ELECTRICAL CHARACTERIZATION AND THE CATALYTIC PROPERTIES OF SnO₂/TiO₂ CATALYSTS AND THEIR Pd-SUPPORTED EQUIVALENTS

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Samples of SnO₂-TiO₂ with different SnO₂ loadings and their Pd-supported homologues were prepared, characterized and tested in propene oxidation reaction. The redox behavior of the samples was studied using AC electrical conductivity measurements performed *in operando* conditions. The results were discussed and correlated with the catalytic properties of the studied samples.
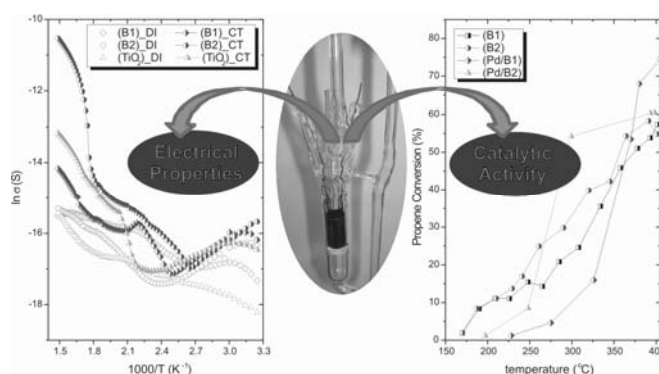
INTRODUCTION

Catalytic combustion is largely used to control the emission of toxic, volatile organic compounds (VOC's) due to its flexibility and energy saving in comparison to thermal combustion.[1] It offers the advantage that VOC's can be removed from the effluents up to very low levels at relatively low temperatures. Typical combustion catalysts are noble metal such as Pt or Pd dispersed on high surface area metal oxides like alumina,[2,3] silica,[4] or activated carbon.[5] These types of catalysts are most active for combustion, but they are rather unstable and expensive.[6]

The hydrocarbon oxidation over less expensive and more stable metal oxides catalysts occurs via a Mars van Krevelen (redox) mechanism,[7] which involves the participation of lattice oxygen. In this case, the redox properties of the catalyst are important factors as they determine its activity and selectivity.

The surface conductivity of catalysts is sensitive to the presence of chemisorbed species and to many other changes undergone by the catalyst during operation (*e.g.* phase and structural changes).[8] Information concerning the changes of the catalyst surface topography exposed to certain oxidizing, reducing or inert atmospheres can be obtained by electrical properties measurements performed in *operando* conditions.[9-16]

The aim of this paper is to study the structural and catalytic properties of SnO₂/TiO₂ catalysts by using the information concerning their reducibility obtained from electrical conductivity measurements. The catalytic performances of the samples were investigated using propene oxidation as a model

reaction for the hydrocarbon removal from air. For comparison, their Pd-supported equivalents were also studied.

EXPERIMENTAL

Synthesis and characterization

The SnO_2/TiO_2 catalysts were obtained by impregnating TiO_2 (Rhone Poulenc, S_{BET}-103m^2/g) with $SnCl_4$x5H_2O dissolved in ethanol, at room temperature. The amounts of SnO_2 deposited on TiO_2 were calculated in order to obtain a sub-monolayer and monolayer coverage,[17] *i.e.* 3% and 30% wt SnO_2. The samples were dried at 120°C, and then calcined in air flow for 5h at 500°C. 1% wt Pd supported samples were prepared by impregnating the SnO_2/TiO_2 catalysts previously obtained with $Pd(OAc)_2$ dissolved in acetone. The materials were treated again at 500°C for 4 hours, after that they were dried at 120°C.

The surface area of the samples was analyzed using a Micromeritics ASAP 2020 physisorption analyzer using N_2-BET adsorption technique. Prior to surface area determination, the powders were outgassed at 400°C.

The XRD analysis was performed on a Rigaku Ultima IV apparatus, with CuK$_\alpha$ λ = 1.5406 Å radiation, in the 2θ = 20-70° range.

The diffuse reflectance UV-Vis spectra were recorded using a spectrophotometer Perkin Elmer Lambda 35, equipped with an integrating sphere. The measurements were carried out at room temperature in the range 700-300 nm, using spectralon as a reference. The reflectance measurements were converted to absorption spectra using the Kubelka-Munk function, F(R).

