

Improved Pd/ γ -Al₂O₃-Ce catalysts for benzene combustion

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Abstract

The catalytic oxidation of benzene on Pd (0.5 wt%)/ γ -Al₂O₃-Ce catalysts with 1, 5 and 10 wt% Ce was investigated. The alumina-Ce supports were prepared by adding a Ce-nitrate precursor to an aluminum boehmite. The presence of Lewis acid sites was determined by FTIR-pyridine adsorption spectroscopy. By FTIR-CO adsorption, it was found that the presence of Ce leads to the stabilization of PdO on the supports. The presence of the PdO species on the Pd/ γ -Al₂O₃-Ce catalysts was confirmed by X-ray photoelectron spectroscopy (XPS). The combustion of benzene (2600 ppm) in air was carried out at atmospheric pressure. Two behaviors were observed: for the catalysts with low Ce content (1%) and without Ce, the combustion occurs in a broad temperature range 100–280 °C, meanwhile, catalysts with high Ce contents (5, 10%), the benzene combustion occurs in the range 220–280 °C. An activation treatment on Pd/ γ -Al₂O₃-Ce catalysts with a reactant mixture at 250 °C for 20 h reduces the temperature of the total combustion to 250 °C. A better stability on Pd/ γ -Al₂O₃-Ce catalysts containing 5 and 10% Ce was observed. These results suggest that the oxidative catalytic properties of cerium oxide are shown at temperatures higher than 220 °C, and that an activation treatment is needed to obtain an optimal Pd⁰/PdO ratio for these species. The stability showed by the catalysts is explained by the effect of the CeO₂, which inhibits the deposition of carbonaceous species on the Pd surface.

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1. Introduction

Air pollution has become one of the most complex environmental problems. Among the most common contamination sources is that produced by volatile organic compounds (VOC). Benzene is one of the main pollutants whose principal sources are petrochemical industries and vehicles [1–4]. The oxidation of the VOCs on a catalyst takes place at temperatures which are lower than those required for thermal destruction [2]. Noble metals such as Pt, Rh and Pd, deposited in conventional supports such as Al₂O₃, SiO₂, etc., have shown to be efficient for this reaction [4]. The Al₂O₃/CeO₂ support is one of the most widely used in three-way automotive catalysts (used for the elimination of the pollutant gases in the exhaust automobile gases). The cerium addition to alumina produces structural changes, improves the dispersion of the metal and it participates

in the stabilization of alumina, avoiding the thermal sinterization. On the other hand, the Ce³⁺/Ce⁴⁺ oxidation–reduction properties make cerium a good promoter for the combustion reaction due to its capacity to deliver oxygen. [5].

The present work is a study of the effect of Ce content on Pd/ γ -Al₂O₃-Ce catalysts for the benzene combustion, as well as the effect of the activation and stabilization of the catalysts after 30 h on stream.

The γ -Al₂O₃-Ce supports were obtained from the addition of cerium nitrate to an aluminum boehmite and the characterizations were carried out by BET nitrogen adsorption, Fourier transform infrared spectroscopy of pyridine (FTIR), FTIR-CO adsorption and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Support preparations

The γ -Al₂O₃ reference support was obtained by calcination in air of the aluminum boehmite phase (Catapal-B Condea high

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purity 99.999%) at 650 °C. The alumina doped with Ce with 1, 5 and 10 wt%, was prepared by adding Ce(NO₃)₃·6H₂O (Strem Chemicals 99.9%) to the aluminum boehmite which were maintained in stirring in an aqueous media for 4 h, the solids were dried in an oven at 120 °C for 12 h and then calcined in air flow at 650 °C for 24 h. The supports were labeled as γ -Al₂O₃-CeX, where X represents the wt% of Ce in the support.

2.2. Catalysts preparation

The Pd/ γ -Al₂O₃ and Pd/ γ -Al₂O₃-Ce catalysts were prepared by impregnation of the supports with a PdCl₂ (Strem Chemicals 99.9%) aqueous solution at pH 2 to obtain 0.5 wt% of Pd in all the catalysts. Afterwards the catalysts were calcined at 500 °C during 4 h and then reduced with hydrogen at 500 °C for 5 h.

2.3. Specific surface area, BET

The determination of the BET surface area and the pore diameter was carried out in a QuantaChrome Multistation Autosorb 3B analyzer. Before performing the adsorption measurements, the samples were outgassed at 400 °C, in a vacuum of 10⁻³ Torr for 3 h. The specific surface area was calculated by the BET equation and the pore diameter by the BJH method.

