



SURFACE PROPERTIES AND CATALYTIC OXIDATION ON V₂O₅-CeO₂ CATALYSTS

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A series of V₂O₅-CeO₂ mixed oxide samples with V/Ce atomic ratios as 1:1 and 2:1 were prepared by co-precipitation (from inorganic precursors) via two different routes: in presence and in absence of diethylene glycol (DEG). The surface behavior of the samples was studied based on the response of the ac electrical conductivity and correlated with their structure (as determined from spectroscopic data: XRD, EPR, UV-Vis). The compounds were also tested in catalytic oxidation of CO and propylene.

INTRODUCTION

V₂O₅ and CeO₂ are well known materials in oxidation catalysis. Besides being used as a catalyst for selective oxidation of hydrocarbons and of other VOC (volatile organic compounds)^{1,2} vanadia is also a main component of the catalysts used for environmental purposes.³ Ceria-based composites are used in composition of catalysts for diesel soot oxidation,⁴ in the three-way catalysts (TWC)⁵ and in combustion catalysts, ceria being well known for its oxygen storage capacity.⁶ Thus, it is to be expected that the combinations of vanadia and ceria will produce efficient oxidation catalysts due to the synergetic effects in terms of the redox behavior of the constituent oxides.

The conductivity of the powders is controlled by Schottky type intergrain barriers, whose heights is strongly dependent on the topography, coverage and dielectric constant of the surface layer in intergrain areas. Since changes induced by reduction/oxidation will be reflected in variations of the height of the intergrain barriers, such

processes could be followed by measuring the electrical conductivity of the surface.

In the present work it was studied the influence of the molar ratio and the presence of chelating agent on the structure of the obtained mixed oxides by spectroscopic data and electrical conductivity measurements. In the same time, the samples were tested in CO oxidation and in propylene combustion, as a model reaction for hydrocarbon removal from air.

EXPERIMENTAL

The samples. Two pairs of samples were prepared by co-precipitation from the corresponding vanadia and ceria precursors (solutions of Ce(NH₄)₂(NO₃)₆ and V₂O₅, in diluted nitric acid, respectively), with V/Ce atomic ratios as 1:1 and 2:1, in absence and in presence of diethylene glycol (DEG).⁷ The adequate concentration of cerium compound was added into the V₂O₅ solution. A suspension was obtained, which was further heated with stirring at 80-90°C on a water bath, for 4 hours, resulting in a clear solution. By addition of NH₄OH (pH=9), precipitates were obtained that were filtered, washed to remove residual ions, dried at 80°C and then thermally treated for 30 minutes at 400°C.

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Samples of mixed V/Ce oxides with the ratio mentioned above were also prepared in the presence of diethylene glycol as complexing and dispersing agent with a molar ratio of: 0.01 V-Ce precursors/0.42 DEG.

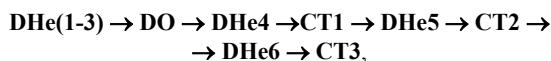
The samples were abbreviated as 1V_1Ce, 2V_1Ce, and 1V_1Ce_DEG, 2V_1Ce_DEG, respectively.

Characterization. The samples were previously characterized by BET surface area measurements, X-ray diffraction, FT-IR, XPS, transmission electron microscopy (TEM) and selected area electron diffraction (SAED).⁸ In this paper, the samples were characterized by EPR, UV-Vis, electrical conductivity and were tested in CO and propylene oxidation.

The EPR spectra were recorded at liquid nitrogen temperature using a Varian 104E spectrometer (X-band spectrometer) having a microwave bridge which generates a microwave radiation with a frequency in the 9 GHz range and provided with a digital data acquisition system.

Diffuse reflectance UV-VIS spectra were recorded using a spectrophotometer Perkin Elmer Lambda 35, equipped with an integrating sphere. The measurements were carried out in the range 900-200 nm, using spectralon as a reference. The reflectance measurements were converted to absorption spectra by using the Kubelka-Munk function, F[R].

Electrical conductivity. The redox behavior of the surface was followed by AC electrical conductivity measurements performed in a cell specially designed to allow measurement in powders, in operando conditions (*i.e.* in gas flow, at atmospheric pressure), by using the differential step technique (DST).^{9,10} The scope was to follow the surface behavior of the samples in various atmospheres, being known that adsorption/desorption/reaction occur with charge transfer. The measurements were performed by successive thermal cycling between 20-400°C, and changing the gases according with the following protocol:



where **DHe**- dry helium, **DO**- dry oxygen, **CT1** - CO:O₂:He as 5:2.5:92.5, **CT2**- CO: He as 5:95, **CT3** – C₃H₆:air as 1:22. The content of inlet/exit gases was permanently monitored by GC.

The conversions for CO and propylene oxidation respectively were measured simultaneously with electrical conductivity measurements, by periodically sampling from the effluent on heating during CT runs. Even if not absolute, as in the case of stationary state data, the values obtained are informative in terms of the trend of CO/propylene conversion

RESULTS AND DISCUSSION

The BET surface areas are listed in Table 1. As shown, the samples prepared *via* DEG route have higher surface areas than the corresponding samples prepared without DEG. The surface areas of the mixed oxides decreased with the increase of vanadium content.

