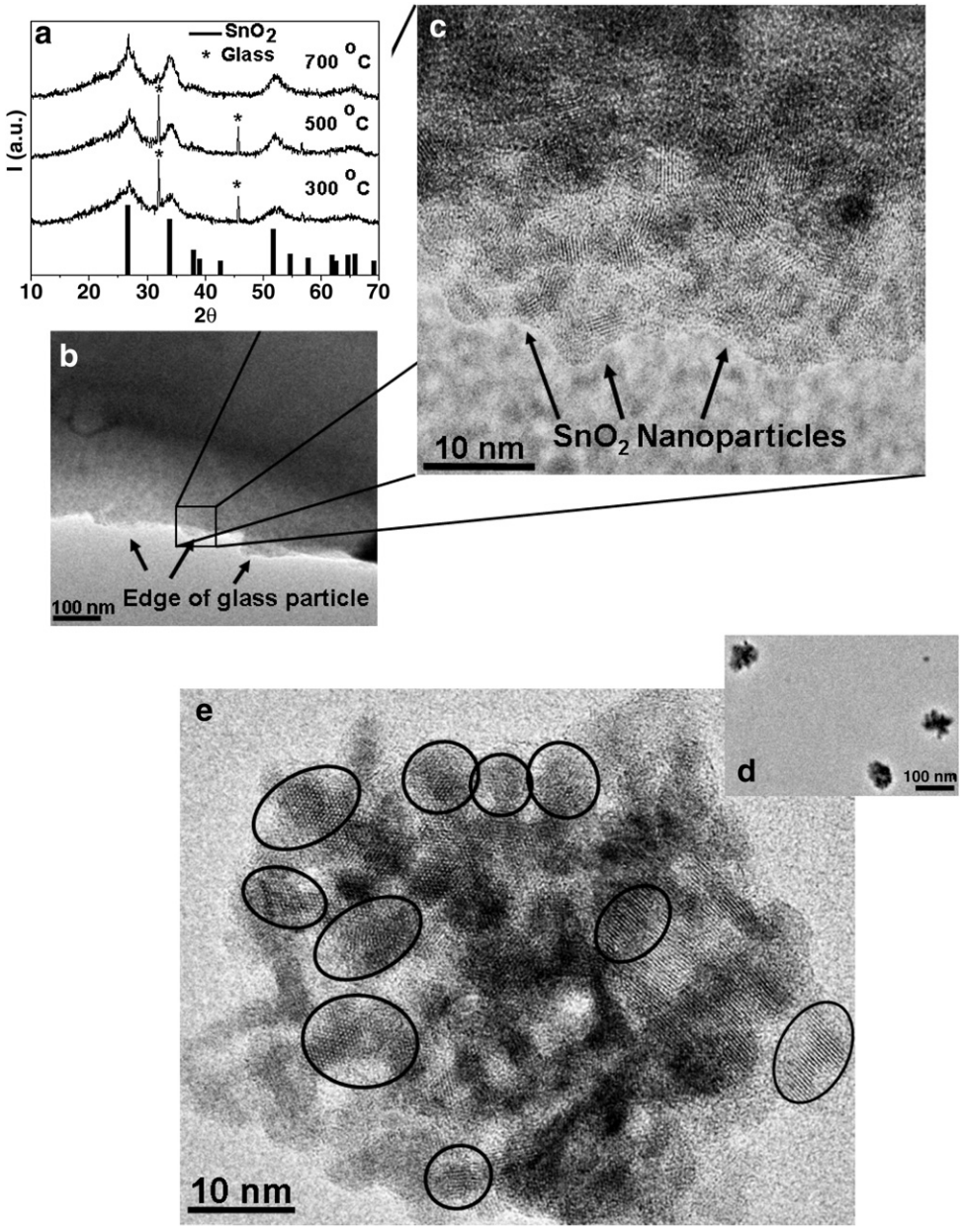

Fig. 4. a) XRD patterns of powdered undoped SnO_2 synthesized by milling SiO_2–CaO functionalized glass; b) TEM images of powders annealed at 700 °C; c) HRTEM images of edge of the SnO_2 functionalized glass particle; d) TEM and e) HRTEM images of SnO_2 nanoparticles (not functionalized on glass surfaces).

dehydration and dehydrogenation reactions (Eqs. (1) and (2), respectively) are promoted over the catalyst surface.

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \quad (1)$$

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \quad (2)$$

On the other hand, H_2 and C_2H_4 were the only products formed during the ethanol steam reforming process over Pr-doped SnO_2/SiO_2–CaO catalyst, indicating that ethanol dehydrogenation to acetaldehyde (Eq.(2)) is negligible. Instead, ethanol dehydration to ethylene (Eq. (1)) and an ethanol decomposition reaction (Eq. (3)) seem to occur as the main reactions.

$$C_2H_5OH \rightarrow 2H_2 + 2C + H_2O \quad (3)$$

The reaction pathway during catalytic ethanol steam reforming comprises a series of simultaneous reactions, including decomposition, dehydrogenation, dehydration and steam reforming reactions. These reactions are more or less promoted depending on the nature of the catalyst, the type of interaction with the surface of the solid material and the different reaction conditions [9,10].