2.4. TPO measurements

The TPO study was carried out in a CHEMBET-3000 apparatus using a thermal conductivity detector (TCD), and 0.1 g of catalyst. In these experiments, the flow rate of the 5% O₂/95% He mixture was 10 mL/min and the heating rate was 10 °C/min. Finally, the spectra were recorded, for fresh and after-combustion samples, from room temperature to 500 °C, only one peak was observed at around 100 °C.

2.5. FTIR-pyridine adsorption

The FTIR spectra for pyridine adsorption were determined with a Nicolet model 170-SX spectrometer. The powdered sample was pressed until a transparent sample was obtained, which was placed in a glass cell equipped with CaF₂ windows. The samples were pretreated in a vacuum of 10⁻⁶ Torr at 400 °C for 30 min in order to clean the surface. The samples were then cooled down to room temperature. The pyridine contained in a glass bulb coupled to the cell was passed on the catalyst. After the pyridine excess was eliminated under vacuum for 10 min, and then the spectra were registered at different desorption temperatures. The pyridine desorbed at each temperature was eliminated under vacuum (10⁻⁶ Torr).

2.6. FTIR-CO adsorption

The study of the FTIR-CO adsorption was carried out at room temperature using a Nicolet-FX710 apparatus. The samples pressed in thin wafers were placed in a Pyrex glass cell

equipped with CaF₂ windows. The samples were pretreated *in situ* at 400 °C for 30 min under vacuum (10⁻⁶ Torr). The CO admission at 20 Torr was carried out at 200 °C, afterwards the cell was cooled down to room temperature, the excess of CO was evacuated under vacuum during 10 min and then the CO absorption spectra were recorded.

2.7. X-ray photoelectron spectroscopy

The XPS analyses were carried out in a THERMO VG ESCALAB 250 spectrometer equipped with an aluminum anode (energy of 1486.8 eV) and with an X-ray system monochromator. The X-ray source was powered at 15 kV and 7.5 mA. In order to correct the effect of charge on the XPS spectra, all binding energies were referenced to the C 1s line of adventitious carbon at 284.6 eV. The reduced samples were placed on a thin sheet of indium and then analyzed. In order to control the sample charge in all experiments, an electron flood gun was used.

2.8. Catalytic activity measurements

The combustion of benzene in vapor phase was carried out in a conventional flow U-shape glass reactor used in the differential mode at atmospheric pressure. The 2600 ppm of benzene in air were used as reactants in a total flow of 90 cm³/min. The catalyst (0.1 g) was first treated under air flow (90 cm³/min) at 500 °C for 45 min, afterwards the catalytic system was treated under a flow of a mixture of benzene (2600 ppm)/air at 500 °C during 15 min. Then, the temperature was diminished to 100 °C, under the reactant mixture flow, at this moment the combustion reaction was carried out at different temperatures: 100, 140, 180, 220, 250 and 280 °C. The activity tests were done once a steady state was reached for each temperature. The conversions were measured during this period, where, in the end, almost constant values were reached.

To measure the effect of the activation treatment on the catalyst conversions, at the different temperatures, we proceeded in the following way: the sample was treated under a benzene (2600 ppm)/air flow at 250 °C and then maintained on stream during 20 h. Afterwards the combustion reaction proceeded at 100 °C and the temperature was increased by steps of 50 °C until 250 °C.

Reactants and products were analyzed by using an on-line gas chromatograph VARIAN 3400 CX equipped with a TCD (thermal conductivity detector) and a FID (flame ionization detector) using a J & W Scientific Megaboro 30 m, with a phase GSQ column that allowed measurements of CO₂ and H₂O concentrations and a PONA of 50 m columns to follow Benzene conversion. The products detected by the HP-GC-MS 5973 gas chromatograph mass spectrometer were, only, CO₂ and H₂O.

3. Results and discussion

3.1. Specific surface area

The specific surface area of γ -Al₂O₃ obtained from the calcination of the boehmite at 650 °C was around 210 m²/g.

Table 1
Characterization of the Pd/ γ -Al₂O₃ and Pd/ γ -Al₂O₃-Ce Catalysts

| Catalyst | Pd (wt%) | Dispersion (%) | Particle size (Å) |
|--|----------|----------------|-------------------|
| Pd/ γ -Al ₂ O ₃ | 0.51 | 85 | 12.4 |
| Pd/ γ -Al ₂ O ₃ -Ce1 | 0.49 | 91 | 11.6 |
| Pd/ γ -Al ₂ O ₃ -Ce5 | 0.52 | 83 | 12.8 |
| Pd/ γ -Al ₂ O ₃ -Ce10 | 0.50 | 68 | 15.6 |

The addition of Ce produced a decrease in the specific surface area. The supports showed specific areas of 153, 145 and 146 m²/g, for γ -Al₂O₃-Ce1, γ -Al₂O₃-Ce5 γ -Al₂O₃-Ce10, respectively. On the other hand, the pore diameter was practically constant (78–94 Å) in all the supports. The lower specific surface areas of the supports containing cerium indicate that probably the ceria crystallites plugged the aperture of the pores of alumina. However, the formation of Al–O–Ce– bonds cannot be discarded [6].