As shown in Figs. 1 a and b, XRD data indicated the formation of CeVO₄ in all samples.

The oxide powders obtained with the higher V content, with and without DEG, contain also orthorombic V₂O₅.⁸

The electrical conductivity data (obtained in operando conditions) between room temperature and 400°C (Figs. 2 a and b) indicate, for all samples, an n-type semiconductor behavior (higher conductivity in inert gas, lower conductivity in oxygen). The Arrhenius representations consist of plots with two linear parts, the change of the slope (*i.e.* of activation energy for conduction) occurring at about 200°C for samples prepared without DEG, and at about 270°C for samples with DEG, respectively. The conductivity is more obviously influenced by the presence of oxygen above these temperatures.

Figs. 2 a and b show also a difference between the two series of samples, those prepared without DEG presenting higher conductivities.

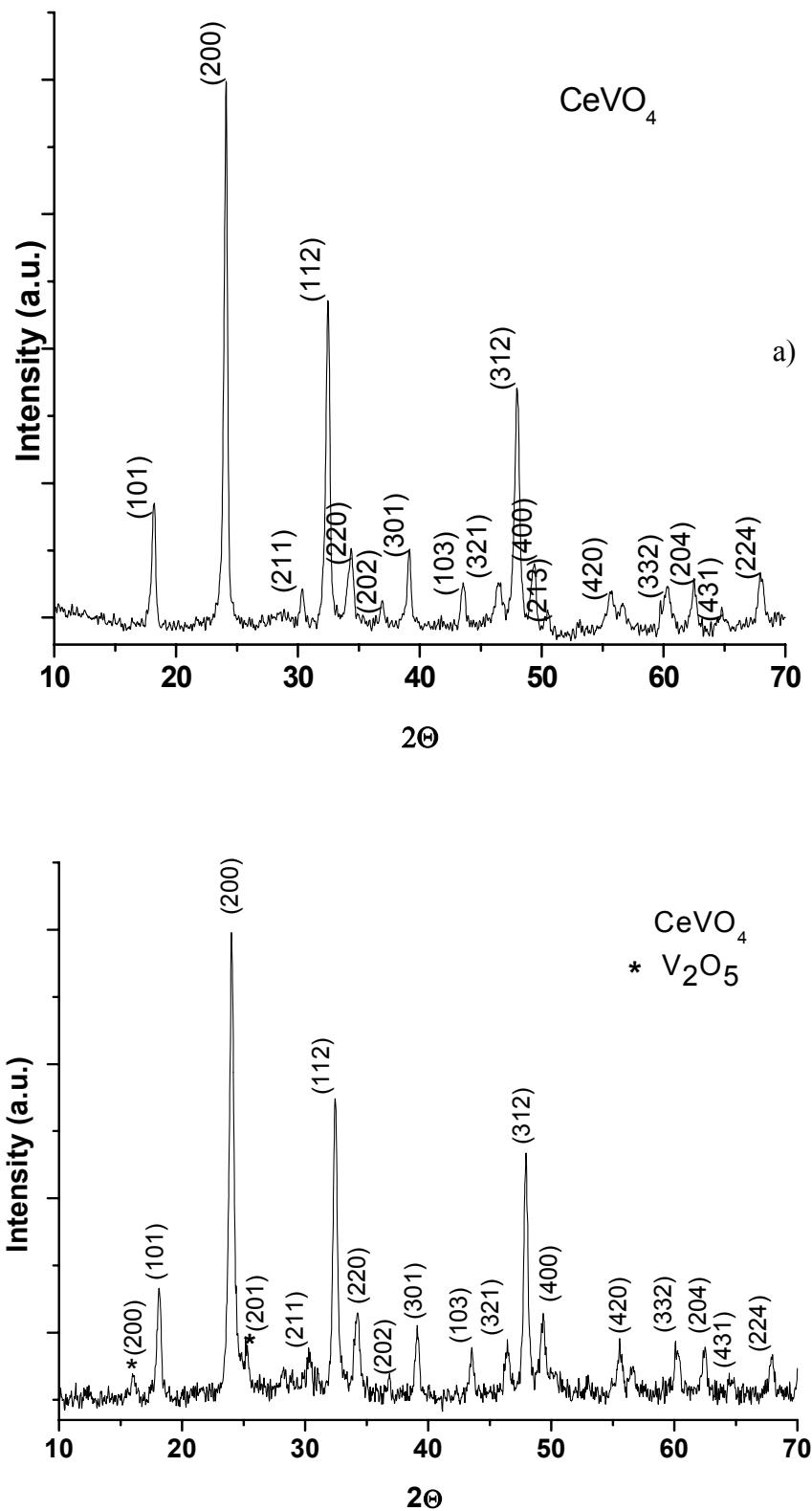
Rather surprisingly, the gas mixtures containing reducing gases (CO, C₃H₆) have also a weak influence on the conductivity for all vanadia-ceria catalysts. The samples prepared with DEG show higher sensitivity to the presence of various atmospheres (Figs. 2 and 3), in correlation with their higher surface areas.

