IN SITU ELECTRICAL CONDUCTIVITY OF PROPENE INTERACTION WITH SnO2-CeO2 MIXED OXIDES

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A series of SnO2-CeO2 mixed oxides samples with 5, 10 and 20 wt% SnO2 prepared by co-precipitation were studied in the reaction of propene oxidation in the presence of air. The surface behavior of the samples was studied based on the response of the AC electrical conductivity and correlated with catalytic conversion of hydrocarbon. The obtained results have been discussed.
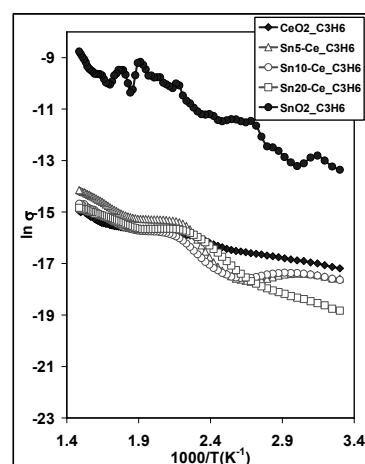
INTRODUCTION

Surface oxidation/reduction of the semiconductor oxides used in catalysis can be investigated by following the evolution of the electrical properties of the solid in relation with a specific atmosphere. The conductivity of the undoped ceria (an n-type material) is directly related to oxygen diffusion.[1] The incorporation of Zr^{4+} into the lattice of CeO_2 strongly favors the creation of structural defects and results in the acceleration of oxygen diffusion in the bulk.[2,3] Ceria-based compounds are used in catalysis particularly for abatement of pollutants due to ceria ability to release and uptake oxygen under different conditions, with the preservation of its fluorite structure. This material contains a high concentration of highly mobile oxygen vacancies, which act as local sources or sinks for the oxygen involved in reactions on its surface. This high oxygen storage capacity[4] relates to the electronic

structure of cerium and is coupled with its ability to switch between reduced and oxidized states (Ce^{3+}/Ce^{4+}).

In the present work the influence of the tin dioxide loading on the surface behavior of ceria was presented by electrical conductivity measurements. The catalytic performances of the synthesized samples were investigated in propene combustion as a model reaction for hydrocarbon removal from air.
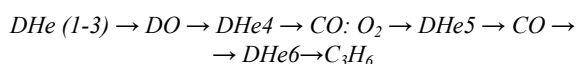
EXPERIMENTAL

Sample preparation: The SnO_2-CeO_2 catalyst samples (with a content of 5, 10 and 20 wt% SnO_2) were obtained by mixing aqueous solutions of tin (II) dichloride dihydrate ($SnCl_2 \cdot 2H_2O > 99\%$, Interkemia) and cerium (IV) ammonium nitrate (($NH_4)_2Ce(NO_3)_6$ 99%, Merck). Co-precipitation was achieved by addition of ammonium hydroxide. A similar procedure was used for obtaining pure SnO_2 and CeO_2 from the same precursors. The preparation of the catalyst samples was as given previously.[5] The obtained catalyst samples were labeled as follows: Sn5-Ce for the sample containing 5 wt% of SnO_2, Sn10-Ce and Sn20-Ce for samples with 10 and 20 wt% tin oxide content, respectively.

Characterization: The samples were characterized previously[5] by surface area and acidity determination (by BET and NH_3 pulse chemisorption method, respectively) and, in this paper, by electrical conductivity and catalytic measurements.

Electrical conductivity and catalytic properties: AC electrical conductivity measurements were carried out in a cell specially designed to allow simultaneous electrical and catalytic activity measurements in powders under **operando** conditions.[6-8] The electrical conductivity (σ) of the sample powder (1.5 cm^3, fraction between 0.25-0.5 mm) was measured at 1592 Hz, in gas flow with a RLC bridge (HIOKI 3522-50) by using the differential step technique (DST) as described previously.[6-8] At this frequency of the measurements the conductivity of the powder was dominated by surface conduction.[9]

