

## MECHANISMS OF CATALYTIC REACTIONS

# Study of the Ru/Ce System in the Oxidation of Carbon Black and Volatile Organic Compounds<sup>1</sup>

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**Abstract**—The relationship between the state of Ru on CeO<sub>2</sub> and catalytic activity in the oxidation of carbon black (CB) and some volatile organic compounds (VOCs) was investigated for Ru/CeO<sub>2</sub> catalysts prepared by wet impregnation. It was demonstrated that the addition of ruthenium to ceria significantly improved the reactivity of the latter. The temperature programmed reduction (TPR) experiments of Ru/CeO<sub>2</sub> showed that the oxygen species of RuO<sub>2</sub> was reduced at low temperatures. In addition, Electronic Paramagnetic Resonance (EPR) studies of outgassed samples at different temperatures showed an anisotropic signal indicating that Ru(IV) was reduced to intermediate valence states like Ru(III) before its total reduction to metallic Ru. It was concluded that Ru–O–Ce bonds in the well-dispersed Ru species are highly fragile and its mobile oxygen is the active species in the catalytic oxidation process.

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## 1. INTRODUCTION

The deleterious effect on human health of particulates present in diesel engine and industrial emissions has become a subject of great concern and has resulted in the formulation of restrictive legislation both in the EU and the US [1–5]. Although physical filtration of the particulate from the emissions is possible, this solution has several drawbacks. Such physical traps suffer from blocking and need periodic regeneration. In the same time, various industrial processes continuously generate air flows containing volatile organic compounds (VOCs). Given the toxicity of these compounds and considering their impact on the greenhouse effect, it is necessary to treat these air flows before release into the atmosphere [6]. Emission control strategies include changes and improvements in the fuel used, engine modifications, or exhaust after-treatment systems. These latter provide satisfactory results for compliance with the emission regulations where the engine modifications or fuel improvements are not sufficient. Using oxidation catalysts in order to oxidize diesel soot is one of the promising after-treatment systems. These catalysts also provide significant reductions in the carbon monoxide (CO) and hydrocarbons (HC) emissions. They were reported to be active in PM reduction especially when low sulfur fuel is used. Recently, it has been reported that the use of supports based on cerium oxide confers interesting properties to soot combustion catalysts due to high availability of surface oxygen and high surface reducibility [7–10]. The success of oxygen storage systems based on ceria is due to their ability to

change oxidation state during operation (i.e., CeO<sub>2</sub> to CeO<sub>2-x</sub>) maintaining structural integrity, thus allowing oxygen uptake and release to occur easily. Ruthenium oxide catalysts have been demonstrated to be active in acetic acid [11] and propane [12] oxidation reactions, but only few studies investigated its reactivity in diesel soot oxidation.

In this paper, we describe the activity of ceria-supported ruthenium catalysts towards the oxidation of carbon black (CB) particulates, propane, toluene, and *ortho*-xylene. Catalysts containing various amounts of ruthenium were prepared, and their catalytic activity and CO<sub>2</sub> selectivity have been investigated.

## 2. EXPERIMENTAL

### 2.1. Solids Preparation

Cerium hydroxide Ce(OH)<sub>3</sub> was prepared by precipitation from cerium(III) nitrate hexahydrated solution Ce(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O with an alkali solution of NaOH. The resulting hydroxide Ce(OH)<sub>3</sub> was filtered, washed, and dried for about 20 h in a drying oven at 100°C, then it was calcined at 500°C to obtain ceria CeO<sub>2</sub>. Different volumes of ruthenium(III) nitrosyl nitrate Ru(NO)(NO<sub>3</sub>)<sub>3</sub> solution have been impregnated on ceria in order to obtain solids with different ruthenium loadings (0.67, 1, 1.5, 2, 3, and 5 wt %). These solids are designated as Ru<sub>x</sub>Ce (x = Ru wt %). After drying at 100°C for about 20 h, solids were stabilized by calcination under dried air (35 ml min<sup>-1</sup>) at 600°C for 4 h. Ele-

<sup>1</sup> This article was submitted by the authors in English.