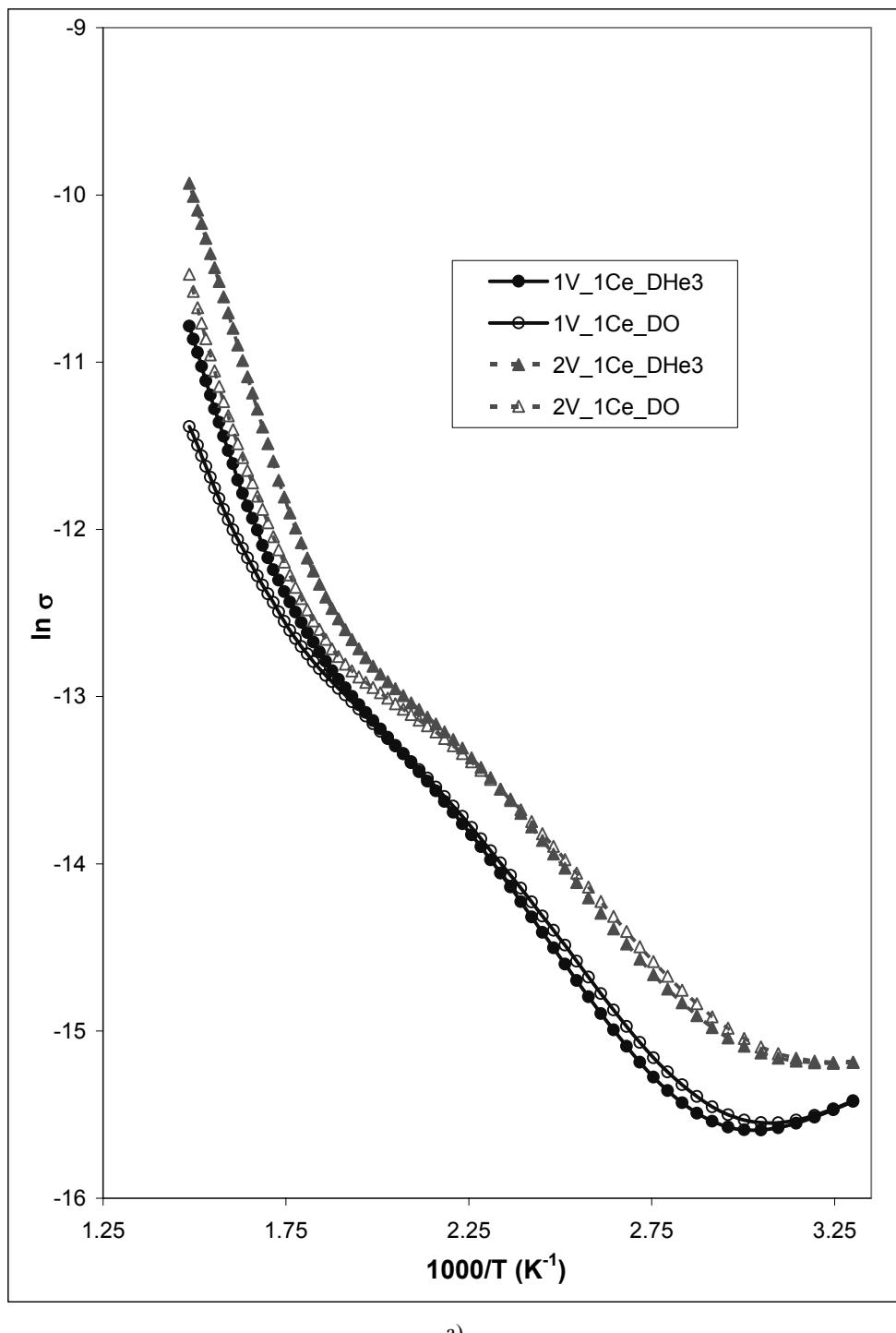
In presence of CO:O₂ mixture (CT1 plot), no significant effects on conductivity were detected for 1V_1Ce and 2V_1Ce samples. Since in the temperature region above 250-300°C the catalytic oxidation of CO on the oxide catalysts occurs via Mars van Krevelen mechanism,¹¹ the apparent stability of the surface in this cycle indicates either a poor adsorption of CO or that the rates of surface reduction and reoxidation should be almost equal. The slightly higher values of σ in CT2 run (CO:He mixture) above 205°C indicates however a slight surface reduction above this temperature. In CT3 cycle the conductivity increases continuously starting with ~100°C; this indicates progressive surface reduction (Fig. 3).