The content of Pd was determined by atomic absorption spectroscopy and the obtained values are reported in Table 1. The palladium content for all the catalysts varied between 0.49–0.52 wt%, which was close to the Pd nominal (0.5 wt% Pd).

3.2. FTIR-pyridine adsorption

The infrared spectra for the pyridine adsorption showed typical vibration bands of Lewis acid sites at 1590, 1490 and 1445 cm⁻¹ in all the supports. In Fig. 1 are shown the μ mol/g of pyridine adsorbed as a function of the desorption temperature for the different catalysts. It is observed a decrease in the number and strength of the Lewis acid sites with the cerium content in the support. The decrease of the γ -alumina acidity with cerium addition can be explained by the deposition of Ce particles on the alumina acid sites.

3.3. FTIR-CO adsorption

In Fig. 2 is shown the FTIR spectra of the CO adsorption for the different catalysts. The adsorption of CO on the Pd/ γ -Al₂O₃ and Pd/ γ -Al₂O₃-Ce catalysts showed the typical absorption bands for CO adsorbed on Pd catalysts [7]. The adsorption band located at 1969 cm⁻¹ in the Pd/ γ -Al₂O₃ and Pd/ γ -Al₂O₃-Ce catalysts, has been assigned to symmetric and non-symmetric

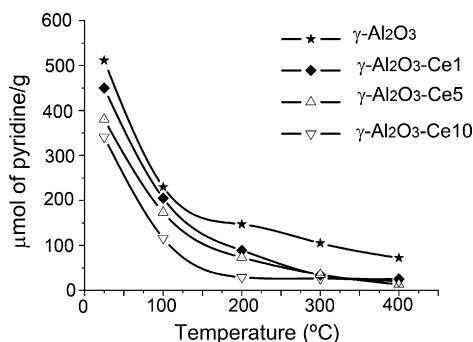


Fig. 1. Pyridine adsorbed (μ mol/g) as a function of the desorption temperature for the catalysts at different cerium contents (0, 1, 5 and 10%) obtained by FTIR.

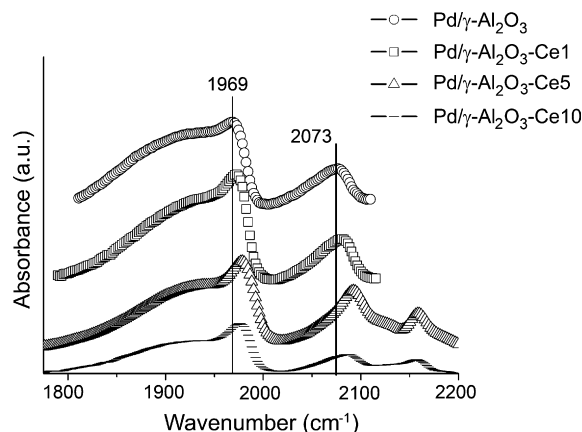


Fig. 2. FTIR spectra of CO adsorbed on Pd/ γ -Al₂O₃ and Pd/ γ -Al₂O₃-Ce catalysts.

adsorptions of CO in the regions 1910–1980 cm⁻¹ [7]. For catalysts containing 5 and 10% Ce the band was slightly shifted to higher frequencies. On the other hand, the adsorption at around 2073 cm⁻¹ also appeared shifted to higher frequencies in catalysts with 5 and 10% of Ce. The band in the 2085–2065 cm⁻¹ is assigned to the CO lineal adsorption on the high index crystallographic planes, i.e. adsorption on edges, corner, terraces and kinks [8]. The adsorption band at 2160 cm⁻¹ in catalysts containing 5 and 10 wt% Ce was assigned to the CO–Pd²⁺ [9]. Palladium in its oxidized state (Pd²⁺) was only detectable in such samples. Then we can assume that the presence of cerium stabilizes the oxidized PdO phase.