Electrical conductivity measurements and catalytic tests

The redox behavior of the surface was monitored using AC electrical conductivity measurements performed in a cell specially designed to allow measurements in powders.[18] The electrical conductivity (σ) of the powder bed was measured at 1592 Hz, in gas flow with a RLC bridge (HIOKI 3522-50) by using the differential step technique (DST).[9,10] The measurements were performed on 1.5 cm^3 of powder catalyst (fraction between 0.25 and 0.5 mm), by successive thermal cycling between 20-400 ^{o}C and changing the gases in accordance with the following protocol:

$$DI_1 \Rightarrow DI_2 \Rightarrow DI_3 \Rightarrow DO \Rightarrow DI_4 \Rightarrow CT$$
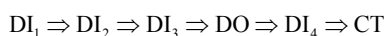
where   DI = dry inert gas (argon or helium) cycle
        DO = dry oxygen cycle
        CT = cycle performed in the mixture used for the catalytic test, namely C_3H_6:air 1:10 molar ratio.

The total flow rate was 72 mL/min.

The conversion for propene oxidation was measured simultaneously with the electrical conductivity measurements. The effluent was periodically analyzed with a gas chromatograph (Pye, TCD detector) attached on-line and equipped with two parallel columns (Porapak Q and molecular sieves 5Å) with helium as carrier gas.

The support and a SnO_2 sample (BDH) were also measured by following the same protocol.

RESULTS AND DISCUSSION

3% and 30% wt SnO_2 and their Pd supported equivalents with their abbreviations and surface area values are listed in Table 1. The BET surface areas of the support and commercial SnO_2 were also given in Table 1. The surface area depends on SnO_2 loading, decreasing with the increase of the SnO_2 amount. The surface areas for Pd supported samples are lower than that of their homologues without Pd, due to the supplementary thermal treatment.

To determine the dispersion and cristallinity of samples, the X-ray diffraction spectra were performed; the data are presented in Fig. 1. The XRD patterns of the studied samples showed the diffraction lines of anatase. The SnO_2 (cassiterite) characteristic diffraction lines were clearly observed only for the samples with high-load while the characteristic lines for palladium do not appear.

The UV-VIS spectra were presented in Fig. 2. A broad band between 400-500 nm centered at 480 nm could be observed in the absorption spectra of Pd containing samples, owing to d-d transition of PdO particles.[19,20] The spectra displays a characteristic absorption edge around 330 nm for TiO_2,[21] due to O^{2-} – Ti^{4+} transition. The band gap energies (E_g), a major factor determining the electrical conductivity of a solid semiconductor metal oxide, were obtained from the linear part of the $(F(R_\infty) \cdot h\nu)^{1/\eta}$ vs. hν graph. The values obtained for η=1/2, characteristic for direct allowed transitions are listed in Table 1.