Table 1

Surface areas for all fresh catalysts

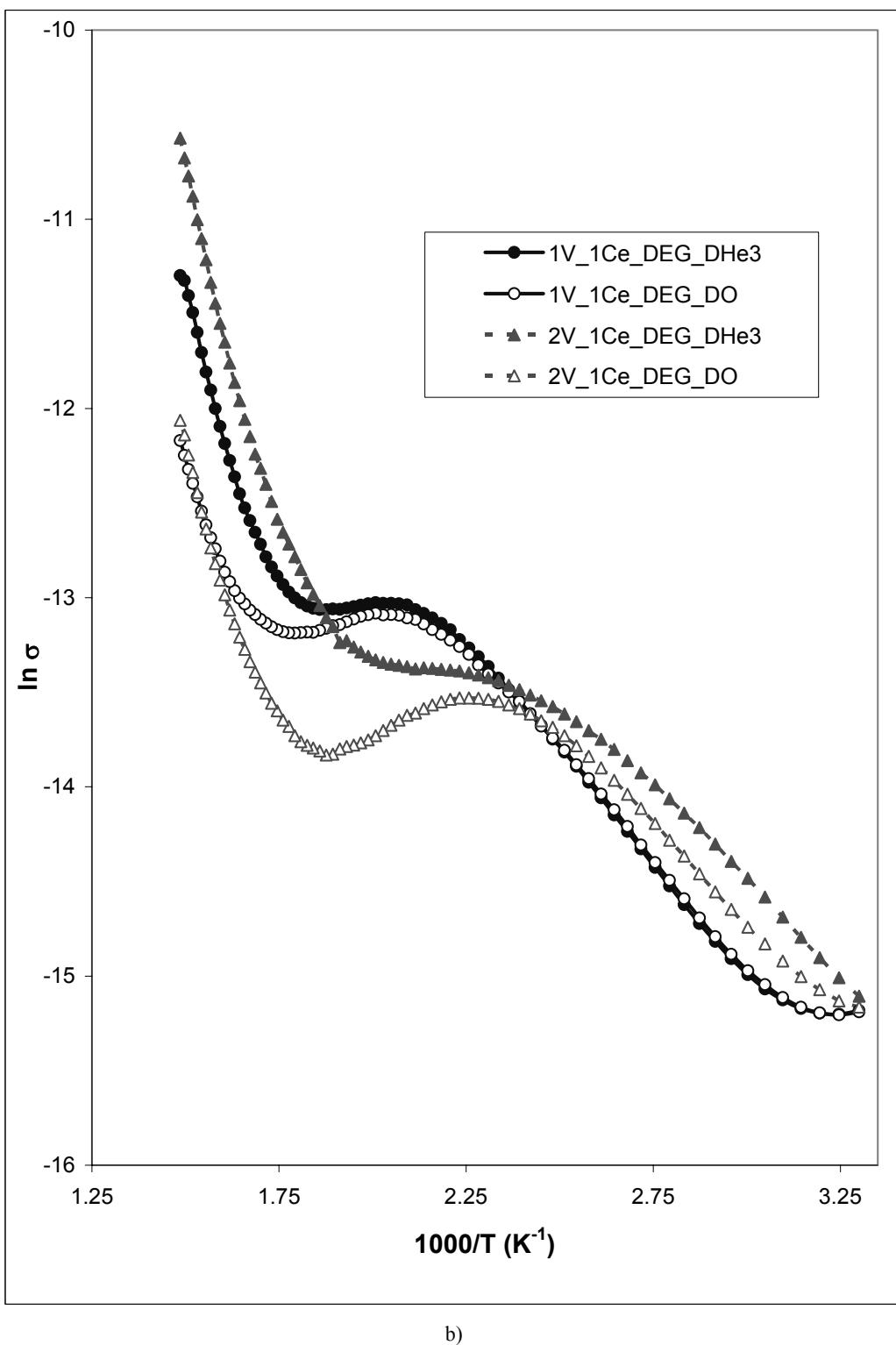
Samples	1V_1Ce	1V_1Ce DEG	2V_1Ce	2V_1Ce DEG
Surface areas (m ² /g)	31	34.6	11.72	20.5

Fig. 1 – XRD patterns of: a) 1V_1Ce; b) 2V_1Ce⁸.



a)

Fig. 2a – The Arhenius plots for temperature dependence of the electrical conductivity on temperature for:
a) $1V_1Ce$ and $2V_1Ce$.



b)

Fig. 2b – The Arhenius plots for temperature dependence of the electrical conductivity on temperature for:
b) 1V_1Ce_DEG and 2V_1Ce_DEG.