3.4. Dispersion determined by FTIR-CO

In this work, information was obtained from the elemental peaks of the CO spectra which were obtained from their deconvolution and the attribution of the vibration bands to determine the dispersion of the Pd catalysts [10,11], similarly, it has been reported in previous works [12]. The deconvolution of the FTIR spectra of the Pd/ γ Al₂O₃ catalysts in the elemental bands is shown in Fig. 3. The (a) and (b) peaks corresponded to the regions of 2050–2100 cm⁻¹ and 2030–2050 cm⁻¹ which are, respectively attributed to the discontinuity between the

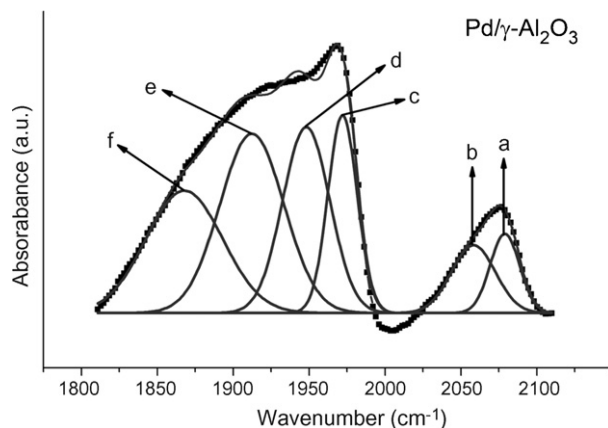


Fig. 3. Deconvoluted FTIR-CO adsorbed spectrum for the Pd/ γ -Al₂O₃ catalyst.

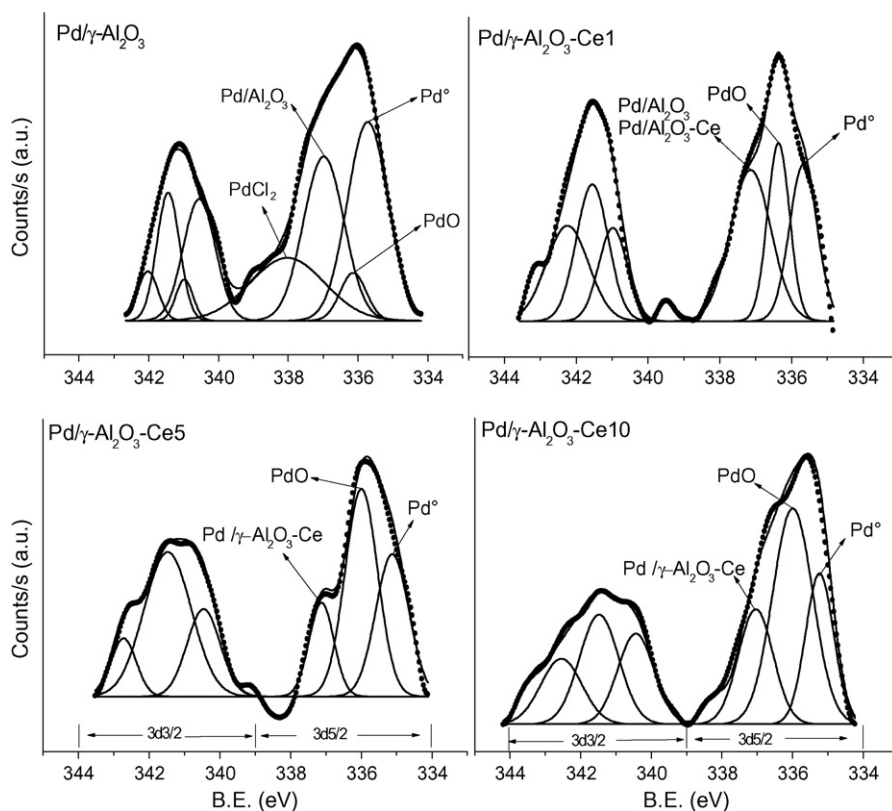


Fig. 4. Pd $3d_{5/2}$ and $3d_{3/2}$ core level spectra of Pd/ γ -Al $_2$ O $_3$ and Pd/ γ -Al $_2$ O $_3$ -Ce catalysts.

plans (edges, corner, terraces and kinks) where CO is linearly adsorbed. The (c) peak at 1950–1990 cm^{-1} was assigned to the 100 planes with bridged CO adsorbed, the domain of 1910–1940 cm^{-1} corresponds to the planes 1 1 1 and also to bridged CO adsorbed (d), whereas the peaks in the ranges of 1840–1880 cm^{-1} and 1810–1940 cm^{-1} (d and e) were associated to the interactions metal–support or the interfaces of the metallic support [13].

