The effect of ceria content on the performance of Pt/CeO$_2$/Al$_2$O$_3$ catalysts in the partial oxidation of methane

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Abstract

The effect of CeO$_2$ loading (1–20 wt.%) on the properties and catalytic behaviors of CeO$_2$–Al$_2$O$_3$-supported Pt catalysts on the partial oxidation of methane was studied. The catalysts were characterized by $S_{\text{BET}}$, X-ray diffraction (XRD), temperature-programmed reduction (TPR) and oxygen storage capacity (OSC). XRD and TPR results showed that the pretreatment temperature of the support influences on the amount of CeO$_2$ with fluorite structure. The pretreatment temperature of the support and CeO$_2$ loading influenced the morphology of Pt. OSC analysis showed a significant increase in the oxygen storage capacity per weight of CeO$_2$ for samples with high CeO$_2$ loading (12 and 20 wt.%). TPR analyses showed that the addition of Pt promotes the reduction of CeO$_2$. This effect was more significant for the catalysts with high CeO$_2$ loading (≥12 wt.%). The dispersion of Pt, measured by the rate of cyclohexane dehydrogenation, increases with increasing of the pretreatment temperature of the support. It was shown that the kind of the support is very important for obtaining of catalysts resistant to carbon formation. The catalysts with high CeO$_2$ loading (≥12 wt.%) showed the highest catalytic activity and stability in the reaction of partial oxidation of methane due to a higher Pt–CeO$_2$ interface.

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References

1. Introduction
The partial oxidation of methane (POM) is one of the most promising methods for producing of synthesis gas from methane. This reaction produces a gas with H₂/CO ratio of 2:1, desirable for the synthesis of hydrocarbons. The exothermic nature of the process of partial oxidation makes this process less costly in terms of energy and capital than the conventional endothermic steam reforming [1]. These characteristics incentive the study of POM and much research has been carried out on this reaction [2, 3, 4, 5, 6, 7] and [8].

A two-step mechanism has been proposed for the partial oxidation of methane consisting of exothermic total oxidation of CH₄, producing CO₂ and H₂O followed by the reforming of the un-reacted CH₄ with the steam and CO₂ produced by the first reaction [2] and [7].

Ceria is a powerful promoter that modifies the structural and electronic properties of many catalysts [9], promotes the reduction of noble metals [10] and, specially, decreases the carbon formation on the surface of catalyst [11]. Moreover, ceria has the important property of storing and releasing oxygen [11]. However, the utilization of ceria alone as support is not suitable due to its low surface area. Therefore, the utilization of alumina together with ceria permits the development of new materials combining the high surface area of alumina with the unique properties of ceria.

In the recent studies [12] and [13] it was shown that Pt/ CeO₂–ZrO₂ catalysts have high stability in the reaction of POM, which was explained by the high reducibility and oxygen storage/release capacity of the support, causing the removal of carbonaceous deposits from the surface of Pt.

In our previous work [14] it was verified that Pt catalysts supported on CeO₂–Al₂O₃ carriers are more stable during CO₂ reforming of CH₄ than Pt/Al₂O₃, and this stability is not dependent on the CeO₂ loading. The recent study of chemical conversion of methane on supported Pt cluster [15] showed that TOF of CH₄ for CO₂ and H₂O reforming increase with increasing of Pt dispersion, but the supports (ZrO₂, γ-Al₂O₃, ZrO₂–CeO₂) did not influence on TOF of CH₄.

The present work is a continuation of the study of Pt catalysts supported on mixed oxides CeO₂–Al₂O₃ with different CeO₂ loading [14] and [16]. The current study attempts to elucidate the effect of CeO₂ loading on the physicochemical characteristics of CeO₂–Al₂O₃ supported Pt. In addition, the effect of CeO₂ loading on the activity and stability of Pt/xCeO₂–Al₂O₃ catalysts in the reaction of partial oxidation of methane was evaluated. The samples were characterized by using surface-area measurements, X-ray diffraction (XRD), temperature-programmed reduction (TPR) and oxygen storage capacity (OSC).

The Pt dispersion was determined from the data of the rate of cyclohexane dehydrogenation.