Table 1

Surface areas and band gap energies for SnO_2/TiO_2 and $Pd/SnO_2/TiO_2$ samples

Sample/abbreviation	S_{BET} (m^2/g)	E_g
3% SnO_2/TiO_2 - **B1**	90.0	3.31
30% SnO_2/TiO_2 - **B2**	59.0	3.23
1%Pd/3% SnO_2/TiO_2 - **Pd/B1**	83.6	3.22
1%Pd/30% SnO_2/TiO_2 -**Pd/B2**	55.1	3.13
TiO_2	103.0	3.38
SnO_2	9.0	3.60
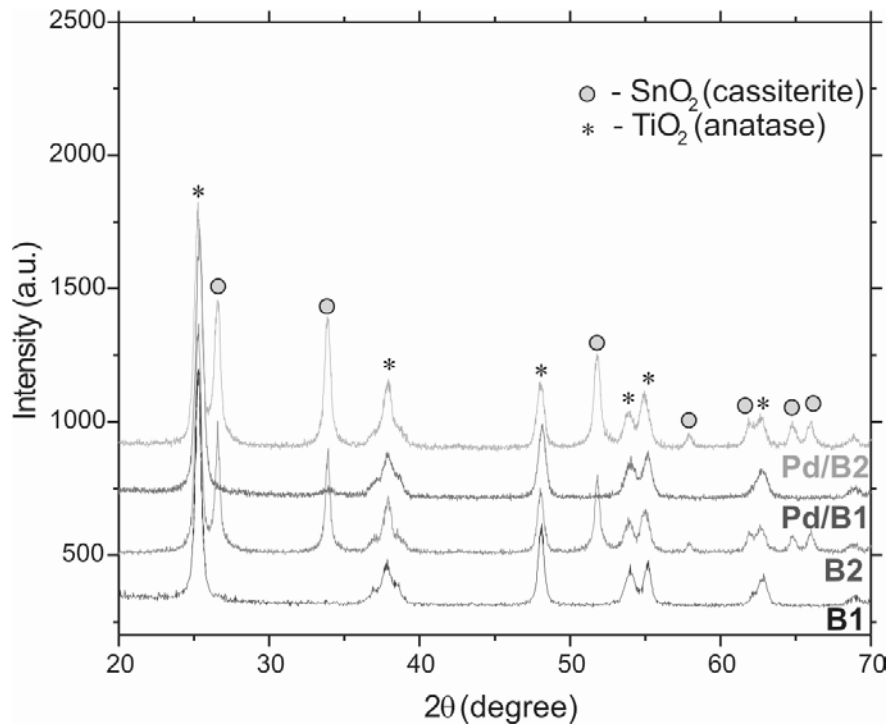
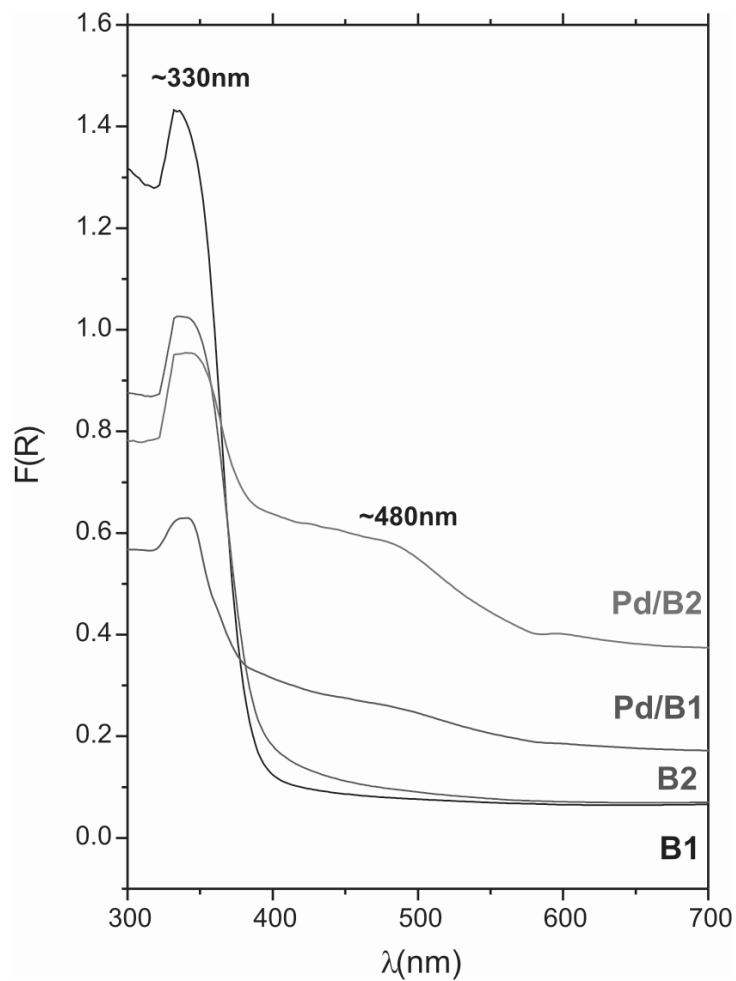Fig. 1 – XRD analysis for SnO$_2$/TiO$_2$ and Pd/SnO$_2$/TiO$_2$ samples.

