Catalytic Complete Oxidation Of Benzene Over Pd Catalysts: Support Effect

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Abstract - In this paper, the effect of various supports on complete benzene oxidation over Pd catalysts was studied. Benzene was selected as a representative model of volatile organic compounds (VOCs) because it is among the most emitted air pollutants with toxic and carcinogenic nature. Complete catalytic oxidation is a very effective and environmentally-friendly approach for the destructive removal of VOCs from waste gas streams due to the opportunity for a total conversion to CO_2 and water at relatively low temperatures. The rational design of catalytic materials with improved efficiency in the elimination of VOCs attracts a substantial interest in the field of environmental catalysis because efficient catalysts should combine high activity with economic feasibility. The aim of the present work was the development of Pd-based catalytic materials with high benzene oxidation activity by using appropriate and economically profitable supports. Two metal oxides, namely Al_2O_3 and CeO_2 were selected, considering the cost-effectiveness of alumina and the beneficial role of ceria in VOCs oxidation. Additionally, high surface area alumina was modified by finely dispersed ceria nanoparticles. The effect of Y-doping of alumina-supported ceria on the activity of Pd catalyst was also studied. Catalytic measurements revealed the best performance of Pd catalyst on Y-doped CeO_2 supported on Al_2O_3. The sample exhibited complete benzene conversion at 175 °C and high stability during 24 hours in a stream. The favorable role of Y-doping in improved oxygen mobility of ceria was evidenced by X-ray photoelectron spectral analysis. A line with g-value 1.964, assigned to Ce^{3+}, was registered in the EPR spectrum of the sample after catalytic test, focusing on the possible role of Ce^{3+} in oxygen activation. This catalytic material demonstrated the potential to meet the challenging emission regulations in an effective and economically profitable way.

Keywords: VOCs abatement, complete benzene oxidation, Pd catalyst, Al_2O_3-supported ceria, Y-doping

1. Introduction

The increasing levels of air pollution represent a serious concern about the environment and human health. Volatile organic compounds (VOCs) are proved as significant contributors to air pollution due to their harmful nature. Complete catalytic oxidation has a high potential for the destructive removal of VOCs from waste gas streams. It is a very effective and environmentally-friendly approach that allows for the total conversion of VOCs to CO_2 and water at relatively low temperatures. The development of catalytic materials with improved efficiency in the elimination of VOCs is currently one of the scientific challenges. It has attracted substantial interest in the field of environmental catalysis because efficient catalysts should combine high activity with economic feasibility [1-3]. Two major types of catalysts, namely noble metal-based and transition metal oxides are currently most intensively studied to meet the challenging environmental regulations [4]. The comparison reveals that the noble metals exhibited superior activity at lower temperatures than transition metal oxides [5]. Pd-based catalysts are recognized as very suitable for VOCs oxidation [6,7]. However, the proper selection of support is of particular importance for the catalytic performance due to the participation of reducible supports in catalytic action, as well as in the stabilization of noble metal particles, thus preventing sintering and deactivation. Moreover, the use of low-cost materials is relevant from an economic point of view. Alumina is one of the most studied supports for Pd [5, 8]. Complete benzene oxidation (CBO) over Pd/Al_2O_3 catalyst, in particular the effects of pretreatment atmospheres, has been investigated [9]. The favorable role of basic sites of support on toluene and isopropyl alcohol oxidation activity of Pd/Al_2O_3 has been demonstrated by doping with MgO, BaO and ZrO_2 [10]. Gil et al. have prepared Pd catalysts supported on various metal oxides (CeO_2, TiO_2, Al_2O_3) and alumina doped by oxides of Ce, Ti, Fe, Mn [11]. A strong effect on the