The measurements were performed by successive thermal cycling, namely heating (2°/5°C min^{-1} heating rate between room temperature and 400°C) – cooling (about 10°C min^{-1} cooling rate) cycles, and changing the gases according to the protocol described below:

$$DHe\ (1\text{-}3) \rightarrow DO \rightarrow DHe4 \rightarrow CO: O_2 \rightarrow DHe5 \rightarrow CO \rightarrow \\ \rightarrow DHe6 \rightarrow C_3H_6$$

where: *DHe*- dry helium (the numbers given above indicate the cycle number), *DO*- dry oxygen,

$$CO:O_2 \text{ - } CO:O_2:He\ (5:5:90),\ CO \text{ - } CO: He\ (5:95),\ C_3H_6 - \\ - C_3H_6: air\ (1:22).$$
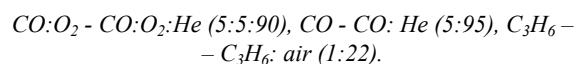
Before each heating run, the sample was flushed for 30 min with the corresponding gas mixture at room temperature.

Cooling was done in the same gaseous atmosphere, then the cell was closed and the sample was kept overnight in the same atmosphere. The measurements were coupled with the permanent monitoring of the composition of the inlet/outlet gas by on-line gas chromatography. The overall flow rate in all cases was 72 mL min^{-1}. Dry gases (except gas mixtures) were obtained by passing the research grade compounds through molecular sieves units.

The catalytic conversion of propene oxidation was measured simultaneously with the electrical conductivity, by periodically sampling from the effluent on heating during catalytic test runs, according to DST protocol. The effluent was periodically analyzed by gas chromatograph. The exit gas analysis was performed with a GC (Pye, TCD detector) attached on-line and equipped with two parallel columns (Porapak Q and molecular sieves 5Å) with helium as carrier gas.

RESULTS AND DISCUSSION

CeO_2 samples containing 5, 10 and 20 wt% SnO_2 and also SnO_2, CeO_2 pure oxides synthesized by co-precipitation method have been primary characterized.[5] It can be seen (Table 1) that S_{BET} of mixed oxides depends on the tin oxide loading. The surface area decreases with increasing amount of SnO_2.

The investigations on the electrical and catalytic properties of the SnO_2-CeO_2 catalysts and of their component single oxides were performed in operando conditions. (*i.e.* in gas flow, at atmospheric pressure). Since the simultaneous effects of the temperature and atmosphere make the interpretation of conductivity data very complex, we have used this technique (*i.e.* DST) in order to be able to separate them. If thermal cycling is performed in identical conditions and between the same temperature limits, the differences between plots at a certain temperature indicate just the particular effect of a certain atmosphere. Thus, using this technique one can obtain valuable information on the evolution of the catalyst surface under reaction conditions, e.g. on the surface dynamics in terms of its relative oxidation level. The interaction with a reducing gas such as hydrocarbon (propene) results either in formation of anion vacancies V_O (Mars-van Krevelen mechanism) acting as electron donors:

$$O_{(lattice)} + hydrocarbon \rightarrow oxidation\ products + V_O$$
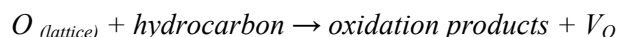
or in the consumption of the oxygen ad-ions. Both variants result in the increase of electrons carrier concentration and thus in the increase of conductivity.

Fig. 1a and 1b shows the influence of propene-air mixture and dry oxygen, respectively, to the variation of electrical conductivity with temperature.