**Table 1.** Specific surface area ( $S_{sp}$ ) and elementary content (wt %) of the solids

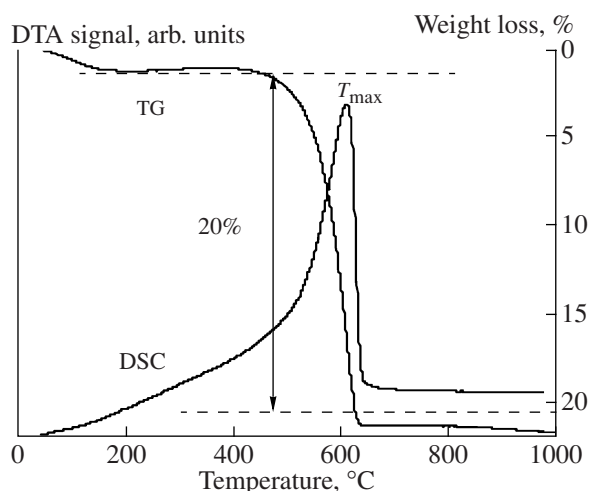
Sample	$S_{sp}$ , m <sup>2</sup> /g	Ru, wt %	Ce, wt %	O, wt %
CeO <sub>2</sub>	93	—	—	—
Ru <sub>0.67</sub> Ce	89	0.56	77.51	21.93
RuCe	86	0.85	76.85	22.3
Ru <sub>1.5</sub> Ce	82	1.31	78.71	19.98
Ru <sub>2</sub> Ce	78	1.79	77.47	20.74
Ru <sub>3</sub> Ce	71	2.53	76.02	21.45
Ru <sub>5</sub> Ce	64	4.15	74.65	21.2
RuO <sub>2</sub>	45	—	—	—

mentary analyses were performed on the obtained solids and element weight percentages are given in Table 1.

## 2.2. Characterization Techniques

Temperature programmed reduction (TPR) analyses were performed on an ALTAMIRA AMI 200 apparatus with a flow type reactor. Hydrogen (5 vol % in Ar) was passed through a reaction tube containing the catalyst at 30 ml min<sup>-1</sup>. The tube was heated with an electric furnace, and the amount of H<sub>2</sub> consumed was monitored with a TC detector.

Electron paramagnetic resonance (EPR) measurements were performed at different temperatures from -196°C up to room temperature on a EMX BRUKER spectrometer with a cavity operating at a frequency of ~9.5 GHz (X band). The magnetic field was modulated at 100 kHz, and the power supply was sufficiently low to avoid saturation effects. The  $g$  values were determined from precise frequency and magnetic field values. Vacuum treatments ( $3 \times 10^{-5}$  mbar) of Ru/CeO<sub>2</sub> catalysts were performed at different temperatures:

**Fig. 1.** Example of DSC-TG curves of “80% CeO<sub>2</sub> + 20% CB” “loose contact” mixture.

room temperature, 100, 200, and 300°C. A 1 K min<sup>-1</sup> temperature rise allowed reaching the treatment temperature which was maintained for 1 h.

## 2.3. Activity and Selectivity Tests

The catalytic test towards the combustion of CB N330 (DEGUSSA) was studied by simultaneous thermogravimetric (TG)–differential scanning calorimetry (DSC) analysis with a NETZSCH STA 409 apparatus. Before the test, 20 wt % of CB and 80 wt % of catalyst were mixed slightly in an appropriate cell for 10 min, “loose contact,” or heavily in a ball miller for 40 minutes, “tight contact.” Even though Neeft et al. [13] found that the practical physical contact between soot and the catalyst in a filter is much closer to a “loose contact” condition, “tight contact” results were displayed to be of use as a comparison scale.