oxidation state of Pd species and the propene oxidation activity has been found. In contrast to the low activity of Pd/CeO_2 due to the interaction of Pd^{4+} species with the support, the modification of alumina by 5 mol.% CeO_2 has produced catalyst with improved performance attributed to the enhanced metal-support interactions and availability of highly dispersed Pd particles. Ren et al. have observed a positive role of the addition of CeO_2 on toluene oxidation activity of Pd/Al_2O_3 [12]. The abundance of oxygen vacancies and active oxygen species on the catalyst surface due to the facile transfer $Ce^{3+} \leftrightarrow Ce^{4+}$ resulted in a decrease of T_{90} (temperature for 90 % conversion) of $Pd/Ce-Al_2O_3$ by 40 °C. Recently, we tuned ceria support properties by Y-doping (1 wt.% Y_2O_3) and analyzed the CBO of supported mono and bimetallic Au-Pd catalysts [13]. Despite the various supports, Pd-based catalysts exhibited higher activity as compared to the corresponding Au-based.

The aim of the present work was the development of Pd-based catalytic materials with high benzene oxidation activity by using appropriate and economically profitable supports. Two metal oxides, namely Al_2O_3 and CeO_2 were selected, considering the cost-effectiveness of alumina and the favourable role of CeO_2 in VOCs oxidation. Then, high surface area alumina was modified by finely dispersed ceria nanoparticles. The effect of Y-doping of alumina-supported ceria on the activity of supported Pd catalyst was also studied. Benzene was selected as a representative model of VOCs because, among the most emitted pollutants, known as BTX (Benzene, Toluene, and Xylene) is very stable and difficult to oxidize.

2. Experimental
2.1. Samples preparation

Ceria was lab-prepared by using an aqueous solution of $Ce(NO_3)_3 \cdot 6H_2O$ as precursor and Na_2CO_3 as precipitant. The synthesis was carried out at 60 °C and pH = 9.0. The precipitate was aged at the same temperature for 1 h, washed with distilled water until the absence of NO_3^- ions and dried at 80 °C. Finally, cerium hydroxide was subjected to thermal treatment at 400°C for 2 hours. Ceria (30 wt.% CeO_2) was supported on commercial γ-Al_2O_3 (Sasol) by mechanochemicall mixing of alumina and cerium hydroxide and calcination at 400 °C. The amount of cerium hydroxide was calculated based on analysis of weight losses during cerium hydroxide treatment at 400 °C. The Y-doping of ceria was performed following the procedure for alumina-supported ceria with the addition of Y_2O_3 (1 wt.% in respect to the ceria content).

Deposition-precipitation method was applied for the preparation of supported Pd samples. All samples contain 1 wt.% Pd. Before the deposition, all supports were dispersed in water by ultrasound. The interaction between $Pd(NO_3)_2 \cdot xH_2O$ and Na_2CO_3 was carried out at pH = 7.0, temperature 60 °C and stirring speed = 250 rpm. After aging at the same temperature for 1 h, the solids were carefully washed, dried and calcined at 400 °C.

2.2. Samples characterization

Textural characteristics of the catalysts were estimated by nitrogen adsorption/desorption experiments carried out by using a Micromeritics ASAP 2020. The specific surface areas were determined from N_2 adsorption–desorption isotherms at -196 °C and calculated through the Brunauer –Emmett–Teller (BET) method at pressure range 0.05–0.3 P/P_0. The mean pore size diameter and total pore volume were calculated by BJH method applied to the desorption branch. Prior to the measurements, the samples were degassed at 250 °C for 2 h.

Powder X-ray diffraction (PXRD) data were recorded on PANalytical Empyrean apparatus equipped with a multichannel detector (Pixel 3D) using Cu Kα radiation in the interval 20–90° 2θ, with a scan step of 0.01° for 20 s.

X-ray photoelectron spectroscopy (XPS) measurements were performed using VG Microtech ESCA 3000 Multilab, equipped with a dual Mg/Al anode. The spectra were excited by the unmonochromatized Al Kα source (1486.6 eV) run at 14 kV and 15 mA. Analyses of the peaks were carried out with the Casa XPS software.