Generally, according to the mechanism previously described for ethanol steam reforming, catalysts that have acidic characteristics, such as SiO_2, are known to favor the dehydration reaction to ethylene and water. In contrast, basic materials, such as La_2O_3, favor dehydrogenation to acetaldehyde. According to the results, it can be seen that dehydration and dehydrogenation reactions are promoted over SnO_2/SiO_2–CaO catalyst. Thus, a combination of catalytic properties can be observed on the surface of this catalyst, indicating that this particular catalyst has a great efficiency in the dehydration of ethanol and a mild capability for dehydrogenation of ethanol. The

increase in the production of ethylene may be indicative of a moderate modification of the material surface due to the doping with Pr. The addition of Pr apparently affects the basicity on the catalyst surface. Light olefins, such as ethylene, are important chemicals in the synthesis processes because of their high chemical activity during reactions. The worldwide demand for and production of light olefins are higher than those of any other chemicals, as they are mostly used to produce plastics, fibers and other chemicals [11].

For comparison with the SnO_2/SiO_2–CaO and Pr-doped SnO_2/SiO_2–CaO samples, the catalytic activity of the Eu-doped SnO_2/SiO_2 sample was evaluated.

From the results in Fig. 6 it can be seen that hydrogen, ethylene and acetaldehyde were the only products detected during the ethanol steam reforming process over the Eu-doped SnO_2/SiO_2 catalyst. Acetaldehyde was the major product formed, with lower amounts of hydrogen and ethylene, and therefore, dehydration and dehydrogenation reactions are promoted over this catalyst.

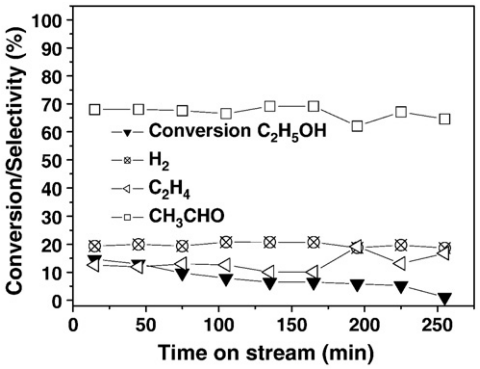

Fig. 6. Catalytic performance in the steam reforming of ethanol over a powdered Eu-doped SnO_2/SiO_2 sample annealed at 900 °C, with a H_2O/C_2H_5OH molar ratio of 3, at 500 °C.

4. Conclusions

The incorporation of stable SnO_2 nanoparticles into SiO_2 materials, doped with rare earth metals and undoped, was achieved. The results indicated that the amorphous silica regions of the material have an important role in the control of SnO_2 particle size.

The physico-chemical changes obtained through the preparation of the material at different temperatures were evaluated and no notable alterations in the structural properties were observed. The catalytic activity of the materials was monitored. It could be observed that the addition of dopants led to changes in the catalytic behavior of the materials with regard to the reaction of ethanol steam reforming.

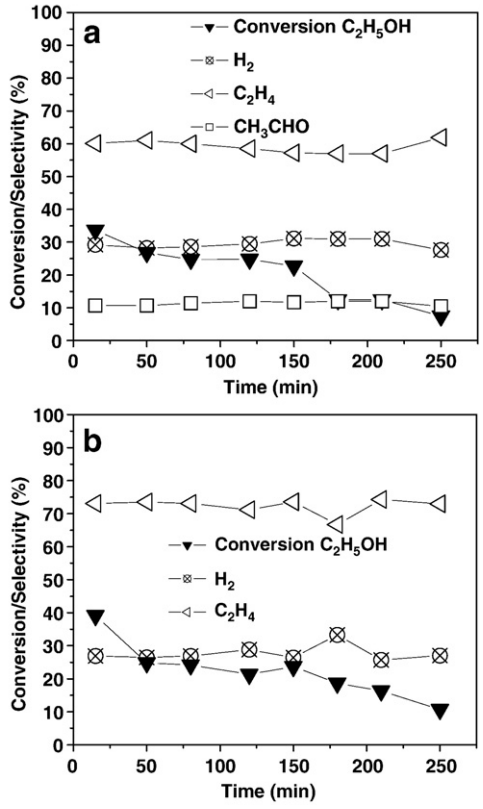

Fig. 5. Catalytic performance in the steam reforming of ethanol over a) undoped and b) Pr-doped SnO_2/SiO_2–CaO glass samples annealed at 700 °C, with a H_2O/C_2H_5OH molar ratio of 3, at 500 °C.

It was also found that the SnO_2/SiO_2–CaO and Pr-doped SnO_2/SiO_2–CaO catalysts were very selective toward ethylene, which is very well known as an important raw material in the polymeric industry.

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