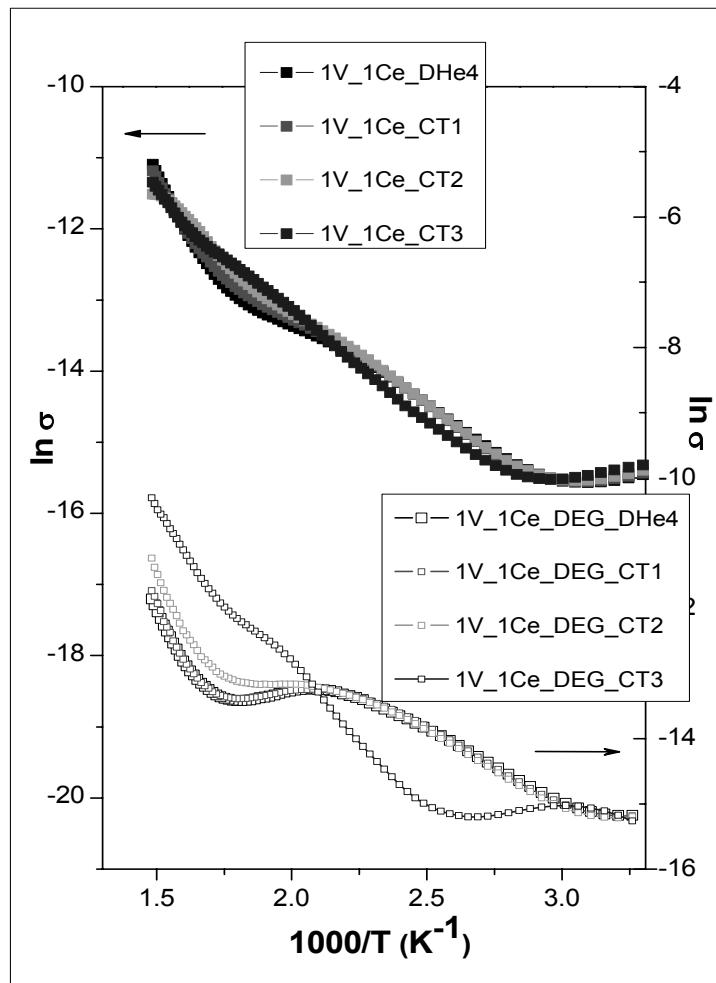


Fig. 3 – The Arrhenius plots for the temperature dependence of conductivity in dry helium (reference) and in CT runs (see the protocol) for 1:1 V:Ce samples.

Based on literature data,¹² the EPR signals shown in Fig. 4, were assigned to Ce^{3+} ions, in good correlation with XRD data, indicating that the main compound present in all the catalysts is CeVO_4 .

For the samples prepared by using DEG, a slight increase in the intensity of the EPR lines after the catalytic test was observed, indicating that these samples are more easily reduced during the catalytic test (being known that the intensity of the EPR lines is directly correlated with the concentration of the Ce^{3+} ions).

For the samples prepared in absence of DEG (not shown), the EPR signals showed virtually no changes of the line shapes in comparison with samples prepared with DEG, the signals obtained for the tested samples being almost identical with those of the fresh samples. This is an indication that the catalyst is relatively stable during the oxidation reaction (concentration of the Ce^{3+} ions

is relatively constant). These observations are in very good agreement with conductivity data, indicating a very weak, or practically no reduction for the samples without DEG.

The UV-VIS spectra are shown in Figs. 5 and 6. In the region 200-300 nm vanadia and ceria have the following absorption bands: V_2O_5 exhibits Ligand Metal Charge Transfer (LMCT) bands at 236, 334 and 481 nm; VO_4 at 260, 300 nm (isolated) or 280, 350 nm (polymerized).¹³ CeO_2 exhibits LMCT bands at 256, 296 nm (Ce(III) , Ce(IV)) respectively. For this reason the large band obtained in this region could not be resolved. The presence of Ce^{3+} is obvious: for all samples one can observe the twin absorption features at about 560 and 600 nm, specific for $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$ transitions.¹⁴ For the samples with the higher content of vanadium another peak appears at 230 nm, assigned to V_2O_5 .