Temperature-programmed reduction (TPR) experiments were carried out in a flow system with H_2 - Ar gas mixture (10% H_2) at a flow rate of 24 ml/min over sample amount 0.05 g. The temperature ramp rate was 15 °C/min. The water (product of reduction) was removed in a cooling trap (-40 °C) installed before the thermal conductivity detector

Electron paramagnetic resonance (EPR) spectra were collected on a JEOL JES-FA 100 EPR spectrometer operating in frequency 9.5 GHz (X-band), equipped with a standard TE_{011} cylindrical resonator. The spectra were recorded at modulation frequency 100 kHz, microwave power 1 mW and modulation amplitude 0.2 mT.

2.3. Catalytic activity measurements

The catalytic tests were performed in a flow fixed bed reactor under the following conditions: catalyst amount – 0.5 cm^3 with particles size 0.25–0.50 mm, temperature range 100 – 300 °C, inlet benzene concentration 42 g/m^3 in air, space velocity 4000 h^{-1}. Gas chromatograph Hewlett Packard 5890 (Agilent 5890A series II) with flame ionization detector and capillary HP Plot Q column was used for the analysis of the products. The sample activation was carried out "in situ" in a flow of purified air at 350 °C for 1 h.

3. Results and discussion
3.1. Catalytic measurements

The results of complete benzene oxidation over Pd-based catalysts are listed in Table 1.

Table 1: Degree of benzene conversion at different temperatures.

Sample	Conversion at 100 °C %	Conversion at 150 °C %	Conversion at 175 °C %	Conversion at 200 °C %	Conversion at 250 °C %	Conversion at 300 °C %
Pd/Al_2O_3	86	89	91	93	94	95
Pd/CeO_2	71	76	88	89	90	90
$Pd/CeO_2-Al_2O_3$	50	92	96	97	98	100
$Pd/Y-CeO_2-Al_2O_3$	91	99	100	100	100	100

The sample $Pd/Y-CeO_2-Al_2O_3$ demonstrated superior activity. Complete benzene conversion was achieved at 175 °C. Intermediate products of partial oxidation were not detected during 24 h stability test at this temperature. $Pd/CeO_2-Al_2O_3$ exhibited also high activity with 96% conversion at 175 °C, achieving total conversion at 300 °C. The temperature dependence of CBO in the low-temperature range is presented in Fig. 1.The effect of Y-doping of ceria is clearly shown by comparing the degree of benzene conversion at 175 °C. It is worth noting that the deposition of Pd on inert Al_2O_3 resulted in a relatively high activity of Pd/Al_2O_3 catalyst (86% conversion at 100 °C). The explanation could be related to the ability of PdO to provide active oxygen. Initial $Pd^{2+}O^{2-}$ reduction by benzene followed by Pd^0 oxidation with O_2 and $Pd^{2+}O^{2-}$ recovering have been proposed by He at al. studying Pd/zeolites catalysts [14]. However, in the present case 100%
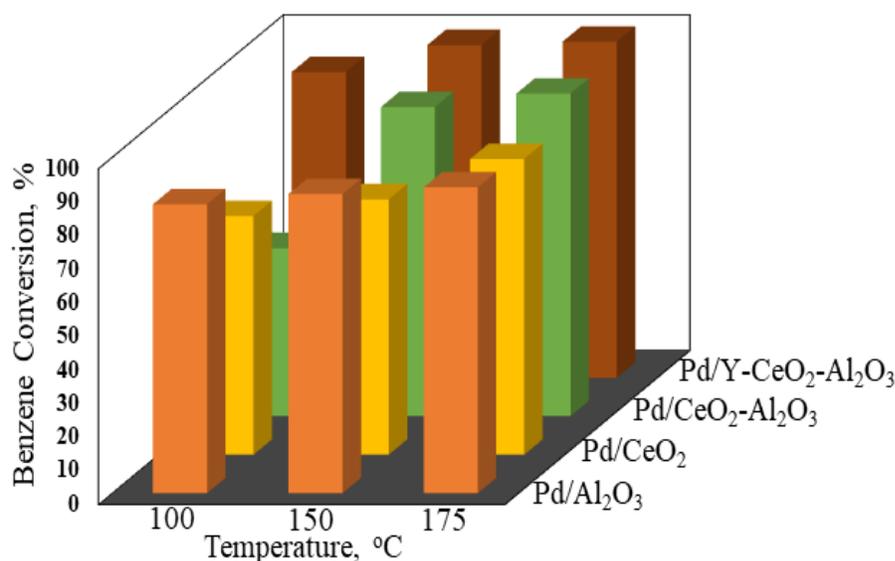
Fig. 1: Temperature dependence of CBO over the studied catalysts.