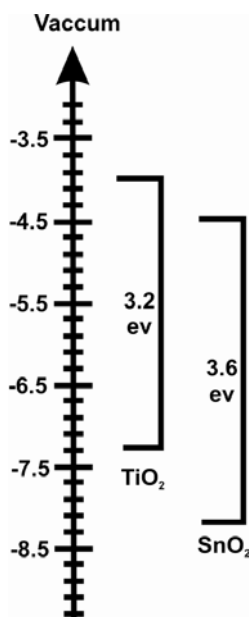Fig. 2 – UV-VIS spectra of SnO$_2$/TiO$_2$ and Pd/SnO$_2$/TiO$_2$ samples.

Fig. 3 – Schematic illustration
of energy levels of TiO_2 (anatase) and SnO_2.

The band gap energies for the supported samples are comparable with the band gap energy of TiO_2 and the values are decreasing with the increase of SnO_2 loading. This could be due to the formation of some defect sites when SnO_2 is adding. Another reason could be originated from the relative energies of valence band – conduction band of TiO_2 and SnO_2. The conduction band edge of SnO_2 is about 500 mV more negative than that of TiO_2 lowering the band gap energy of supported samples. Fig. 3 shows the schematic illustration of the energy levels of the conduction band (CB) and the valence band (VB) of TiO_2 and SnO_2.[22]

The presence of Pd leads to a larger decrease of the band gap energies.

The electrical properties of semiconductor oxide powders are determined by the mobility of charge carriers over the Schottky-type barriers at the contact between the adjacent grains. Surface reduction/oxidation and/or adsorption/desorption/ reaction are reflected in the topography of inter-grains areas and thus in the height of inter-grains Schottky-type barriers. The corresponding modification of the nature and mobility of the surface dipoles produces the changes in the electrical properties of the surface layer.[23] By using measurements of the electrical conductivity *in operando* conditions, it is possible to follow the changes in the oxidation states of the catalysts surfaces under reaction conditions.[9-16]

The conductivity measurements were performed starting with three heating-cooling cycles in inert flow (not shown here) which are used to clean the surface of atmospheric contaminants. Fig. 4 presents the conductivity plots before and during DO run for the B samples, the support and a commercial SnO_2. The conductivity for SnO_2 has much higher values over the whole temperature range. The conductivity behavior of supported samples follows the pattern of the support. This behavior was confirmed also by the band gap energy values calculated from the UV-Vis spectra.

At higher temperatures the conductivity is mostly electronic with a general *n*-type behavior: i.e. higher conductivity in inert, lower conductivity in oxygen, due to the adsorption on the surface of oxygen species, consuming electrons. The same phenomenon was noticed for their palladium doped equivalents (Fig. 5b).

Despite of the oxygen presence in the feed, heating in reaction mixture atmosphere (C_3H_6:air 1:10 molar ratio) induces a higher increase of sample conductivity compared with the electrical conductivity measured in inert atmosphere (Fig. 5a and b). The increased conductivity indicates the dominant surface reduction with hydrocarbon. The effect of the hydrocarbon presence in the feed is more important at higher temperatures. For Pd-supported samples, the conductivity in reaction mixture is higher than that in inert atmosphere over the whole temperature range in accordance with the literature data[24] which states that the presence of PdO increases the reducibility of TiO_2. For $3\%SnO_2/TiO_2$ (B1) sample, the increase of conductivity is significantly lower than for the other studied samples and begins at temperatures above 250°C. This indicates that the lattice reoxidation in this case is faster.

