



“Gheorghe Asachi” Technical University of Iasi, Romania



ELIMINATION OF GAS POLLUTANTS USING SnO₂-CeO₂ CATALYSTS

Anca Vasile^{1*}, Monica Caldararu¹, Cristian Hornoiu¹, Veronica Bratan¹,
Niculae I. Ionescu¹, Tatiana Yuzhakova², Ákos Rédey²

¹“Ilie Murgulescu” Institute of Physical Chemistry, Romanian Academy, 202 Splaiul Independentei, 060021 Bucharest, Romania

²Institute of Environmental Engineering, University of Pannonia, 10 Egyetem Street, Veszprém, 8200 Hungary

Abstract

The surface behavior of a series of SnO₂ (5, 10 and 20 wt.%) - CeO₂ catalyst samples prepared by impregnation method and also pure SnO₂, CeO₂, was studied based on the response of the ac electrical conductivity. The electrical measurements were carried out in operando conditions in order to obtain information about the surface interaction with reactants during CO/hydrocarbon oxidation over these catalysts. The apparent activation energies of conduction in presence of CO:O₂ and C₃H₆:air mixtures were presented. The catalyst samples were tested in catalytic oxidation of CO and C₃H₆ at temperature range of room temperature up to 400°C. The catalytic activity in both oxidation reactions and selectivity towards CO₂ in propylene oxidation at 400°C exhibited by the SnO₂-CeO₂ systems were significantly higher to those exhibited by the pure ceria catalyst.

Key words: CO/hydrocarbon oxidation, electrical conductivity, SnO₂-CeO₂ catalysts

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1. Introduction

The low temperature catalytic oxidation of carbon monoxide (Taylor and Rhodes 2006; Kunkalekar and Salker 2010; Xu et al. 2010) and hydrocarbons (Gluhoi et al., 2006; Lamallem et al. 2009; Yoon et al., 1995) is of great practical importance due to its relevance in applications such as air purification, pollution control or cleaner automobile emissions. Many catalysts have been designed and tested for CO/C_xH_y oxidation under low temperature. Metal oxides like cerium oxide (Tang et al., 2004; Yuzhakova et al., 2009) have been used in this process.

The role of ceria as a support for other metal oxides is not only related to its oxygen storage capacity, but also to the ability of improving dispersion of the second component. Ceria provides the unique capability of promoting oxidation reactions, due to its ability to easily generate oxygen vacancies acting as active sites.

SnO₂ is among the oxides frequently used as a material for sensors and as a component of oxidation catalysts; however, its activity and electrical response to the ambient are limited by its low surface area. The SnO₂ deposition on supports having higher surface area was expected to increase the activity/electrical response properties of the catalysts.

Some mixed oxides were found to exhibit better catalytic properties as compared with the individual pure oxides (Liu and Liu, 2011). A number of studies on Ce-Sn (Sasikala et al., 2001; Mihaiu et al., 2004; Yuzhakova et al., 2009) mixed oxides systems were carried out, in order to achieve an increase in the oxygen storage/release capacity.

The present work focuses on a series of SnO₂ (5, 10 and 20 wt % content) - CeO₂ catalysts, abbreviated as Sn5-Ce, Sn10-Ce and Sn20-Ce obtained by impregnation method, and also deals with SnO₂, CeO₂ samples. The research objective was to analyze the influence of the amount of SnO₂ on the activity of cerium-tin mixed oxides in different

*Author to whom all correspondence should be addressed: e-mail: avasile@icf.ro, Phone: +4021.316.79.12, Fax: +4021.312.11.47

oxidation reactions (CO and C₃H₆) and to understand the surface properties and the redox behavior of these ceria-based catalyst samples in order to obtain systems with improved surface/catalytic properties in depollution processes.

The surface dynamics and the reducing ability of the catalysts were studied by electrical conductivity measurements in similar conditions with those encountered in practical catalytic applications. Electrical conductivity measurements and catalytic tests were carried out in heating/cooling cycles between room temperature and 400°C under different atmospheres (inert gas, O₂, CO, hydrocarbon). Data on the oxidation activity of the catalyst are discussed in the paper regarding the oxidizing properties of these catalysts in the oxidation reactions of carbon monoxide and various hydrocarbons.