conversion was not attained even at 300 °C over Pd/Al_2O_3. It could be suggested that the observed best performance of $Pd/Y-CeO_2-Al_2O_3$ catalyst originated from the oxidation activity of both PdO dispersed on alumina and PdO located on ceria or Y-doped ceria phase with the important contribution of ceria phase in the oxygen supply.

3.2. Sample characterization

Textural characteristics, namely specific surface area (SSA), pores volume (V_{pore}) and average pores size (D_{pore}) of the samples supported on $\gamma-Al_2O_3$ and CeO_2 are very close to that of the parent oxides (Table 2). A slight decrease of SSA was found for mixed $CeO_2-Al_2O_3$ and Y-doped $CeO_2-Al_2O_3$, related mainly to the mechanical mixing of high surface area alumina (200 m^2/g) with 30 wt.% ceria with significantly lower specific surface area (63 m^2/g). The average pore diameter and pore volume were also slightly affected. Our recent studies of the impact of the preparation method of $CeO_2 – Al_2O_3$ mixed oxides on the textural properties indicated, that impregnation caused almost twice lowering of the specific surface areas and pore volume of the samples with the same composition in comparison with bare $\gamma-Al_2O_3$. These changes resulted from the deep penetration of Ce^{3+} ions in the pores of alumina [15]. The formation of ceria crystallites inside the pores limited to some extend the access of reactant to the active sites and affected catalytic activity. Having in mind these findings we selected mechnochemically prepared alumina-supported ceria as support of Pd catalysts.

Table 2: Textural characteristics, average particle size and cell parameter of CeO_2 estimated by PXRD.

Sample	SSA m^2/g	V_{pore} cm^3/g	D_{pore} nm	D_{ceria} nm	α_{ceria} nm
$\gamma-Al_2O_3$	200	0.53	10.6	-	-
CeO_2	63.0	0.29	20.3	6.3	0.5424(2)
$CeO_2-Al_2O_3$	165.0	0.39	9.5	6.1	0.5422(1)
$Y-CeO_2-Al_2O_3$	168.0	0.43	10.0	6.1	0.5421(2)
Pd/Al_2O_3	195.8	0.52	9.7	-	-
Pd/CeO_2	67.6	0.28	16.5	6.2	0.5424(4)
$Pd/CeO_2-Al_2O_3$	161.2	0.45	9.5	5.8	0.5424(1)
$Pd/Y-CeO_2-Al_2O_3$	166.4	0.40	9.6	5.8	0.5420(1)

The PXRD patterns of supports and supported Pd samples are shown in Fig. 2. In the diffractograms of all Ce-containing samples reflections at $2\theta = 28.5°$, $33.1°$, $47.6°$, $56.4°$, related to (111), (200), (220) and (311) planes of the ceria phase in the cubic crystal structure of fluorite type were observed. The patterns were very similar in terms of the peak position and intensity. The average size of ceria particles (D_{ceria}) was calculated according to Scherrer's equation using FWHM of the peak at $2\theta = 28.5°$ (Table 2). It was quite similar, in the range 5.8-6.3 nm. Very weak contribution of Al_2O_3 was visible at about $2\theta = 38°$, as well as a broadening of the ceria peak at $2\theta = 47.6°$. Reflections due to the presence of Y_2O_3 phase were not detected. The analysis revealed that the deposition of Pd and second thermal treatment at 400 °C affected neither particle size nor unit cell parameter of ceria (α_{ceria}). The absence of any palladium related phase should be attributed to its small content and high dispersion.