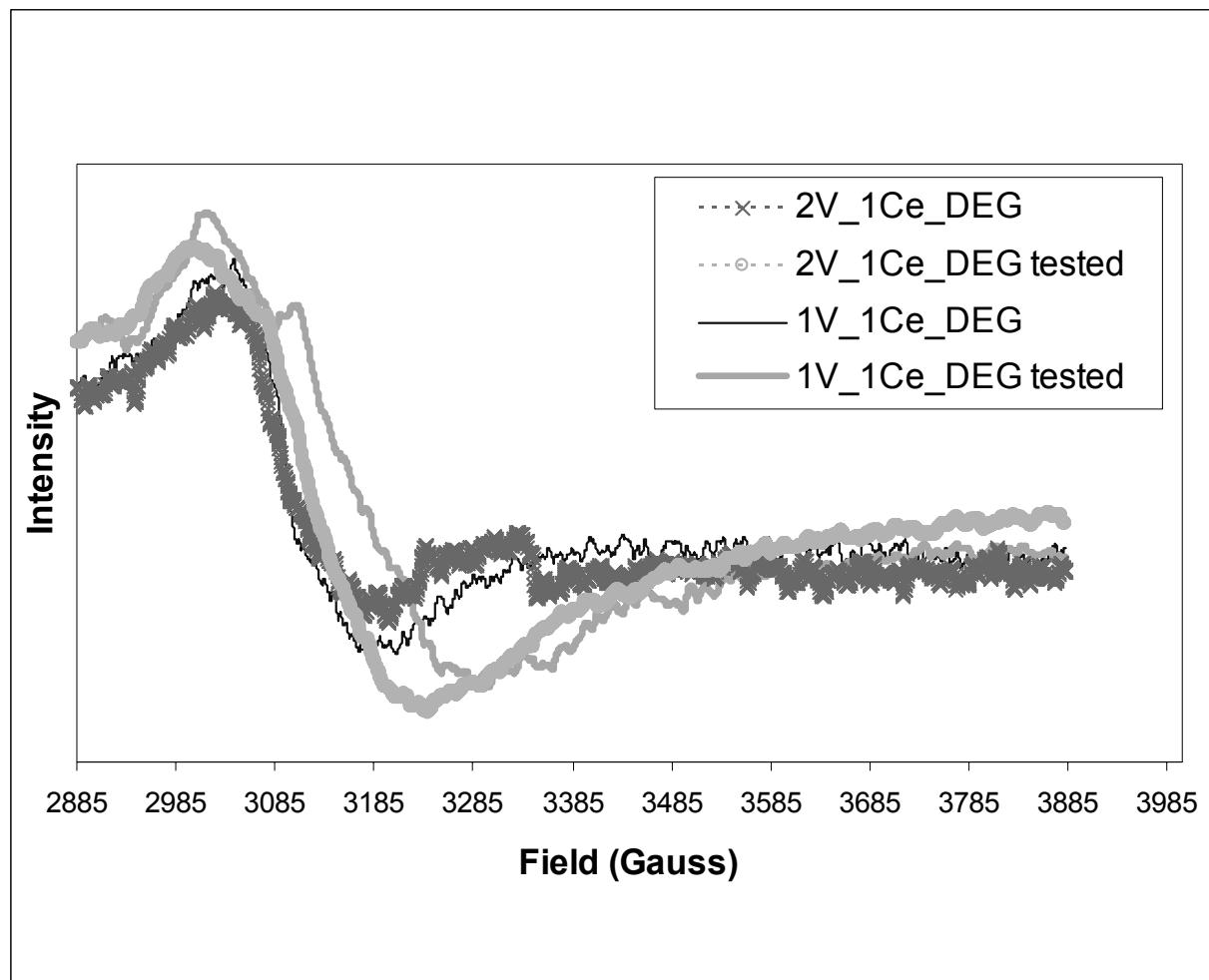


Fig. 4 – EPR spectra for fresh and tested samples with: 1:1 V:Ce molar ratio and 2:1 V:Ce molar ratio prepared by DEG route.