2. Experimental

2.1. Catalyst preparation

The CeO₂–Al₂O₃ carriers with various CeO₂ loading were prepared by impregnation of γ-alumina (Strem, SBET = 205 m²/g) with an aqueous solution of diammonium hexanitrate cerate (NH₄)₂[Ce(NO₃)₆] (99.99% pure product from Aldrich) as described previously in [17]. CeO₂ carrier was obtained by calcination of (NH₄)₂[Ce(NO₃)₆] at 923 K in a flow of synthetic air for 2 h. Pt/Al₂O₃, Pt/CeO₂ and Pt/CeO₂–Al₂O₃ samples were prepared by impregnation of the corresponding carrier with a solution of H₂PtCl₆·6H₂O (Degussa) in ethanol. The appropriate amount of chloroplatinic acid was dissolved in ethanol and the support material was then added. After stirring for 2 h at room temperature ethanol was removed by Rotavapor at 343 K. The samples were dried at 333 K overnight and calcined at 773 or 1173 K for 2 h in air. For all samples the amount of Pt was about 1 wt.%. The prepared samples were referred to as Pt/Al₂O₃, Pt/CeO₂, Pt/xCeO₂–Al₂O₃, where x is the theoretical CeO₂ content (1, 3, 6, 12 and 20 wt.%).
2.2. Characterization

Chemical analysis was obtained by inductively coupled plasma-atomic emission spectroscopy (ICP). The composition of the samples is summarized in Table 1.

Table 1. Chemical analysis, surface area ($S_{BET}$), pore volume ($V_p$) and particle size ($D_{XRD}$) of CeO$_2$–Al$_2$O$_3$ supports and Pt/CeO$_2$–Al$_2$O$_3$ catalysts calcined at 773 and 1173 K

<table>
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<th>Supports</th>
<th>CeO$_2$ (wt.%)</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_p$ (c m$^3$/g)</th>
<th>$D_{XRD}$ (nm)</th>
<th>Catalys</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_p$ (c m$^3$/g)</th>
<th>$D_{XRD}$ (nm)</th>
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<td>Al$_2$O$_3$</td>
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<td>153 (78)$^a$</td>
<td>0.24 (0.20)</td>
<td>-</td>
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<td>157</td>
<td>0.24 (0.20)</td>
<td>-</td>
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<td>27.5</td>
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<td>0.23</td>
<td>n.d. $^b$</td>
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<tr>
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<td>170 (87)</td>
<td>0.23 (0.21)</td>
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<td>0.22</td>
<td>n.d.</td>
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<td>4.4 (10.4)</td>
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<td>0.22</td>
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<td>12CeO$_2$–Al$_2$O$_3$</td>
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<td>7.0 (17.4)</td>
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<td>0.18 (0.19)</td>
<td>7.3 (17.4)</td>
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<tr>
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<td>8.9 (27.8)</td>
<td>Pt/20CeO$_2$–Al$_2$O$_3$</td>
<td>130 (69)</td>
<td>0.18 (0.18)</td>
<td>10.7 (19.9)</td>
</tr>
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</table>

$^a$ Values in parenthesis correspond to calcination temperature of 1173 K.

$^b$ Not detected.

Surface areas ($S_{BET}$) and pore volumes ($V_p$) were measured by N$_2$ adsorption at liquid nitrogen temperature using Micromeritics ASAP 2000 apparatus. The results of nitrogen adsorption measurements are given in Table 1.

X-ray diffraction spectra of the samples were collected with a Rigaku DMAX 2500 PC diffractometer, using Cu Kα radiation. The step-scans were taken over the range of 2θ from 10° to 75° in steps of 0.020° and the intensity data for each one were collected for 10 s. The size of the crystallites ($D_{XRD}$) of ceria was determined using Scherrer equation [18].

TPR profiles were recorded on a Micromeritics Pulse Chemisorb 2705 fitted with a thermo conductivity detector (TCD) and controlled by a computer. In order to remove surface contaminants, the sample (0.100 g) loaded in a quartz reactor was pretreated at 423 K in a He stream for 1 h. After cooling to room temperature, a flow of 10% H$_2$/Ar (30 ml/min) was passing through the sample and the temperature was raised at a rate of 10 K/min up to 1373 K while the TCD signal was recorded.