Table 1

Surface areas of the studied catalysts

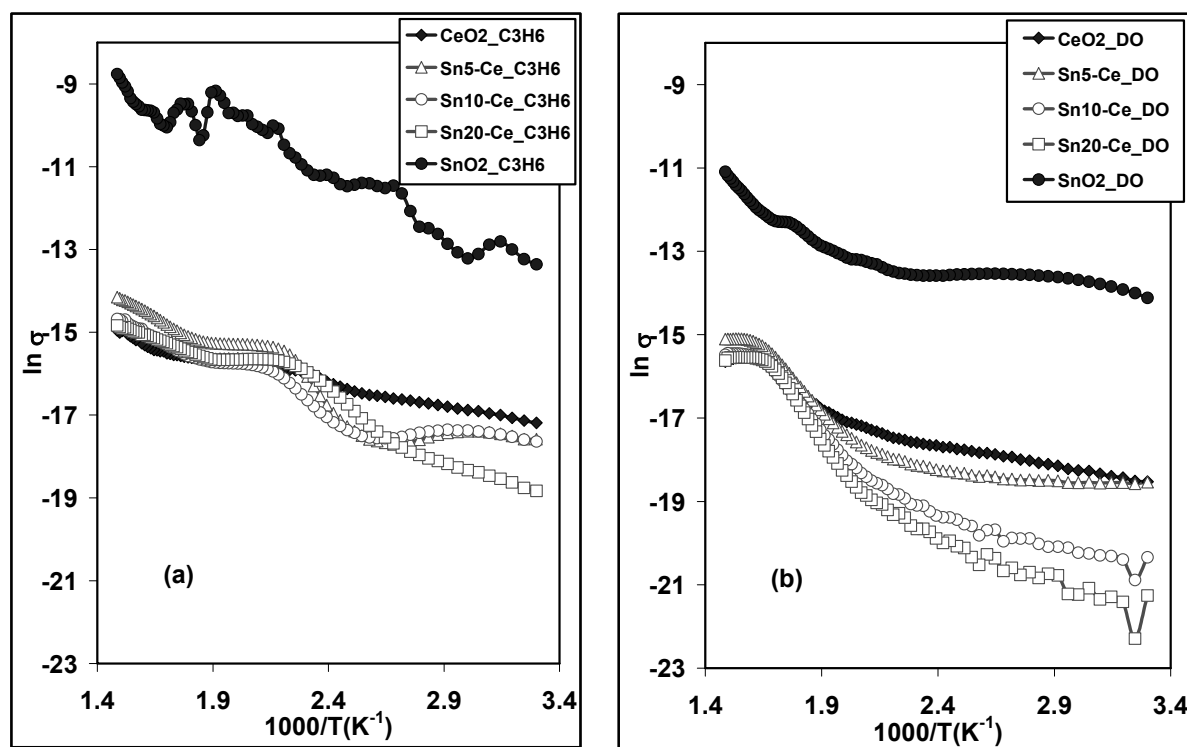| Samples	Abbreviation	$S_{BET} [m^2/g]$
CeO_2	CeO_2	46
5% SnO_2/CeO_2	Sn5-Ce	105
10% SnO_2/CeO_2	Sn10-Ce	99
20% SnO_2/CeO_2	Sn20-Ce	93
SnO_2	SnO_2	13

Fig. 1 – The Arrhenius plots for the temperature dependence of electrical conductivity σ *(S/m)* for all catalyst samples:
a) in the presence of gas mixture (C_3H_6: air); b) in dry oxygen.

In the presence of propene: air mixture (Fig. 1a) the conductivity values and general behavior of the mixed oxides are dictated by the dominant matrix of cerium oxide. At the same time, in the case of SnO_2-containing ceria samples, Arrhenius type curves show several peaks, which are evident also in the case of SnO_2, indicating a different interaction in different temperature ranges of reaction mixture with the solid surface. Reducing effect of the hydrocarbon mixture, marked by much higher values of conductivity, is most evident in the case of SnO_2, despite its much lower specific surface area (see Table 1), due to its special features in hydrocarbon adsorption, as the much lower mobility of oxygen from the bulk. Exposure to oxygen (Fig. 1b) leads to the decrease of conductivity with respect to that in gas mixture (propene: air), the electrons provided by the surface of the oxide being trapped by the adsorbed oxygen. The effect of oxygen atmosphere, as a result of the presence of some adsorbed species is

mainly observed at low temperature. On increasing the temperature, the dipoles of the lattice (as for example cation-oxygen or cation-oxygen vacancy pairs) become more mobile, which explains the increasing values of conductivity. This increase in conductivity turns into a plateau at high temperature. It could be explained by the surface re-oxidation of the SnO_2-CeO_2 and CeO_2 samples.

In order to have a better understanding regarding the conduction process and the change in conductivity related to the progressive loading of SnO_2 to CeO_2, the apparent activation energy of conduction was estimated from the slope of *ln (σ)* versus *1/T* plots. The Arrhenius type representations (Fig. 1a) obtained on flushing of catalyst samples in C_3H_6: air mixture shows two major linear parts, the change in the slope (i.e. of apparent activation energy of conduction) occurs at 200 and 270°C. The apparent activation energy of conduction values were estimated in the temperature range 270-400°C and are summarized in Table 2.