Thirty milligrams of this mixture were loaded in an alumina crucible and heated from room temperature up to 1000°C (5 K min<sup>-1</sup>) under air flow of 75 ml min<sup>-1</sup>. The VOCs (propene, toluene, and *ortho*-xylene) oxidation was realized in a catalytic micro reactor coupled to a Varian 3600 gas chromatograph using a double detection FID and TCD. A hundred milligrams of the catalyst were tested in the presence of VOCs (air + propene = 100 ml min<sup>-1</sup>; 6000 ppm of propene or 1800 ppm of toluene or 2000 ppm of *ortho*-xylene).

As CB is consumed during the reaction, we can only calculate the total selectivity which is given by the ratio  $n_{CO_2}/(n_{CO_2} + n_{CO})$  where  $n_{CO_2}$  and  $n_{CO}$  represent the mole numbers of emitted gas during the combustion. CB/catalyst mixtures are introduced in a calcination reactor, and then the temperature is raised by a mean of 5 K min<sup>-1</sup>. Gas samples are taken with syringes during the thermal phenomenon and mainly around the  $T_{max}$  temperature ( $T_{max}$  determined by an earlier DSC-TG test of the mixture). Then the syringe's content is injected in a gas chromatography (GC) VARIAN 3600. The GC consists of two filled columns, one PORAPACK Q (column 1) and the other consists of a molecular sieve 5 Å (column 2), connected with each other by a six-way commutation valve. By extracting the compounds only on the PORAPACK Q, a first composite peak is detected, followed by a second peak corresponding to CO<sub>2</sub>. The O<sub>2</sub>, N<sub>2</sub>, and CO gas are then oriented to the molecular sieve 5 Å to be separated then analyzed by a TCD to determine catalyst selectivity in CB oxidation.

## 3. RESULTS AND DISCUSSION

### 3.1. Carbon Black (CB) Catalytic Combustion

Figure 1 shows the example of DSC-TG curves of an “80% CeO<sub>2</sub> + 20% CB” “loose contact” mixture. A weight loss of ~20 wt % is observed, corresponding to the combustion of the total mass of carbon black.  $T_{max}$

is the temperature of the maximum of the DSC-curve and corresponds to the temperature of the highest rate of CB combustion. Catalytic properties of solids are evaluated by comparing these temperatures with those of CB combustion without the catalyst in the same conditions. Table 2 shows  $T_{\max}$  obtained for different “catalyst + CB” mixtures. The total combustion of CB without any catalyst was performed using SiC as an inactive support and has exhibited only one exothermic peak with a maximum of the combustion temperature at about 629°C. For “tight contact” mixtures, a decrease of about 250°C of the CB  $T_{\max}$  value was observed in the presence of ceria. This was not the case of the “CeO<sub>2</sub> + CB” “loose contact” mixture as a nonsignificant temperature shift was observed (17°C). Thus, even if ceria was shown as a very active support in the CB combustion in “tight contact” mixtures [14], it appears that it does not favor this same reaction under “loose contact” conditions. However, when ruthenium is added to ceria, a decrease of about 100 to 120°C of the temperature values was observed for “loose contact” mixtures, and about 270 to 280°C for “tight contact” mixtures, showing that the presence of ruthenium enables the soot particle combustion at lower temperatures. Nevertheless, the catalytic reactivity is stable for ruthenium loading  $\geq 1.5\%$  as  $T_{\max}$  remains unchanged at about 490°C (“loose contact”) and 345°C (“tight contact”) despite the increase of Ru loading from 1.5 to 5%. In the case of CB combustion without a catalyst, 87% CO<sub>2</sub> selectivity is observed, while there is no CO production during the same combustion in the presence of different catalysts. Ru<sub>x</sub>Ce catalysts have shown a 100% selectivity for CO<sub>2</sub> formation in the two types of mixtures. In fact, ceria is entirely selective to CO<sub>2</sub> formation because of several of its properties in oxidation catalysis like its capacity to capture and release oxygen easily [15]. The interaction between the ruthenium and