Oxygen storage capacity measurements were carried out in a micro-reactor coupled to a quadrupole mass spectrometer (Omnistar, Balzers). Prior to OSC analysis, the samples were reduced under H$_2$ at 773 K for 1 h and heated to 1073 K in a flow of He. Then, the samples were cooled to 723 K and remained at this temperature during the analysis. The mass spectrometer was used to measure the composition of the reactor effluent as a function of the time while a 5% O$_2$/He mixture was passed through the catalyst. Oxygen consumption was calculated from the curve corresponding to $m/e = 32$ taking into account a previous calibration of the equipment.

The Pt dispersion was determined from the data of cyclohexane dehydrogenation rate and compared with a standard sample. The reaction of cyclohexane dehydrogenation was
performed in a fixed-bed reactor at atmospheric pressure. The catalysts were reduced at 773 K for 1 h and the reaction was carried out at 543 K and WHSV = 170 h\(^{-1}\). The reactants were feed to the reactor by bubbling H\(_2\) through a saturator containing cyclohexane at 285 K (H\(_2\)/HC = 13.6). The exit gases were analyzed using a gas chromatograph (HP5890) equipped with a HP-INNOWAX capillary column.

2.3. Test reaction
Catalytic reaction runs of partial oxidation of CH\(_4\) were conducted in a fixed bed quartz reactor at atmospheric pressure. The catalyst (20 mg) was diluted with SiC (36 mg) in order to minimize heat effects. The length of the catalytic bed was such that there was no temperature gradient along the catalytic bed. Prior to reaction, the samples were reduced in situ at 773 K for 1h in 10% H\(_2\)/N\(_2\) flow (50 ml/min) and then heated up to 1073 K under N\(_2\). The catalytic activity of different catalysts were carried out at 773 K and WHSV = 260 h\(^{-1}\). A reactant mixture with CH\(_4\):O\(_2\) ratio of 2:1 and a flow rate of 100 cm\(^3\)/min was used. The stability test of the catalysts was carried out at 1073 K in the conditions like the catalytic activity measurements. The exit gases were analyzed using a gas chromatograph (Agilent 6890) equipped with a thermal conductivity detector and a CP-carboplot column.

3. Results

3.1. Characterization of the supports and catalysts
Chemical analysis, \(S_{\text{BET}}\) and pore volume of Al\(_2\)O\(_3\), CeO\(_2\) and CeO\(_2\)–Al\(_2\)O\(_3\) supports with different CeO\(_2\) loading after treatment in air at different temperature of calcination are summarized in Table 1. The surface areas and pore volume of CeO\(_2\)–Al\(_2\)O\(_3\) samples with lower CeO\(_2\) loading (CeO\(_2\) ≤ 6 wt.\%) and treated at 773 K are similar to that of un-promoted with CeO\(_2\) Pt/alumina (Table 1). The textural properties of higher CeO\(_2\)-loaded samples (≥12 wt.% ) decrease with increasing of CeO\(_2\) loading, due to an agglomeration of CeO\(_2\). The increase in the temperature of calcination from 773 up to 1173 K leads to a significant decrease in the \(S_{\text{BET}}\) and \(V_p\) corresponding to formation of micropores. The observed influence of CeO\(_2\) loading on the thermal stability of alumina is similar to previous observations in the literature \([19]\) and \([20]\). Pt catalysts supported on Al\(_2\)O\(_3\), CeO\(_2\) and CeO\(_2\)–Al\(_2\)O\(_3\) show surface areas and pore volume similar to those of the supports (Table 1).