The increase in conductivity above 250°C is related to a sharp increase of conversion in C_3H_6 oxidation over the studied catalysts. The electrical conductivity and the catalytic data indicate that propene oxidation on these samples occurs following a Mars van Krevelen mechanism: the catalyst is reduced by propene (thus the increase in conductivity) and then it is slowly re-oxidized with the oxygen from air.
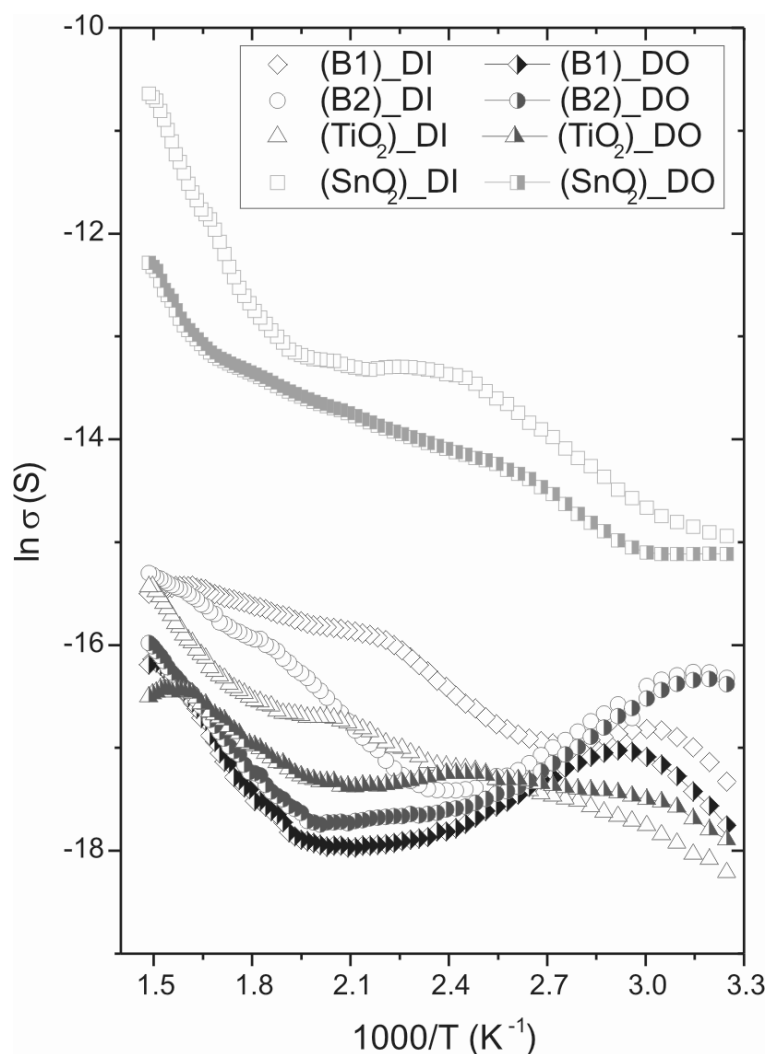
Fig. 4 – Comparison between the Arrhenius dependence of conductivity for TiO$_2$, SnO$_2$ and B samples in dry inert (DI3) and in dry oxygen (DO).

The calculated conversions, based on the decrease of propene peak with respect to the reference mixture at zero conversion, were also measured and the results obtained at 400°C are listed in Table 2. The conversions of the supported oxides are comparable with the conversion of TiO$_2$, but the selectivity to CO$_2$ is higher.

The temperature of the onset of the reaction (conversion of about 1.5%) varies in order:

PdB2 ~ PdB1 (160°C) < B2 (200°C) < B1 (230°C).

The lower temperature obtained when using Pd-containing catalysts could be correlated with the increase of reducibility of these samples, as resulted from the conductivity data.

The oxidation products were mainly CO and CO$_2$ with rather high selectivity for CO$_2$. The highest CO selectivity was obtained for 30%SnO$_2$/ TiO$_2$ (B2) sample. On the other side this is the sample showing the highest increase of conductivity which indicates that for this catalyst the reoxidation must be slower than reduction over the whole temperature range. The supra-reduction of the catalyst leads to more CO formation.