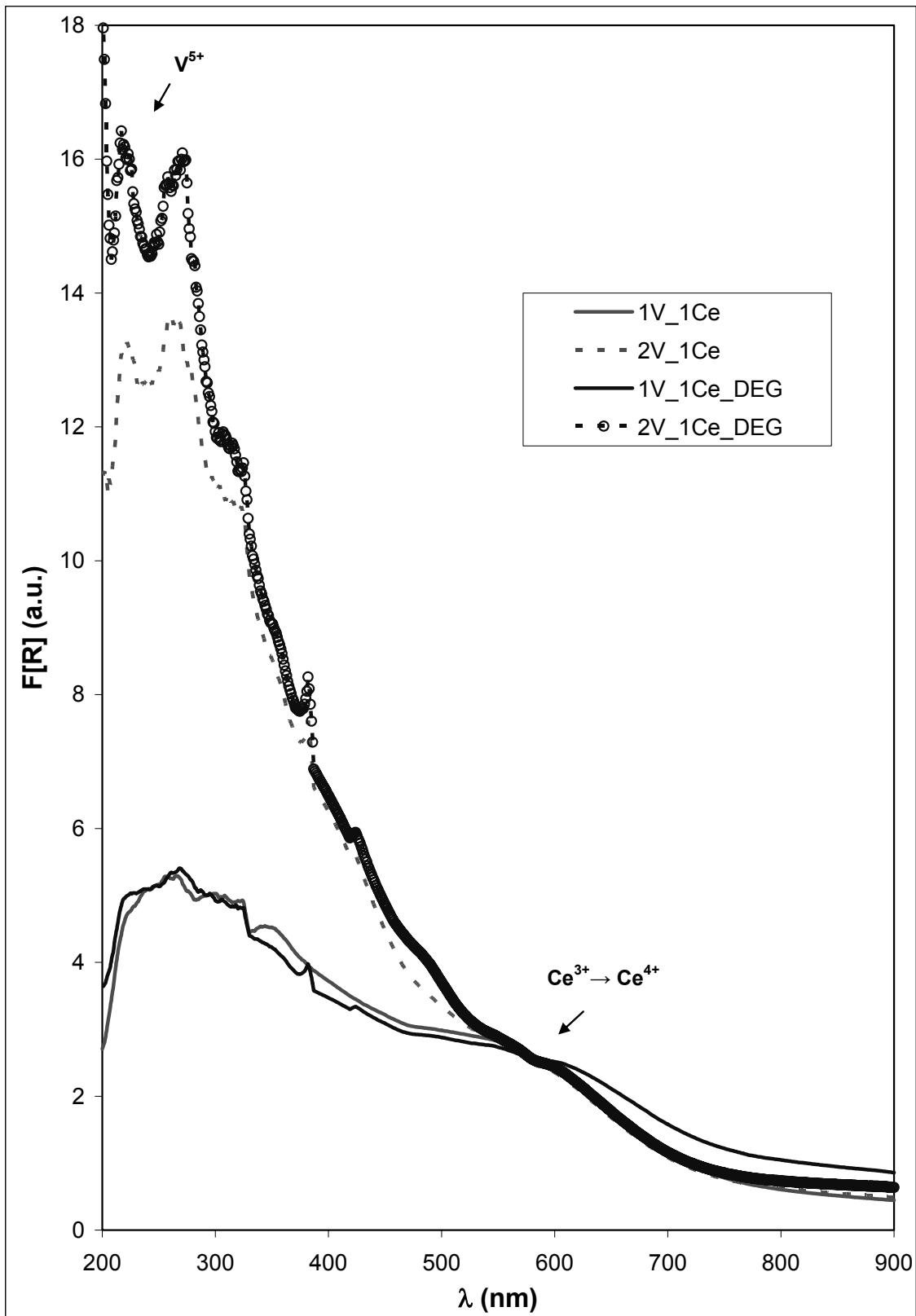


Fig. 5 – UV-Vis spectra of the fresh vanadia-ceria catalysts.

After the catalytic test the pattern of curves is changed for samples with V:Ce ratio 1:1. The

absorption band corresponding to V_2O_5 becomes visible (Fig. 6).

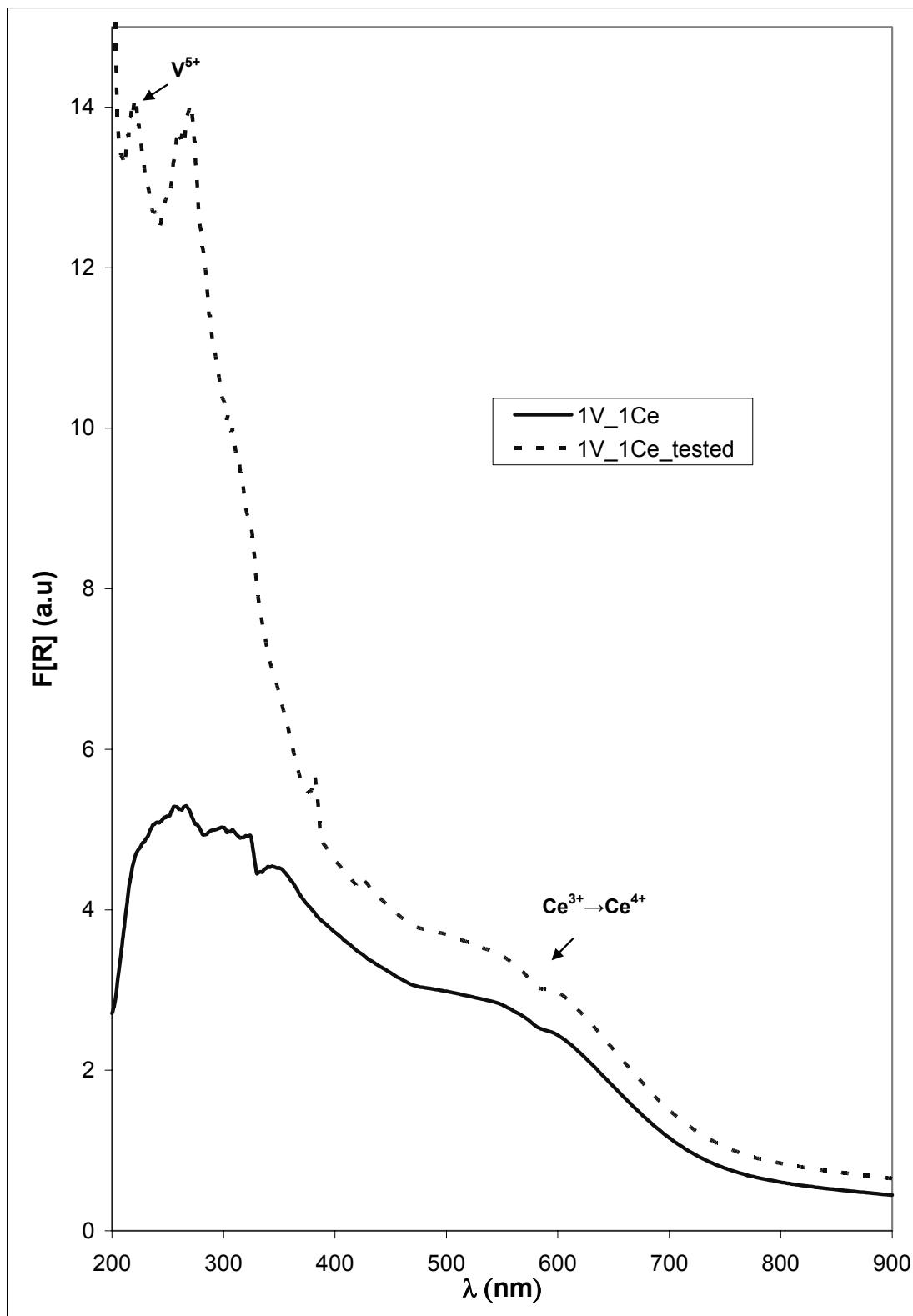


Fig. 6 – Comparison between the UV-Vis spectra of the fresh and used 1V_1Ce catalyst.