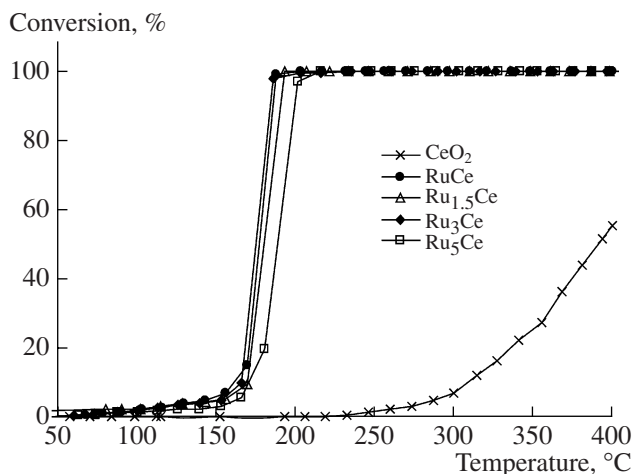
**Table 2.**  $T_{\max}$  for different 80% Ru<sub>x</sub>Ce + 20% CB mixtures

Mixtures	$T_{\max}$ , °C	
	“loose contact”	“tight contact”
SiC + CB	629	—
CeO <sub>2</sub> + CB	612	375
Ru <sub>0.67</sub> Ce + CB	506	358
RuCe + CB	492	350
Ru <sub>1.5</sub> Ce + CB	490	345
Ru <sub>2</sub> Ce + CB	490	349
Ru <sub>3</sub> Ce + CB	493	350
Ru <sub>5</sub> Ce + CB	490	352

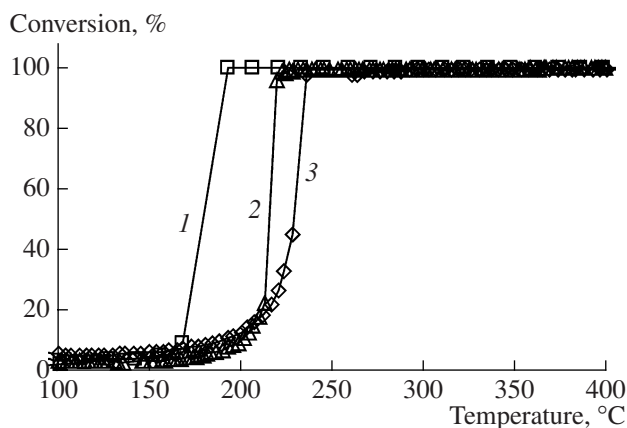
the support probably maintains or improves oxygen transfer making its permanent presence on the solid surfaces easier.

### 3.2. Catalyst Performance in VOCs Oxidation

The catalytic activity results of CeO<sub>2</sub> and Ru/CeO<sub>2</sub> are presented in Fig. 2 in terms of propene conversion versus temperature. While CeO<sub>2</sub> gives a light-off curve with a  $T_{50\%} \approx 390^\circ\text{C}$ , all Ru<sub>x</sub>Ce catalysts showed a  $T_{50\%} \approx 175\text{--}185^\circ\text{C}$ . CeO<sub>2</sub> is less active than Ru/CeO<sub>2</sub> catalysts, and a gain of about 200°C is obtained in the oxidation reaction. On the other hand, the catalytic activity of Ru<sub>1.5</sub>Ce was also investigated in the oxidation of two other VOCs, toluene and *o*-xylene (1800 and 2000 ppm, respectively). Figure 3 shows light-off curves for propene, toluene, and *o*-xylene over Ru<sub>1.5</sub>Ce.  $T_{50\%}$  for propene, toluene, and *o*-xylene conversion are respectively 175, 215, and 230°C. Knowing that total conversion of these VOCs alone does not occur before 600°C and that propene conversion did not



**Fig. 2.** Propene conversion vs. reaction temperature over ceria and different Ru<sub>x</sub>Ce.



**Fig. 3.** Propene, toluene, and *ortho*-xylene conversion vs. reaction temperature over the Ru<sub>1.5</sub>Ce catalyst. (1) Propene, (2) toluene; (3) *ortho*-xylene.