2. Experimental

2.1. Sample preparation

SnO₂-CeO₂ samples were prepared by impregnation method using the tin(II) 2-ethylhexanoate (C₁₆H₃₀O₄Sn ~95,0%, Sigma, viscous liquid) and commercial cerium(IV) oxide (CeO₂ ~99.9%, Sigma, fine powder). C₁₆H₃₀O₄Sn was dissolved in n-hexane (CH₃(CH₂)₄CH₃ ≥ 98,0%) before impregnation. Solution for impregnation had a mass ratio of 1 tin(II) 2-ethylhexanoate: 5 n-hexane in order to achieve total dissolution solution of tin compound in hexane. The calculated amount (for preparation 5, 10 and 20 wt% of SnO₂) of C₁₆H₃₀O₄Sn dissolved in n-hexane was added to cerium(IV) oxide fine powder and was mixed mechanically. The obtained mixture was dried under infrared lamp up to the evaporation of n-hexane. The thin layer of obtained mixture of paste consistency was put on flat form of crucible and inserted in oven for calcinations in air.

Table 1. The list of catalysts studied

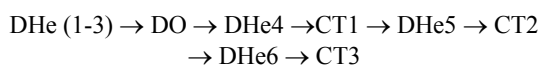
Samples	S_{BET} m ² /g	NH ₃ adsorption μmol/g
CeO ₂	7.8	29.69
Sn5-Ce	7.4	22.44
Sn10-Ce	9.0	25.45
Sn20-Ce	10.0	23.11
SnO ₂	17.2	11.20

The calcinations program was the following: heating in air up to 100 (200, 300)°C and keeping the sample at indicated temperature for 30 min, followed by heating and calcinations at 400°C for 5 hrs. A similar procedure was used for obtaining pure SnO₂ from the same organic precursor. CeO₂ samples containing 5, 10 and 20 wt.% SnO₂ were abbreviated as Sn5-Ce, Sn10-Ce and Sn20-Ce. The specific surface areas of samples were determined by the low-

temperature nitrogen adsorption (BET) method. The acidity of the samples was studied by temperature programmed isotherm (30°C) NH₃ adsorption (TPA). The list of the catalyst samples studied, their surface areas and the TPA data on acidity are summarized in Table 1.

2.2. Sample characterization

AC electrical conductivity measurements were carried out on the catalyst powder in a cell specially designed to allow simultaneous electrical and catalytic activity measurements in powders, under operando conditions i.e. in gas flow, using the differential step technique (DST) (Caldararu et al., 1996; Caldararu et al., 2003; Caldararu et al., 2007) and monitoring permanently the composition of the inlet/exit gas (on-line coupled GC) at atmospheric pressure. The sample powder (1.5 cm³, fraction between 0.25-0.5 mm) was placed in the annular space between the electrodes and supported on a frit. The electrical conductivity (σ) and the capacitance (C) of the powder bed were simultaneously measured at 1592 Hz, in gas flow with a RLC bridge (HIOKI 3522-50). At this frequency of the measurements the conductivity of the powder is dominated by surface conduction (Fripiat et al. 1965). The measurements were performed by successive thermal cycling, namely heating (2°/5°C min⁻¹, between room temperature and 400°C) – cooling (about 10°C min⁻¹) cycles, and changing the gases according with the following protocol:



where DHe- dry helium, DO- dry oxygen, CT1 - CO:O₂:He as 5:5:90, CT2- CO: He as 5:95, CT3 – C₃H₆:air as 1:22. The numbers given above indicate cycle number.

The catalytic performances in CO and C₃H₆ oxidation (by measurement of reactants conversions) were evaluated during the catalytic (CT) run of the electrical conductivity protocol, by periodically sampling the effluent into the gas chromatograph. The content of inlet/exit gases was permanently monitored by GC (Pye, TCD detector) attached on-line, on two parallel columns (Porapak Q and molecular sieves 5Å) with helium as carrier gas.

3. Results and discussion

3.1. Electrical measurements data

By comparing the Arrhenius plots obtained in these heating cycles it is possible to have a deeper insight on the influence of various gas atmospheres and on the surface dynamics in conditions similar to those encountered in the practical use in catalysis.

Fig. 1 presents the plots for the change of the conductivity for the CeO₂, SnO₂ and Sn5-Ce samples conductivity with temperature in successive heating-

cooling cycles under dry inert atmosphere (i.e. DHe3) and under dry oxygen (DO).