The dispersion values calculated from the deconvolution of the FTIR-CO adsorption spectra for all the catalysts are reported in Table 1. By the metal dispersion, defined as $D (\%) = N(\text{CO})_{\text{surf}}/N(\text{Pd})_{\text{total}} \times 100$ and applying the Beer–Lambert law, we calculated the total number of CO molecules adsorbed on the surface by $N(\text{CO})_{\text{surf}} = A_i S/W\varepsilon$, where A_i = integrated absorbance of the total bands obtained by the IR spectra, S = area of the wafer used in IR experiment, W = weight of the catalyst wafer and ε = molar extinction coefficient (total) of CO adsorbed for Pd: 2.9×10^{-7} cm^2/mol [14]. For the Pd/ γ -Al $_2$ O $_3$ catalyst, the dispersion was 85%, while for the Pd catalysts with 1, 5 and 10 wt% Ce, the dispersions were 91, 83 and 68%, respectively. The catalyst with 1% Ce showed the highest dispersions, this results are in agreement with those reported in the literature, where is well-known that the presence of Ce at low concentrations favors the dispersion of the metal on Al $_2$ O $_3$ -CeO $_2$ or La $_2$ O $_3$ -Al $_2$ O $_3$ supports.

In the Pd/ γ -Al $_2$ O $_3$ -Ce10 catalyst with high load of Ce (10%), the dispersion decreases giving a value of 68%. This dispersion diminution could be explained by the deposition of

cerium oxide on the surface of the metal, blocking some Pd sites [15].

3.5. XPS spectra characterization

The deconvoluted XPS photoelectron spectra for the Pd 3d core level region of the Pd/ γ -Al $_2$ O $_3$ and Pd/ γ -Al $_2$ O $_3$ -Ce catalysts are shown in Fig. 4. The deconvolution of the peaks showed three components for $3d_{5/2}$ and for $3d_{3/2}$ core levels in Pd/ γ -Al $_2$ O $_3$ -Ce catalysts. The binding energies of Pd $3d_{5/2}$, Al 2p core levels and the percent of Pd species are reported in Table 2. The binding energy of the Pd $3d_{5/2}$ core level for Pd in the pattern catalysts, Pd/ γ -Al $_2$ O $_3$, is 335.7 eV, which corresponds to Pd 0 [16]. The peak placed at 337.9 eV in the pattern catalyst Pd/ γ -Al $_2$ O $_3$ has been related to Pd-chlorine species indicating that Pd is in a higher oxidation state likely Pd $^{2+}$ [17]. In the catalysts containing cerium, the PdO species was observed at $3d_{5/2}$ core level with binding energies in the range of 336.3–336.0 eV for all the catalysts. As it can be seen, the Pd 0 is present in all the Pd catalysts, however, the signal at 337.9 eV is only observed in the catalyst pattern, whose relative percent of this species, calculated from the deconvoluted peak, is around 21% (Table 2). The PdO was observed in catalysts where Ce was added: in catalysts with 1% Ce this species had 7%, for higher contents of Ce, 5 and 10%, the relative percent of this specie was 50 and 53%, respectively, Table 2.

The binding energies corresponding to 337.1–337.3 eV, for Pd/ γ -Al $_2$ O $_3$ -Ce, have been assigned to the interaction of small Pd clusters with the support. The interaction of small clusters

Table 2
Data from the XPS analyses of the Pd/ γ -Al₂O₃-Ce catalysts

| Catalyst | Binding energy (eV) | | Pd species (%) |
|--|----------------------|-------|--|
| | Pd 3d _{5/2} | Al 2p | |
| Pd/ γ -Al ₂ O ₃ | 335.7 | 74.5 | 41 (Pd ⁰) |
| | 336.1 | | 7 (PdO) |
| | 337.1 | | 31 (Pd/Al ₂ O ₃) |
| | 337.9 | | 21 (PdCl ₂) |
| Pd/ γ -Al ₂ O ₃ -Ce1 | 335.6 | 74.5 | 32 (Pd ⁰) |
| | 336.3 | | 28 (PdO) |
| | 337.2 | | 40 (Pd/Al ₂ O ₃ -Ce, Pd/Al ₂ O ₃) |
| Pd/ γ -Al ₂ O ₃ -Ce5 | 335.1 | 74.5 | 34 (Pd ⁰) |
| | 336.0 | | 50 (PdO) |
| | 337.3 | | 16 (Pd/Al ₂ O ₃ -Ce) |
| Pd/ γ -Al ₂ O ₃ -Ce10 | 335.2 | 74.5 | 28 (Pd ⁰) |
| | 336.0 | | 53 (PdO) |
| | 337.3 | | 19 (Pd/Al ₂ O ₃ -Ce) |

with oxide substrates such as Pd-Al₂O₃ [18] and Pd-CeO₂ has been studied [19], the results showed a shift to a higher binding energy in the Pd- γ -Al₂O₃ and Pd-Ce systems.