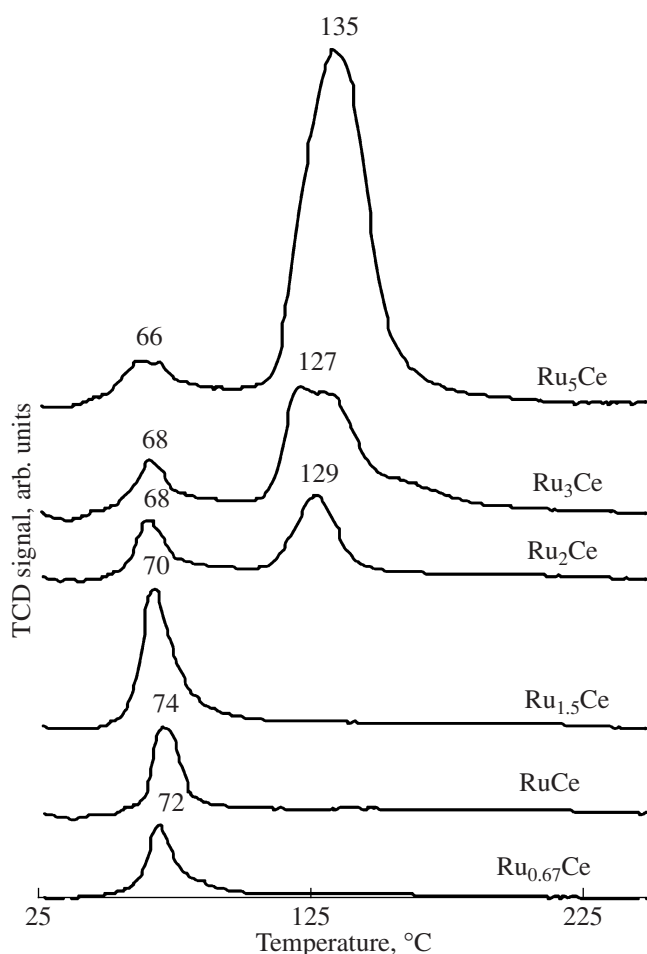


Fig. 4. TPR profiles for the different calcined catalysts.

exceed 22% over alumina at 500°C [16], the high  $\text{Ru}_x\text{Ce}$  activity observed can be attributed to a strong synergetic effect obtained by combining Ru and  $\text{CeO}_2$ . In fact, in a previous work, it was shown that, for the same content of Ru (wt %), a better activity of Ru–Ce–Al catalysts is obtained when the ceria content in the support increases [17]. This can confirm the presence of a synergetic effect between Ru species and ceria, which is less expressed when Ru is in interaction with other supports. It is evident to note that in the propene oxidation reactions, all catalysts showed approximately the same activity, which is in accordance with the results observed in CB oxidation.

As in the CB oxidation reaction, no CO formation in VOCs catalytic oxidation reactions was observed.

### 3.3 Characterization of Catalysts

Table 1 shows the specific area of the different solids after their calcination at 600°C. It was observed that the specific area of  $\text{Ru}_x\text{Ce}$  catalysts is lower than that of ceria and it decreases with increase of the ruthenium content. This is probably caused by ruthenium occupation of ceria surface sites due to the impregnation method or the formation of ruthenium oxide clusters on the support surface. In fact, the ruthenium oxide  $\text{RuO}_2$  specific area (45  $\text{m}^2/\text{g}$ ) is lower than cerium oxide area (93  $\text{m}^2/\text{g}$ ) which could explain the decrease of specific areas with increase of the ruthenium content.

TPR study was realized for all the catalysts after their calcination at 600°C. Figure 4 shows hydrogen consumption profiles of the different catalysts. According to the literature [11], ruthenium(IV) in  $\text{RuO}_2$  is totally reduced into metallic  $\text{Ru}^0$  under hydrogen (1.9 vol % in Ar) flow at temperatures close to 110°C.  $\text{RuO}_2$  hydrogen consumption is found by calculating the surface going between 25 and 250°C for each catalyst. The theoretical values for this same consumption are calculated while being based on the following reaction:

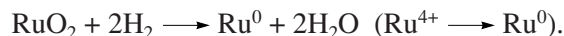


Table 3 recapitulates the values of hydrogen consumption necessary for the reduction of various  $\text{Ru}_x\text{Ce}$  catalysts. A smaller amount of  $\text{H}_2$  consumption than the theoretical value may indicate that the reduced state Ru is formed even during calcinations at 600°C [11]. The first reduction peak (Fig. 4) observed at low temperatures for each catalyst corresponds to the reduction of ruthenium oxide [11, 18]. Moreover, this first peak is broad and seems to be composed of two or more peaks. This can be due to the fact that ruthenium takes different states of valence while reducing from  $\text{Ru}^{4+}$  ( $\text{RuO}_2$ ) to  $\text{Ru}^0$ . When the quantity of ruthenium increases, its reduction occurs at lower temperatures. Moreover, for  $\text{Ru}_2\text{Ce}$ , there is the presence of a rather broad peak at 129°C, this peak also exists and is broader and more intense for  $\text{Ru}_3\text{Ce}$  and  $\text{Ru}_5\text{Ce}$  at 127 and 135°C, respectively. These peaks probably correspond to a part of the ruthenium oxide that agglomerated on the surface of ceria, which explains its reduction at higher temperatures. On the other hand, for contents lower than ~2%, this peak does not exist, which indicates the absence of

Table 3. Hydrogen consumption for the catalysts

Theoretical/experimental data	$\text{Ru}_{0.67}\text{Ce}$	$\text{RuCe}$	$\text{Ru}_{1.5}\text{Ce}$	$\text{Ru}_2\text{Ce}$	$\text{Ru}_3\text{Ce}$	$\text{Ru}_5\text{Ce}$
Th $[\text{H}_2]$ ( $\text{mmol g}^{-1}$ )	0.132	0.198	0.297	0.396	0.594	0.990
Exp $[\text{H}_2]$ ( $\text{mmol g}^{-1}$ )	0.127	0.190	0.246	0.325	0.494	0.844



agglomerated ruthenium. Starting from a content of approximately 2%, the quantity of agglomerated ruthenium increases with increase of the Ru content in the solid, since  $\text{Ru}_3\text{Ce}$  and  $\text{Ru}_5\text{Ce}$  peaks at 127 and 135°C are more intense and broader than the  $\text{Ru}_2\text{Ce}$  peak at 129°C. Consequently, for  $\text{Ru}_2\text{Ce}$ ,  $\text{Ru}_3\text{Ce}$ , and  $\text{Ru}_5\text{Ce}$ , the ceria surface is saturated with ruthenium oxide which causes cluster formation of this oxide. Finally, as was shown earlier, the reactivity of catalysts in carbon black and VOCs oxidation is stable for catalysts containing 1.5% and more of Ru. This can be confirmed by TPR study, which has shown the formation of  $\text{RuO}_2$  clusters for Ru percentages exceeding 1.5%. Then, it was considered that Ru species with reduction peaks at low temperature ( $\sim 70^\circ\text{C}$ ) are in tight interaction with the support "Ru–O–Ce" and seem to be responsible for the activity of the catalysts in carbon black and VOCs oxidation. This reactivity is due to the weakness of the Ru–O bonds [11], which allows the mobility of oxygen and then an easy reduction of Ru oxide species at low temperatures and thus the complete oxidation of CB and VOCs.

In order to deepen the reducibility study of  $\text{Ru}_x\text{Ce}$  catalysts, EPR measurements were carried out after a vacuum treatment of catalysts at high temperatures, knowing that a vacuum treatment can cause a partial reduction of the catalysts. Figure 5 shows EPR spectra recorded at room temperature for the  $\text{Ru}_3\text{Ce}$  catalyst treated at different temperatures. The EPR spectrum presents two anisotropic signals of axial symmetry (called A and B) characterized by the following parameters:  $g_\perp = 1.967$ ,  $g_\parallel = 1.939$  for A, and  $g_\perp = 1.967$ ,  $g_\parallel = 1.946$  for B. This spectrum is similar to those observed in the literature [19, 20] where it was attributed to  $\text{Ce}^{3+}$  ions ( $f^1$  ions:  $g_e > g_\perp > g_\parallel$ ) or more exactly to a trapped electron in a  $\text{Ce}^{4+}$  free orbital which confers to ceria a paramagnetic character.