The electrical conductivity data (obtained in operando conditions) between room temperature and 400°C for all tin oxide containing ceria samples (here only Sn5-Ce plot is presented as an example), indicate an n-type semiconductor behavior, i.e. higher conductivity in inert or reducing gas atmospheres, lower conductivity in oxygen as a result of electrons consumption by formation of oxygen adsorbed species. For CeO₂ there was no significant change in conductivity values up to approximately 200°C ($1000/T(K) = 2.11 \text{ K}^{-1}$). Moreover, the conductivity of tin oxide impregnated samples follows the pattern obtained for CeO₂, namely, conductivity exhibits a continuous increase at low temperature and shows sharp increase at temperature above 235°C ($1000/T(K) = 1.96 \text{ K}^{-1}$). It should be noted that higher conductivity can be observed with increasing tin oxide content.

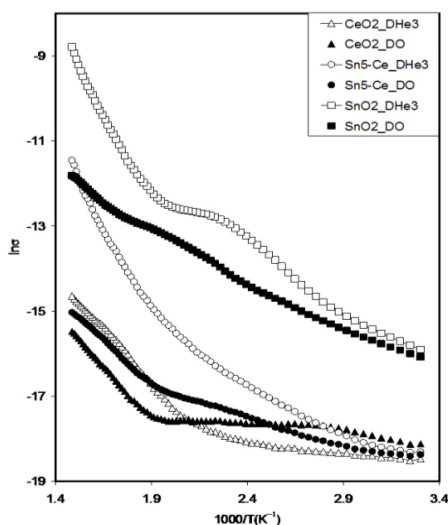


Fig. 1. Arrhenius plots for the variation of conductivity σ (S/m) on progressive heating of the samples in dry inert and in dry oxygen

The Figs. 2 and 3 show a comparison between the variation of conductivity obtained by flushing in CO:O₂ (1:1) and in C₃H₆:air (1:22) mixtures, respectively, for all catalyst samples.

SnO₂ shows a much higher conductivity during CO oxidation (CT1 run) and propylene oxidation (CT3 run), respectively. The other tin oxide containing samples exhibit lower conductivity values and a behavior similar to CeO₂. An increase in conductivity was observed for all studied samples, indicating surface reduction during the catalytic tests. The higher values of σ (S/m) in CT1 and in CT3 run (CO:O₂ and C₃H₆:air mixtures) above 200°C ($1000/T(K) = 2.11 \text{ K}^{-1}$), indicate a highly extent of reduction with the increase in temperature. A higher conductivity with increasing tin content can be observed as well.

The Arrhenius type representations obtained on flushing of catalyst samples in various atmospheres shows two major linear parts on Figs. 2 and 3, the change in the slope (i.e. of apparent activation energy of conduction) occurs at about 200°C ($1000/T(K) = 2.11 \text{ K}^{-1}$).

In order to have a better understanding regarding the change in conductivity the apparent activation energy of conduction values on progressive heating in reducing atmosphere are summarized in Table 2.

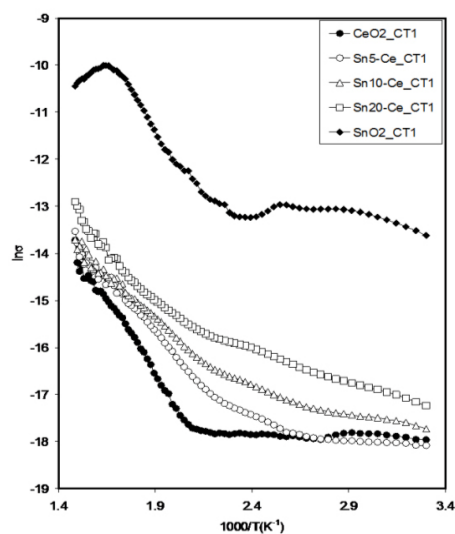


Fig. 2. Comparison between the conductivity σ (S/m) of the samples during the catalytic test of CO oxidation in presence of oxygen