XRD spectra of the Pt catalysts supported on Al\(_2\)O\(_3\), CeO\(_2\) and CeO\(_2\)–Al\(_2\)O\(_3\) and calcined at 773 K are shown in Fig. 1. Fig. 1A and B corresponds to the samples, whose supports previously are calcined at 773 and 1173 K, respectively. No XRD patterns of Pt oxide species were observed in the samples calcined at 773 K that is similar to the observations in Ref. \([16]\). The results suggest that independently from the treatment temperature of the CeO\(_2\)–Al\(_2\)O\(_3\) supports the Pt particles are well dispersed on the surface of Pt/CeO\(_2\)–Al\(_2\)O\(_3\) samples after their calcination at 773 K. It should be noted that the characteristic diffraction lines of CeO\(_2\) fluorite structure at \(2\theta = 28.5^\circ\), 33.3\(^\circ\), 47.5\(^\circ\) and 56.4\(^\circ\) were clearly observed for the CeO\(_2\)–Al\(_2\)O\(_3\) samples with higher CeO\(_2\) loading (≥6 wt.\%). The diffraction lines of CeO\(_2\) fluorite structure became stronger at higher temperature of calcination (1173 K) of the CeO\(_2\)–Al\(_2\)O\(_3\) supports, suggesting a progressive crystallization of CeO\(_2\) on the surface of the carriers. This is confirmed by the higher values of the calculated size of CeO\(_2\) particles (Table 1). The same trend in the change of particle size of CeO\(_2\) with increasing of CeO\(_2\) loading and calcination temperature of the support is observed for Pt/CeO\(_2\)–Al\(_2\)O\(_3\) samples (Fig. 1A and B and Table 1). The diffraction patterns of the Pt/CeO\(_2\)–Al\(_2\)O\(_3\) samples show a decrease in the intensity of CeO\(_2\) fluorite structure after reduction in H\(_2\) (Fig. 1A (curve h) and B (curve d)).
The TPR profiles of CeO$_2$ and CeO$_2$–Al$_2$O$_3$ supports with different CeO$_2$ loading, previously calcined at 773 and 1173 K, are shown in Fig. 2A and B, respectively. The TPR profile of CeO$_2$ shows peaks in a lower (623–773 K) and in a higher (above 873 K) temperature region (Fig. 2A (curve a)), which can be interpreted as a stepwise reduction of CeO$_2$, similar to the results in Refs. [21] and [22]. The peaks in the low temperature region are assigned to the reduction of the surface capping oxygen (O$_2^-$ or O$^-$ anions) (723 K) and to the formation of nonstoichiometric cerium oxides at 850 K (CeO$_x$ with $x$ ranging from 1.9 to 1.7, or the $\beta$ phase) [23]. The contribution of the peaks depends on the specific surface area of CeO$_2$ with fluorite structure [21]. The peak in the high temperature region would be assigned to the deep reduction of bulk ceria by elimination of O$_2^-$ anions of the lattice and formation of Ce$_2$O$_3$ [24]. The TPR profiles of CeO$_2$–Al$_2$O$_3$ supports with different CeO$_2$ loading and calcined at 773 K (Fig. 2A) show main peaks at around 830 with a shoulder at 730, 1120 and 1250 K. The contribution of the different peaks depends strongly on the CeO$_2$ loading. The CeO$_2$–Al$_2$O$_3$ samples with low CeO$_2$ loading (≤3 wt.%) and calcined at 773 K show main peaks at 880 and 1250 K. Considering the previous study of CeO$_2$–Al$_2$O$_3$ supports [17] with XPS analysis, it can be supposed that these peaks are associated with the reduction of a small amount of CeO$_2$ that is agglomerated. The peak at 1120 K becomes pronounced with increasing of CeO$_2$ loading (≥6 wt.%). This species would be assigned to the reduction of CeAlO$_3$ precursor, which is formed by ceria in interaction with alumina and partially reduced. The reduction of CeAlO$_3$ precursor is followed by formation of CeAlO$_3$. The TPR profiles of the high CeO$_2$-loaded samples (≥12 wt.%) show main peak at around 830 K with a shoulder at 730 K; the peak at 1240 K becomes more intensive with increasing of CeO$_2$ loading from 12 to 20 wt.%. The peaks at around 880 and 1240 K would be assigned to the reduction of CeO$_2$ species that is agglomerated and the ceria loading exceed monolayer coverage on alumina [17] and [22]. In the TPR profiles of xCeO$_2$–Al$_2$O$_3$ samples with low CeO$_2$ loading (≤6 wt.%) and calcined at high temperature (1173 K) the peak at 1120 K, assigned to the reduction of CeAlO$_3$ precursor, becomes more pronounced relative to that for the samples calcined at low temperature (see Fig. 2A (curve c) and B (curve c)). No species is observed for CeO$_2$–Al$_2$O$_3$ sample with 6 wt.% CeO$_2$ at reduction temperature lower than 1100 K. The results reveal that the CeAlO$_3$ precursor is favored with increasing of the reduction temperature before the agglomeration of CeO$_2$. The partial reduction of ceria is followed by the formation of CeAlO$_3$, which occur during the previous thermal treatment in air. Due to the strong interaction between CeO$_2$ and alumina surface no removal of oxygen from CeAlO$_3$ precursor occurs until the temperature at around 1100 K is reached for CeAlO$_3$ formation. Similar results have been described by Shyu et al. [23]. In the TPR profiles of CeO$_2$–Al$_2$O$_3$ samples with high CeO$_2$ loading (≥12 wt.%) and calcined at 1173 K the main peaks at around 850, 1120 and 1240 K become more pronounced relative to those for the samples calcined at low temperature (773 K). This means that the main species in the samples with higher CeO$_2$ loading and calcined at higher temperature are CeAlO$_3$ precursor and agglomerated CeO$_2$. 