The typical Ce 3d region spectrum for the Pd/ γ -Al₂O₃-Ce10 catalyst is shown in Fig. 5. The characteristic peaks for Ce₂O₃ and CeO₂ with binding energies of 880 and 882.6 eV for Ce³⁺ and Ce⁴⁺ species, respectively are observed. It was also observed a peak which has been associated to the interaction of cerium and palladium CePd₃ with the corresponding energy of 884.4 eV [20]. The characteristic Al 2p binding energy of 74.5 eV is observed in all the samples, Table 2. The atomic percent of the different species and the surface atomic ratios calculated for Pd/ γ -Al₂O₃ and Pd/ γ -Al₂O₃-Ce catalysts determined by XPS are reported in Tables 3 and 4, respectively. From this information, it is observed that the Ce/Al ratio increased and the Pd/Ce ratio decreased, this suggests that cerium could be segregated on the surface as the cerium content increases. The Cl/Pd ratio is around 2 in Pd/Al₂O₃ catalyst, which confirms the presence of the PdCl₂ in this catalyst, that ratio decreases with the amount of Ce in the catalyst. The Cl/Ce ratio follows the same trend, also decreases with the cerium

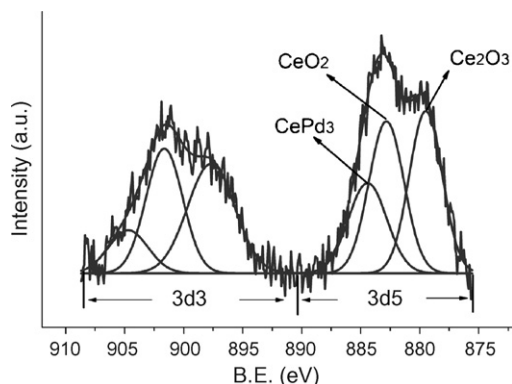


Fig. 5. XPS spectra at Ce 3d region of the Pd/ γ -Al₂O₃-Ce10 catalyst, showing the deconvoluted peaks.

Table 3
Atomic percent of the different elements of the Pd/Al₂O₃-Ce catalysts determined by XPS

| Catalyst | Atomic% | | | | |
|--|---------|-------|------|------|------|
| | Al | O | Pd | Cl | Ce |
| Pd/ γ -Al ₂ O ₃ | 41.33 | 58.45 | 0.07 | 0.15 | – |
| Pd/ γ -Al ₂ O ₃ -Ce1 | 42.30 | 57.56 | 0.08 | 0.06 | 0.20 |
| Pd/ γ -Al ₂ O ₃ -Ce5 | 41.95 | 57.12 | 0.16 | 0.05 | 0.71 |
| Pd/ γ -Al ₂ O ₃ -Ce10 | 41.96 | 57.13 | 0.15 | 0.05 | 0.79 |

Table 4
XPS atomic ratios for the Pd/ γ -Al₂O₃-Ce catalysts

| Catalyst | Pd/Al | Ce/Al | Pd/Ce | Cl/Pd | Cl/Ce | Cl/Al |
|--|--------|--------|--------|--------|--------|--------|
| Pd/ γ -Al ₂ O ₃ | 0.0017 | – | – | 2.1429 | – | 0.0036 |
| Pd/ γ -Al ₂ O ₃ -Ce1 | 0.0019 | 0.0047 | 0.4000 | 0.7500 | 0.3000 | 0.0014 |
| Pd/ γ -Al ₂ O ₃ -Ce5 | 0.0038 | 0.0169 | 0.2254 | 0.3125 | 0.0704 | 0.0012 |
| Pd/ γ -Al ₂ O ₃ -Ce10 | 0.0036 | 0.0188 | 0.1899 | 0.3333 | 0.0633 | 0.0012 |

load. The Pd/Al₂O₃ and Pd/Al₂O₃-Ce1 catalysts show the highest Cl/Al ratios.