The results from XP spectral analysis are shown in Table 3. The binding energy (BE) of Al 2p peak is not listed, because it was located at 75.1 ± 0.1 eV in the spectra of all samples. Components at BE around 336.7 ± 0.1 eV, typical of Pd^{2+} were registered in the Pd $3d_{5/2}$ spectra of Pd-based samples. Important information was provided by XPS derived Pd/(Ce+Al) atomic ratio. Higher values, namely 0.044 and 0.041, as compared to the analytical value of 0.006 were observed for $Pd/CeO_2-Al_2O_3$ and $Pd/Y-CeO_2-Al_2O_3$. These ratios indicate a better surface dispersion of palladium. The much higher atomic ratio of 0.14 obtained for Pd/CeO_2 reflects the lower surface area of the support, maximising the Pd photoelectrons with respect to the support Ce, but it is in accord with the role of ceria in favoring a high dispersion of the supported noble metals.
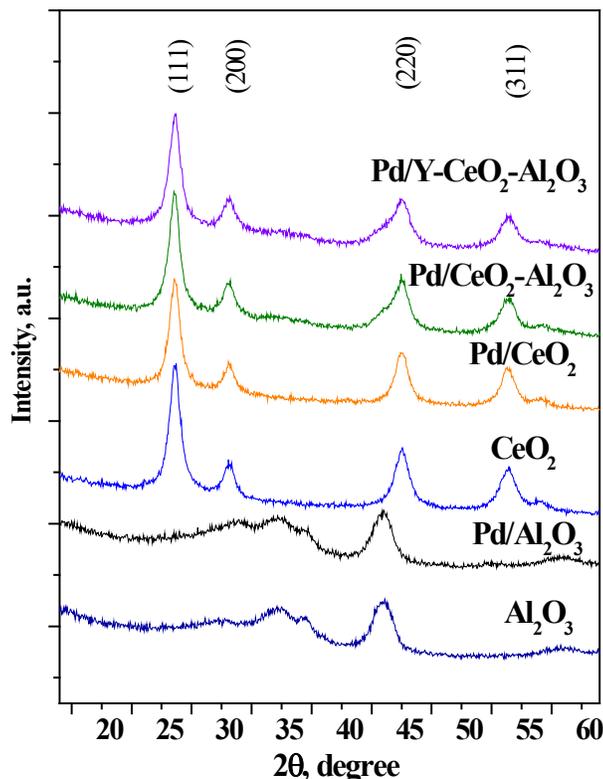
Fig. 2: PXRD patterns of the studied samples.

Both Ce^{4+} and Ce^{3+} oxidation states were detected in the Ce 3d spectra of all Ce-containing samples. The atomic ratios $Ce^{3+}/(Ce^{4+}+Ce^{3+})$ were calculated, following the consensus about the relationship between the concentration of Ce^{3+} and oxygen vacancies formed for the charge compensation. The values were in the interval 0.25–0.38, i.e. higher than the typically calculated values of 0.06–0.10 for bulk ceria [16]. These results revealed the existence of defective ceria structure with oxygen vacancies formation on the catalyst surface.

The Y 3d spectrum of the Y-containing sample was characterised by the Y $3d_{5/2}$ binding energy of 157.8 eV assigned to Y^{3+}. The effect of Y-doping on defectivity of ceria was clearly demonstrated. The effect was well visible by comparing the values of $Ce^{3+}/(Ce^{4+}+Ce^{3+})$ for Pd/Y-CeO₂-Al₂O₃ (0.38) and undoped Pd/CeO₂-Al₂O₃ (0.25).