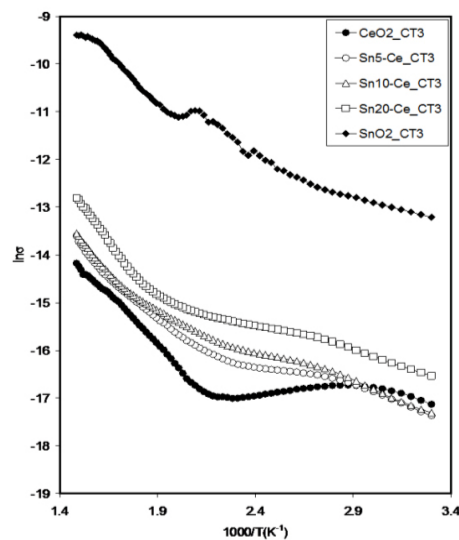


Fig. 3. Comparison between the conductivity σ (S/m) of the samples during the catalytic test of C₃H₆ oxidation

For tin oxide containing ceria samples on heating in CT1 run (CO oxidation in presence of oxygen) a decrease of apparent activation energy values compared to pure tin and cerium oxide was observed. The increasing tin oxide content in the

samples results in minor changes in the apparent activation energy values. This decrease of the apparent activation energy of conduction is an indication that the surface adsorption of the reactant gases in both oxidation reactions is favored.

Table 2. The apparent activation energy of conduction by CO and C₃H₆ oxidation

Sample	Apparent activation energy of conduction (eV)	
	CT1 run (235-400°C)	CT3 run (250-400°C)
CeO ₂	0.51 ± 0.01	0.33 ± 0.01
Sn5-Ce	0.35 ± 0.01	0.34 ± 0.01
Sn10-Ce	0.31 ± 0.01	0.33 ± 0.01
Sn20-Ce	0.38 ± 0.01	0.44 ± 0.01
SnO ₂	0.59 ± 0.01	0.35 ± 0.01

3.2. Catalytic tests data

CO oxidation (CT1 run) was performed in a mixture CO:O₂ as 1:1 balanced with helium (i.e. CO:O₂:He as 5:5:90) under programmed heating (2°/min) ramp between room temperature and 400°C.

In Table 3 the CO conversion values are listed with different reaction temperatures during CO oxidation on the CeO₂ samples and the impregnated tin dioxide-ceria samples.

Table 3. CO conversion at different reaction temperatures

Sample	Temperature(°C)	Conversion (CO:O ₂) (mol%)
CeO ₂	180	0.2
	360	51.4
	411	70.4
Sn5-Ce	150	0.1
	297	48.4
	410	90.0
Sn10-Ce	193	0.6
	301	51.0
	408	90.7
Sn20-Ce	177	2.2
	284	43.7
	408	91.9

It should be noted that the presence of SnO₂ increases the CO conversion at lower temperatures, which indicates a higher mobility of the lattice oxygen in tin oxide-ceria compounds in comparison with pure ceria (Table 3). Catalytic tests of CO oxidation in the presence of oxygen indicated that the conversion to CO₂ at about 400°C increases with the increase of the tin oxide content.

The Sn20-Ce sample exhibits the highest conversion value. However, finally for all the tin oxide containing ceria samples almost the same conversion can be reached. Under the given conditions, it can be concluded that the optimum

SnO₂ loading was 5 wt% in order to obtain a high conversion at 400°C for CO oxidation.

Moreover, in tin oxide-ceria samples about fifty percent of CO conversion at lower temperature (280-300°C) than pure ceria (360°C) was observed.

The catalytic tests for hydrocarbon oxidation (CT3 run) were carried out in C₃H₆: air mixture as 1:22 under programmed heating (2°/min) ramp between room temperature and 400°C. The propylene conversion and the CO₂ selectivity values obtained during C₃H₆ oxidation on the impregnated samples and pure CeO₂ are listed in Table 4.

Table 4. Propylene conversion and selectivity to CO₂ in propene oxidation at 400°C (contact time, τ = 1.25 s)

Sample	Conversion(C ₃ H ₆ :air) mol%	Selectivity to CO ₂ mol%
CeO ₂	32.9	92.5
Sn5-Ce	45.8	99.0
Sn10-Ce	41.7	99.8
Sn20-Ce	50.2	98.6

Similar results were obtained with these catalyst samples in the case of C₃H₆ oxidation, however with lower values of conversion as shown in the Table 4. Propylene conversion at high temperature (400°C) on cerium oxide was lower than that on impregnated samples. A decrease in the propylene conversion value for the Sn10-Ce sample was observed; this could be correlated with the increasing number of acidic sites in comparison with the other impregnated samples (see Table 1). Also the Sn20-Ce sample exhibited the highest activity in propylene oxidation reaction. As shown in Table 4, adding tin oxide to pure ceria results in an increase in CO₂ selectivity at 400°C; selectivity values around 100% for impregnated samples are obtained.