3.6. Catalytic activity

The catalytic behavior of the Pd/ γ -Al₂O₃ and Pd/ γ -Al₂O₃-Ce catalysts in the combustion of benzene as a function of the temperature is reported in Table 5. Two different behaviors can be observed, the first presented by the Pd/ γ -Al₂O₃, Pd/ γ -Al₂O₃-Ce1 catalysts and the second by the Pd/ γ -Al₂O₃-Ce5 and Pd/ γ -Al₂O₃-Ce10 catalysts. In the Pd/alumina catalyst without cerium and with 1% Ce, the benzene combustion occurred in a wide range of temperatures starting from 100 °C and rising to the total conversion, towards CO₂, at 280 °C. On the other hand, the catalysts containing 5 and 10% Ce, the combustion of benzene was produced in a low interval of temperatures, 250–280 °C, with selectivity towards CO₂ of 100%. We assume that two different mechanisms of benzene oxidation occurred in both cases.

In the first case, the behavior of the Pd/ γ -Al₂O₃ and Pd/ γ -Al₂O₃-Ce1 catalysts can be explained by the acidic character of the alumina support. According to the literature the catalysts with supports showing high acidity present a good performance for the combustion reactions [21]. It has been reported that the organic compounds interact with the strong Lewis acid sites which activate the organic compounds [22]. We can assume that both catalysts, without Ce and containing 1% Ce have enough

Table 5
Benzene combustion on Pd/ γ -Al₂O₃-Ce catalysts with 0, 1, 5, 10 wt% Ce

| Catalyst | Combustion of benzene (%) | | | | | |
|--|---------------------------|--------|--------|--------|--------|--------|
| | 100 °C | 140 °C | 180 °C | 220 °C | 250 °C | 280 °C |
| Pd/ γ -Al ₂ O ₃ | 38 | 74 | 78 | 85 | 90 | 100 |
| Pd/ γ -Al ₂ O ₃ -Ce1 | 31 | 35 | 75 | 88 | 97 | 100 |
| Pd/ γ -Al ₂ O ₃ -Ce5 | 0 | 0 | 0 | 0 | 99 | 100 |
| Pd/ γ -Al ₂ O ₃ -Ce10 | 0 | 0 | 0 | 0 | 82 | 100 |

acid sites (Fig. 1) in the catalyst to lead the combustion. Another factor that could be playing a role is the metal dispersion. The sensitive structure of the benzene combustion has been pointed out by various authors [23,3]. The Pd/ γ -Al₂O₃ and Pd/ γ -Al₂O₃-Ce1 catalysts showed a high dispersion of palladium (85 and 91%), then, it cannot be discarded a positive effect because of the small metal particles present in this catalysts.

On the other hand, the Pd/ γ -Al₂O₃-Ce5 and Pd/ γ -Al₂O₃-Ce10 catalysts did not show activity in the range of temperatures of 100–220 °C, however, a shot in the conversion of benzene at 250 °C is observed, with values of 99 and 82%, respectively. In both catalysts the total benzene conversion was obtained at 280 °C. These results can be explained by a promotion effect of the cerium oxide which is revealed only at high temperatures. In the present case, we assume that the presence of Ce at 5 and 10% favors the oxidizing state of Pd to PdO on the support. Evidence of PdO in these catalysts was shown by infrared spectroscopy CO adsorption (Fig. 2) and by XPS results (Fig. 4). It has also been reported that the maximum in the catalytic activity in the combustion is reached when an optimal Pd⁰/PdO ratio is reached [24]. The no activity showed by the catalysts with 5 and 10% Ce at low temperatures could be due to the fact that cerium requires a high temperature or a long activation time to reach this ratio.

3.7. Activation effect on the catalytic activity

In order to study the effect of the activation of the catalysts on the conversion of the benzene combustion, the catalysts were thermally treated with a reactant mixture. The catalysts were maintained on stream under a benzene (2600 ppm)/air flow at 250 °C during 20 h. After this, the benzene combustion was carried out from 100 to 250 °C. The results of the conversion of benzene at different temperatures are reported in Table 6. Combustion is observed in all the catalysts with and without cerium, beginning from 100 °C. This conversion is increased with the increment of the temperature, being slightly higher in the catalysts with cerium. In the Pd/ γ -Al₂O₃-Ce catalysts, no effect of the cerium concentration was observed on the conversion, which is very similar for the different samples, at the different temperatures. In the catalysts containing cerium the total conversion was obtained at 250 °C while in the pattern catalyst, Pd/ γ -Al₂O₃, the conversion at this temperature was 94%. As it can be observed, the effect of the activation on the catalysts with cerium leads to the activation of the species Pd⁰/PdO which allows conversion at lower temperatures.