From a vacuum treatment temperature of 100°C, a new signal for which intensity increases with the increase of the vacuum treatment temperature is observed. In addition, this new signal becomes sharper when the treatment temperature increases. It consists of three distinct components; it seems thus that it is a phenomenon of general anisotropy. The  $g$  factor values of this signal are the following:  $g_{xx} = 1.827$ ,  $g_{yy} = 1.926$ , and  $g_{zz} = 2.047$  then  $g_{\text{iso}} = (g_{xx} + g_{yy} + g_{zz})/3 = 1.933$ . Moreover, the vacuum treatment does not have much influence on ceria. Consequently, the effect observed (general anisotropy) is due to the ruthenium which undergoes a partial reduction during this vacuum treatment to pass from Ru(IV) to Ru(III). Indeed, the electronic configuration of Ru(III) is "4d<sup>5</sup>," then it possesses 5 single electrons which contributes to the EPR signal.

EPR analysis confirms the TPR results obtained previously by the fact that it shows the reduction of ruthenium at low temperatures because the orthorhombic signal due to ruthenium appears as the vacuum treat-

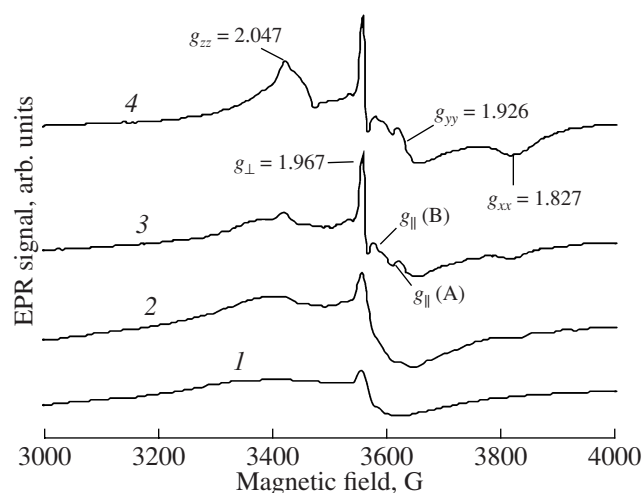


Fig. 5. EPR spectra of  $\text{Ru}_3\text{Ce}$  treated under vacuum at different temperatures: (1) room temperature, (2) 100, (3) 200, and (4) 300°C.

ment temperature reaches 100°C. These data can be correlated with the presence of a double peak at low temperature in TPR indicating that the reduction of ruthenium Ru(IV) to give Ru(0) passes by different valence states among which Ru(III) is responsible for the EPR signal.

#### 4. CONCLUSIONS

In conclusion, the  $\text{Ru}_x\text{Ce}$  catalysts are active in the total oxidation of carbon black and VOCs. Even in the case of a "loose contact," these doped ruthenium catalysts allowed the combustion of the CB at temperatures close to  $\sim 490^\circ\text{C}$ , largely lower than those obtained with ceria ( $612^\circ\text{C}$ ) under practical conditions. These catalysts were also very reactive under "tight contact" conditions with a gain of about  $280^\circ\text{C}$  in CB oxidation. They all also showed important reactivity in VOCs oxidation. This reactivity is due to the weakness of the Ru–O bonds, which allows the mobility of oxygen, an easy reduction of ruthenium oxide species at low temperatures, and thus the complete oxidation CB and VOCs. Moreover, the reactivity of catalysts increases with the ruthenium content until a content of 1.5%. In fact, for this quantity of ruthenium, there is ruthenium oxide saturation on the ceria surface, which explains stabilization of catalyst reactivity from  $\geq 1.5\%$  out of ruthenium. These catalysts were also shown to be selective in the oxidation reactions with only  $\text{CO}_2$  as product, which is promising for the use of these catalysts in the struggle to control the carbonaceous particle pollution.

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