4. Conclusions

The AC electrical conductivity measurements indicated that all the samples behaved as n-type semiconductors. The presence of tin oxide improves the catalytic performances of the pure ceria for CO and C₃H₆ oxidation reaction. The tin oxide supported on ceria samples exhibited a high activity for CO oxidation and a moderate activity for deep propylene oxidation. They also showed a fifty percent of CO conversion at lower temperature than that of pure cerium oxide. By adding tin oxide to ceria compared to pure ceria selectivity increase can be observed towards CO₂ in propylene oxidation at 400°C..

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References

- Caldararu M., Munteanu C., Chesler P., Carata M., Hornoiu C., Ionescu N.I., Postole G., Bratan V., (2007), Supported oxides as combustion catalysts and as humidity sensors. Tuning the surface behavior by inter-phase charge transfer, *Microporous and Mesoporous Materials*, **99**, 126-131.
- Caldararu M., Postole G., Carata M., Chelu M., Hornoiu C., Ionescu N.I., Juchakova T., Redey A., (2003), In situ electrical conductivity study of propylene interaction with alumina surface, *Applied Surface Science*, **211**, 156-165.
- Caldararu M., Sprinceana D., Popa V.T., Ionescu N.I., (1996), Surface dynamics in tin dioxide-containing catalysts II. Competition between water and oxygen adsorption on polycrystalline tin dioxide, *Sensors and Actuators, B: Chemical*, **30**, 35-41.
- Fripiat J.J., Jelli A., Poncelet G., André J., (1965), Thermodynamic Properties of Adsorbed Water Molecules and Electrical Conduction in Montmorillonites and Silicas, *The Journal of Physical Chemistry*, **69**, 2185-2197.
- Gluhoi A.C., Bogdanchikova N., Nieuwenhuys B.E., (2006), Total oxidation of propene and propane over gold-copper oxide on alumina catalysts: Comparison with Pt/Al₂O₃, *Catalysis Today*, **113**, 178-181.
- Kunkalekar R.K., Salker A.V., (2010), Low temperature carbon monoxide oxidation over nanosized silver doped manganese dioxide catalysts, *Catalysis Communications*, **12**, 193-196.
- Lamallem M., Cousin R., Thomas R., Siffert S., Aïssi F., Aboukais A., (2009), Investigation of the effect of support thermal treatment on gold-based catalysts' activity towards propene total oxidation, *Comptes Rendus Chimie*, **12**, 772-778.
- Liu H., Liu Y., (2010), Removal of p-xylene by a DBD-type plasma combined with catalyst, *Environmental Engineering and Management Journal*, **10**, 749-753.
- Mihaiu S., Postole G., Carata M., Caldaranu M., Crisan D., Dragan N., Zaharescu M., (2004), The structure properties correlation in the Ce-doped SnO₂ materials obtained by different synthesis routes, *Journal of the European Ceramic Society*, **24**, 963-967.
- Sasikala R., Gupta N.M., Kulshreshtha S.K., (2001), Temperature-programmed reduction and CO oxidation studies over Ce-Sn mixed oxides, *Catalysis Letters*, **71**, 69-73.
- Tang X., Zhang B., Li Y., Xu Y., Xin Q., Shen W., (2004), Carbon monoxide oxidation over CuO/CeO₂ catalysts, *Catalysis Today*, **93-95**, 191-198.
- Taylor S.H., Rhodes C., (2006), The oxidation of carbon monoxide at ambient temperature over mixed copper-silver oxide catalysts, *Catalysis Today*, **114**, 357-361.
- Xu H., Chu W., Luo J., Liu M., (2010), New Au/FeOx/SiO₂ catalysts using deposition-precipitation for low-temperature carbon monoxide oxidation, *Catalysis Communications*, **11**, 812-815.
- Yoon Y.S., Fujikawa N., Ueda W., Moro-oka Y., Lee K.W., (1995), Propane oxidation over various metal molybdate catalysts, *Catalysis Today*, **24**, 327-333.
- Yuzhakova T., Redey A., Caldaranu M., Kovacs J., Postole G., Hornoiu C., Vasile A., Domokos E., (2009), SnO₂-CeO₂ Oxidation Catalysts, *Environmental Engineering and Management Journal*, **8**, 1403-1406.