Table 3: X-ray photoelectron spectral analysis

Sample	Ce $3d_{5/2}$ BE (eV)	Pd $3d_{5/2}$ BE (eV)	Pd/(Ce+Al)	$Ce^{3+}/(Ce^{3+}+Ce^{4+})$
Pd/Al₂O₃	-	336.7	0.017 (0.048)*	-
Pd/CeO₂	881.7	336.8	0.140 (0.0163)*	0.35
Pd/CeO₂-Al₂O₃	881.8	336.6	0.044 (0.0062)*	0.25
Pd/Y-CeO₂-Al₂O₃	881.8	336.7	0.041 (0.0063)*	0.38

∗ values in brackets refer to analytical ratio

The reducibility was evaluated by TPR with hydrogen. In Fig. 4 are presented TPR profiles of the samples. The profile of Pd/Al_2O_3 sample contained a weak symmetric peak centered at 21 °C. This peak was attributed to the reduction of PdO to Pd^0 (the presence of Pd^{2+} was shown by XPS), because alumina is nonreducible oxide. Two peaks were observed in the profiles of ceria-containing samples. It is already well known that the reduction of ceria proceeds in two steps: the reduction of the surface layers at around 500 °C and the bulk reduction at higher temperatures (over 800 °C) [17]. Noble metals significantly facilitate ceria surface layer reduction and boost the first reduction peak to much lower temperatures [5]. The narrow peaks in the interval 44-60 °C were attributed to the redox transfer $PdO \leftrightarrow Pd^0$ and some oxygen atoms from ceria surface layers in close vicinity to Pd particles. The broad peaks in the temperature range 300-500 °C corresponded to the further ceria surface reduction. The lowest peak intensity was observed in the profile of the catalyst with 30 wt.% CeO_2 on alumina. Doping of ceria by yttrium affected oxygen mobility and caused improved reducibility of $Pd/Y-CeO_2-Al_2O_3$. Reasonably, the highest peak intensity was registered in the profile of the sample with the highest ceria amount, i.e. Pd/CeO_2.
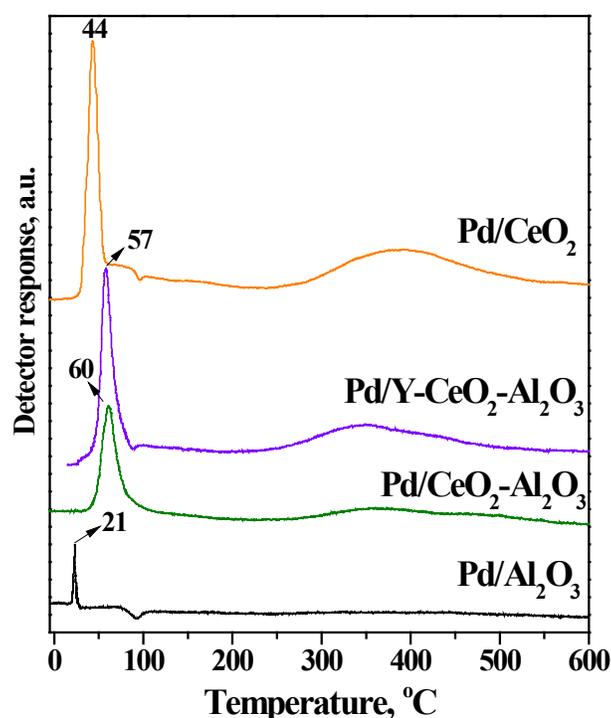
Fig. 4: TPR profiles of the studied catalysts.