For 3%SnO$_2$/TiO$_2$ (B1) sample, the oxidation reaction starts at higher temperature than for the other samples, but it presents the highest conversion at 400°C (see Table 2). The high conversion and the high selectivity for CO$_2$ could be correlated with a faster reoxidation of the lattice, as results from conductivity data. For a reaction which takes place via Mars van Krevelen mechanism, an easily reducible catalyst has initially good catalytic activity but its long term use depends also on a facile reoxidation.
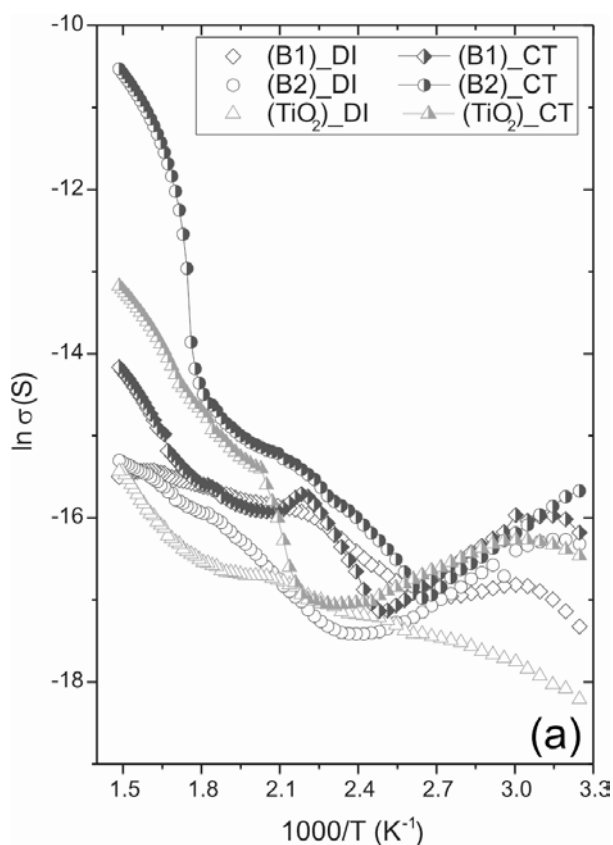
Fig. 5a – The Arrhenius dependence of conductivity of B1, B2 and TiO$_2$ samples during the catalytic test (DO run was used as reference).
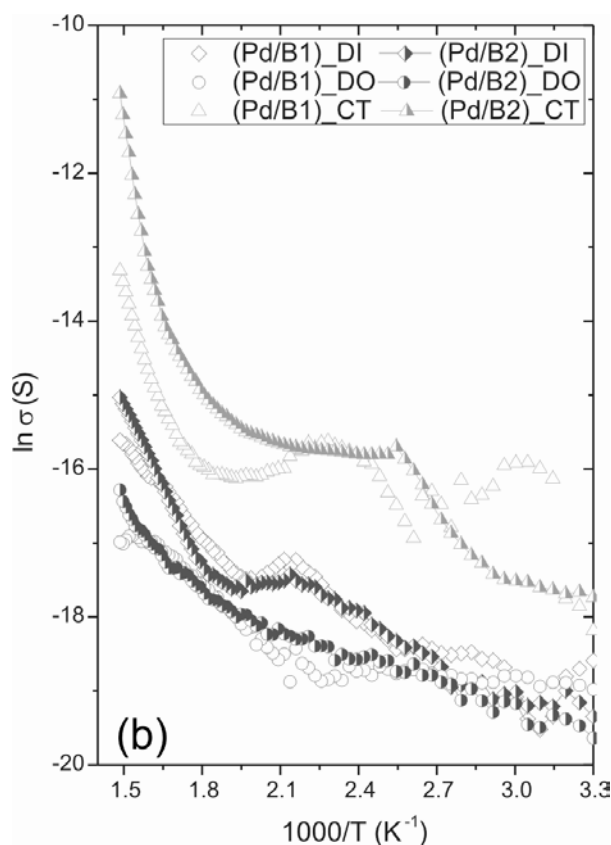
Fig. 5b – Comparison between the Arrhenius dependence of conductivity for Pd/B1, Pd/B2 samples in dry inert (DI3), dry oxygen (DO) and CT runs.

Table 2

Conversions and selectivities in propene oxidation (C$_3$H$_6$-air 1:10)

Catalyst	Temperature (°C)	Conversion (%)	S$_{CO}$ (%)	S$_{CO2}$ (%)
TiO$_2$	400	56.7	25.6	74.4
SnO$_2$	395	30.0	16.4	83.6
B1	405	74.6	9.9	89.9
B2	400	60.4	17.4	82.6
Pd/B1	403	52.4	7.1	87.8
Pd/B2	401	54.8	9.9	90.0

CONCLUSIONS

The surface modifications of various SnO$_2$/TiO$_2$ samples were investigated as a function of SnO$_2$ loading, in the presence or absence of palladium.

The electrical conductivity measurements indicated that propene oxidation on these tin oxide supported titania catalysts occurs via a Mars van Krevelen mechanism. It was also shown that the presence of Pd facilities the reduction of the sample at low temperature.

Because the 3%SnO$_2$/TiO$_2$ sample showed the highest propene conversion and also the highest selectivity for CO$_2$ at 400°C, these results recommend it as a possible catalyst for environmental purposes.

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