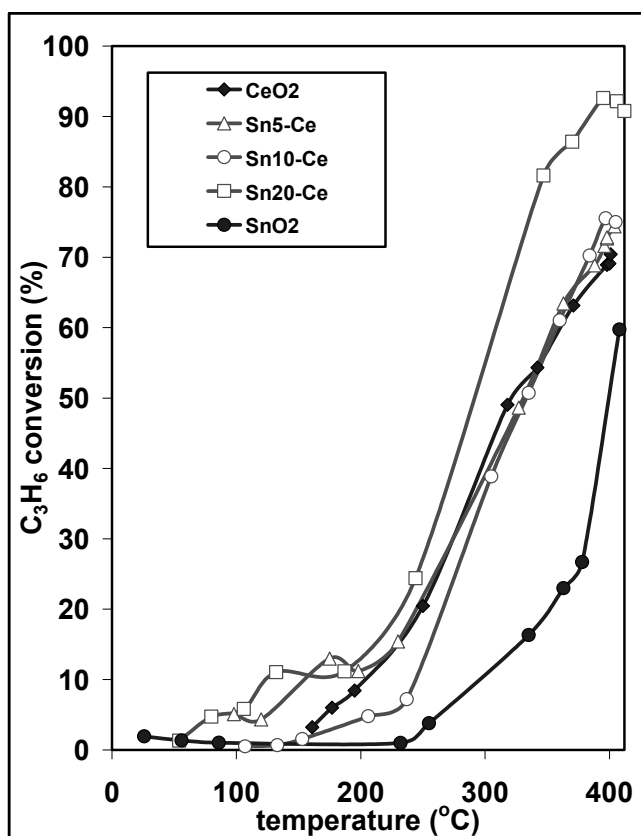| Sample	CeO$_2$	Sn5-Ce	Sn10-Ce	Sn20-Ce	SnO$_2$
Temperature range (°C)	330-390	270-400	270-400	270-400	355-400
$E_{a\,(C3H6:air)}$ (eV)	0.28±0.01	0.27±0.02	0.25±0.02	0.18±0.02	0.72±0.03

Fig. 2 – Propene conversion in the C$_3$H$_6$ cycle (C$_3$H$_6$: air =1:22).

For mixed oxide catalysts a decrease of apparent activation energy of conduction values compared to single component oxides was observed. This decrease of E_a, more evident in case of Sn20-Ce sample, is an indication of the enhancement of the surface adsorption of the reactant gases in propene oxidation reaction, possibly associated with a much higher lattice mobilization in this temperature range, in agreement with catalytic tests data presented below. The activation energy may be related to a variation of the defects formation energy. These defects (*i.e.* oxygen vacancies) can influence the catalytic behavior of mixed oxides.

The catalytic tests for hydrocarbon oxidation (C$_3$H$_6$ run) were performed in C$_3$H$_6$: air mixture 1:22 under programmed heating (2°/min) ramp between 30-400°C. The main products were in all cases CO$_2$ and H$_2$O. Propene conversion value on single oxides was lower than that on mixed compounds, the highest conversion (92.6%) being obtained for Sn20-Ce catalyst sample (Fig. 2). The other two mixed catalyst samples exhibits propene conversion values (around 75%) close to the ceria catalyst sample.

The onset of lattice mobilization with sharply increase of propene conversion values is above 250°C in good correlation with electrical

conductivity data (see Fig. 1a). The conversion curves passes from the kinetic regime in the low temperature range up to 250°C to the diffusion regime over this temperature.

CONCLUSIONS

Mixing SnO_2 with CeO_2 by co-precipitation induces the increase of the catalytic conversion value measured by deep propene oxidation reaction. The role of tin dioxide loading to ceria was evidenced also by enhancement of the surface interaction process of compounds with propene, related with the higher mobility of their lattice, the formation of anion vacancies and/or the consumption of oxygen ad-ions, as resulted from the measurement of electrical properties.

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