Table 6
Benzene combustion on Pd/ γ -Al₂O₃-Ce catalysts with 0, 1, 5, 10 wt% Ce, after 20 h of activation at 250 °C

| Catalysts | Combustion of benzene (%) | | | |
|--|---------------------------|--------|--------|--------|
| | 100 °C | 150 °C | 200 °C | 250 °C |
| Pd/ γ -Al ₂ O ₃ | 25 | 59 | 88 | 94 |
| Pd/ γ -Al ₂ O ₃ -Ce1 | 28 | 69 | 94 | 100 |
| Pd/ γ -Al ₂ O ₃ -Ce5 | 33 | 69 | 91 | 100 |
| Pd/ γ -Al ₂ O ₃ -Ce10 | 37 | 70 | 92 | 100 |

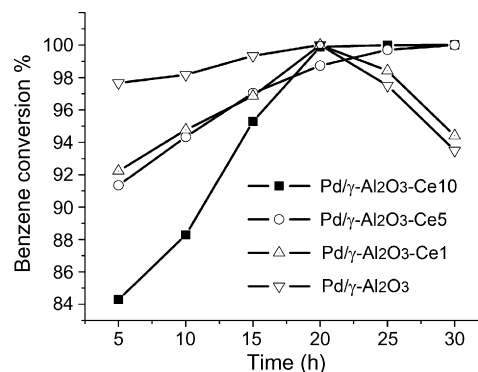


Fig. 6. Conversion of benzene after 30 h of reaction at 250 °C on Pd/ γ -Al₂O₃ and Pd/ γ -Al₂O₃-Ce catalysts.

3.8. Catalytic stability

In addition, the presence of cerium could play an important role in the stabilization of the Pd catalysts. In line with the aforementioned, a study of the stability of the catalysts was carried out in samples without activation treatment. The catalysts were maintained under the combustion reaction at 250 °C during 30 h, see Fig. 6. Again, two types of behavior were observed. For the Pd/ γ -Al₂O₃ and Pd/ γ -Al₂O₃-Ce1 catalysts a decrease in the conversion was observed after 20 h of reaction, whereas in the catalysts Pd/ γ -Al₂O₃-Ce5 and Pd/ γ -Al₂O₃-Ce10, the maximum in activity was reached up to 20 h on stream and then remained constant. In the catalysts with low cerium content and without cerium it can be assumed that the deposition of carbon on palladium becomes important after 20 h of work. However, for the catalysts with high cerium contents, it is observed that it is required a period of induction to reach 100% of conversion. This phenomenon can be related to the formation of the Pd⁰/PdO species which require a relative narrow abundance to show their oxidant power, which was achieved after 20 h of reaction.

The amount of carbon deposited on the catalysts after 30 h of reaction, calculated from TPO measurements, is reported in Fig. 7. It can be observed that the lowest amount of carbon corresponds to the catalysts with the highest Ce content. The fact that the activity does not decay once the maximum CO₂

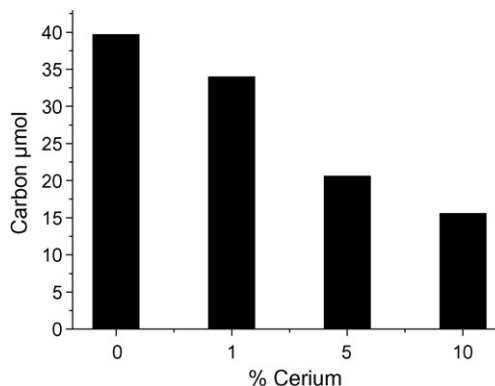


Fig. 7. Amount of carbon deposited on used catalysts after 30 h on stream as a function of the Ce content.

formation is reached is an evidence that cerium acts as a source of active oxygen which cleans continuously the carbonaceous species deposited on the surface of the catalyst.

4. Conclusions

The cerium addition to the aluminum boehmite followed by calcination produces γ -Al₂O₃-Ce supports. Two behaviors can be distinguished in the benzene combustion on the Pd/ γ -Al₂O₃ and Pd/ γ -Al₂O₃-Ce catalysts. The Lewis acidic sites on the γ -Al₂O₃ and γ -Al₂O₃-Ce1 supports and the dispersion of the Pd catalysts are the responsible of the benzene combustion in catalysts containing 1% Ce and free of Ce. At high Ce contents (5 and 10%), the characteristic oxidation–reduction cycle of cerium serves as oxygen source and it allows Pd⁰ and PdO to co-exist in a proportion that favors benzene combustion. A period of activation of the catalysts with the reactant mixture at 250 °C for 20 h, leads to the combustion at lower temperatures in the catalysts with cerium. These results are explained by the effect of cerium oxide, which stabilizes Pd in oxidized species, PdO, allowing Pd⁰ and PdO to co-exist in a proportional ratio, which favors the combustion and inhibits the deposit of carbonaceous species on the Pd surface.

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