EPR measurements were carried out over selected samples after catalytic tests aiming to shed more insight on the oxidation activity. The purpose of the EPR study was to detect eventual coke formation on the catalyst surface. The spectrum of Pd/CeO_2 is shown in Fig. 5 because this sample demonstrated lower activity in comparison with the other samples. A single EPR line with g factor 2.003, which is characteristic of carbon-centered radical and coke, was recorded. Another line related to carbon-centered radicals with g-value of 2.0023 was registered in the EPR spectrum of the best-performing $Pd/Y-CeO_2-Al_2O_3$. This line is typical for free electrons [18]. Additionally, two EPR lines with g values 2.0249 and 2.0054 were observed in the spectrum of $Pd/Y-CeO_2-Al_2O_3$, indicating a presence of oxygen species. Well defined line at magnetic field (334–335 mT) with g-value 1.964, assigned to Ce^{3+} was also observed, focusing on the possible role of Ce^{3+} in oxygen activation [19]. It is important to underline that such line was not detected in the spectrum of Pd/CeO_2. This finding reveals that the modification of commercial alumina by highly dispersed ceria nanoparticles using mechanochemical mixing is a promising approach in the design of catalytic materials with high efficiency in VOCs elimination.
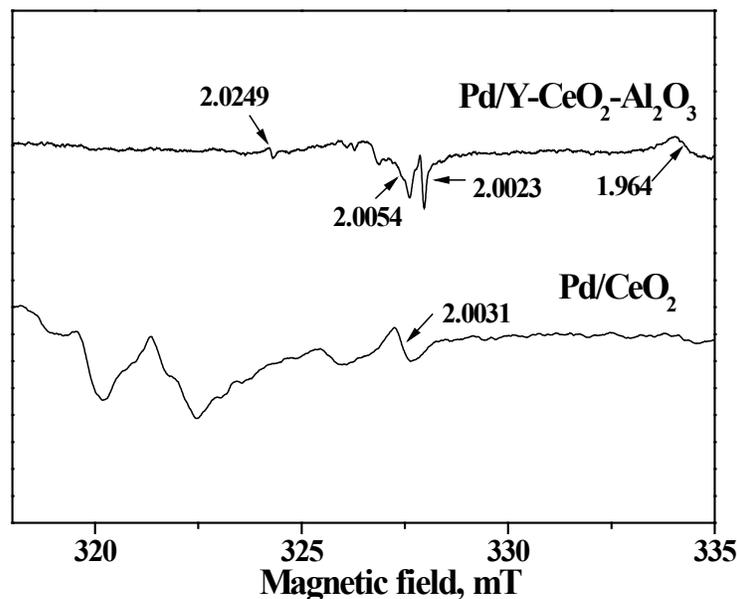
Fig. 5: EPR spectra of Pd/CeO$_2$ and Pd/Y-CeO$_2$-Al$_2$O$_3$ catalysts.

4. Conclusion

The effect of the nature of support on the performance of supported Pd catalysts for CBO was studied. Two metal oxides, namely Al$_2$O$_3$ and CeO$_2$ were selected. Aiming the developing of cost effective catalytic materials with improved efficiency in the elimination of VOCs, alumina-supported ceria and Y-doped ceria were prepared by mechanochemical mixing. Pd–based sample on alumina-supported Y-doped ceria exhibited the highest activity. The best performance of Pd/Y-CeO$_2$-Al$_2$O$_3$ catalyst was related to the redox transfer Pd^0 $\leftrightarrow$ PdO, better surface dispersion of palladium and high atomic ratio Ce^{3+}/(Ce^{4+}+Ce^{3+}) revealed by XPS analysis. The registration of line with g-value 1.964 assigned to Ce^{3+} in the EPR spectrum of the most active catalyst after catalytic test implied the beneficial role of surface modification of alumina with highly despersed fraction of Y-doped ceria. Taking into account high activity of Pd/Al$_2$O$_3$, it was suggested that the superior activity of Pd/Y-CeO$_2$-Al$_2$O$_3$ originated from contribution to the oxidation activity of both Pd located on ceria or Y-doped ceria phase and Pd dispersed on alumina. The potential of this catalytic material to meet emission regulations in an effective and economically profitable way was demonstrated.

Acknowledgements

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