Table 2
CO conversion in CT1 run (CO:O₂:He as 5:2.5:92.5)

1V_1Ce	1V_1Ce_DEG	2V_1Ce	2V_1Ce_DEG
30.62 (408°C)	6.86 (406°C)	3.48 (406°C)	2.26 (400°C)

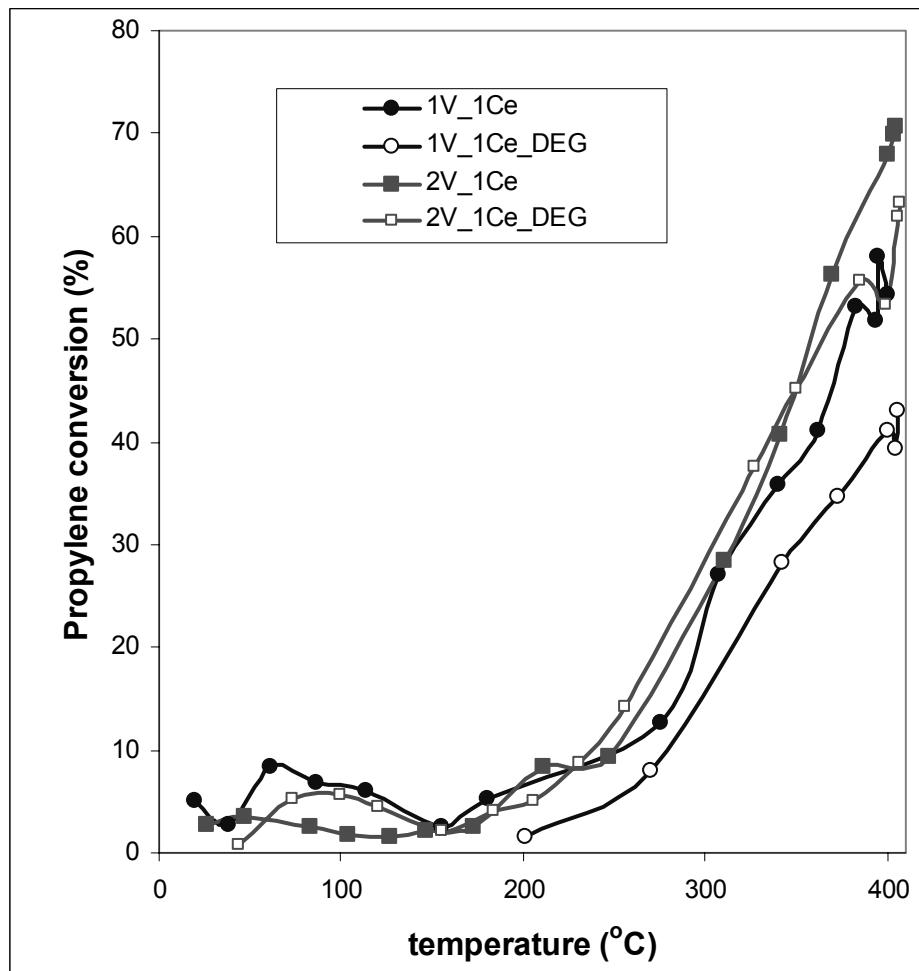


Fig. 7 – Propylene conversion in the CT3 cycle ($\text{C}_3\text{H}_6:\text{O}_2=1:22$).

In Table 2 were summarized the CO conversions in CT1 run (in brackets was indicated the temperature of the test.). As is shown, the V-Ce compounds were not active in CO oxidation (except 1V_1Ce).

A completely different behavior was observed in deep oxidation of propylene, when the conversions were rather high, especially for the 2V_1Ce sample (70.58% at 400°C).

It seems that the CeVO_4 lattice is rather stable in the conditions used for catalytic testing. The higher conversions in propylene oxidation could be tentatively related mostly to the excess V_2O_5 phase existing in higher amounts for samples with higher vanadia content. The lower conversions of samples prepared with DEG must be related with the higher crystallization of these samples.⁸

CONCLUSIONS

As shown by XRD results, the main constituent of the V-Ce-O samples prepared by co-

precipitation in presence or in absence of DEG is CeVO_4 (with Ce^{3+} and V^{5+}), the former having higher surface areas. This is in good correlation with the EPR and the UV-Vis measurements performed on these samples. The samples with V/Ce ratio 2/1 contain also excess V_2O_5 . The AC electrical conductivity measurements indicated that the samples behave as n-type semiconductors; those prepared with DEG being more sensitive to reducing atmospheres, in relation with their higher surface areas. On the other hand, the samples prepared without DEG presented higher values of conversion in oxidation reactions.

After the thermal cycling, a slight increase of the V_2O_5 content indicated partial decomposition of CeVO_4 . Since it seems that the well known reducibility of vanadia is blocked by interaction with ceria, the slight reduction detected during testing is probably mostly due to the excess vanadia present on the surface. The much higher conversion in propylene oxidation indicates a preferential dissociative adsorption of propylene on the surface of these compounds.

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