Fig. 1. XRD spectra of Pt/CeO$_2$, Pt/Al$_2$O$_3$ and Pt/CeO$_2$–Al$_2$O$_3$ samples with different CeO$_2$ loading calcined at 773 K (A) and 1173 K (B). (A) CeO$_2$ (a); Pt/Al$_2$O$_3$ (b); 1 wt.% (c); 3 wt.% (d); 6 wt.% (e); 12 wt.% (f); 20 wt.% CeO$_2$ (g); sample with 20 wt.% reduced at 773 K (h). (B) 3 wt.% (a); 12 wt.% (b); 20 wt.% CeO$_2$ (c); sample with 20 wt.% reduced at 1173 K (d).
Fig. 2. TPR patterns of bulk CeO$_2$ (a) and CeO$_2$–AlO$_3$ with different CeO$_2$ loading calcined at 773 K (A) and 1173 K (B) 1 wt.% (b); 3 wt.% (c); 6 wt.% (d); 12 wt.% (e) and 20 wt.% CeO$_2$ (f).

The TPR profiles of supported Pt samples after calcination at 773 K, whose supports were previously calcined at different temperatures (773 and 1173 K), are shown in Fig. 3. The TPR profile of Pt/CeO$_2$ sample (Fig. 3 (curve b)) shows main peaks at around 520, 740 and 1280 K. The peak at 520 K and the higher H$_2$ consumption relative to the amount of PtO$_2$ could be attributed to both, the reduction of Pt and the superficial CeO$_2$, which is in interaction with Pt. The peaks at approximately 740 and 1280 K are assigned to the formation of nonstoichiometric cerium oxides and formation of Ce$_2$O$_3$, respectively [22]. Interestingly, in the TPR profile of Pt/CeO$_2$ sample the peak attributed to superficial reduction of CeO$_2$ is moved to a lower temperature relative to that of the support, suggesting that the superficial reduction of CeO$_2$ is promoted by the presence of Pt. The higher temperature peak of bulk ceria is moved to a higher temperature, due to the difficulty to transfer oxygen from the bulk to the reduced surface of Pt–CeO$_2$. As described in our previous work [14], the higher TPR peak could be a consequence of the residual chlorine that substitutes the oxygen ions in the ceria lattice, which decreases the hydrogen chemisorption by ceria. These results are in a good agreement with the studies in Ref. [21] suggesting that the presence of noble metals over ceria surface causes easier reduction of the surface of CeO$_2$, affected by the hydrogen spillover from the metallic Pt particles to CeO$_2$.

Fig. 3. TPR patterns of Pt/Al$_2$O$_3$ (a), Pt/CeO$_2$ (b) and Pt/CeO$_2$–Al$_2$O$_3$ whose supports are previously calcined at 773 K: 1 wt.% (c); 3 wt.% (d); 6 wt.% (e); 12 wt.% (f) 20 wt.% CeO$_2$ (g) and at 1173 K 3 wt.% (h); 12 wt.% (i) and 20 wt.% CeO$_2$ (j).

The TPR profile of Pt/Al$_2$O$_3$ sample (Fig. 3 (curve a)) shows peak at 560 K with high intensity and a small peak at 707 K. According to the literature data[25] the peak at 560 K would be assigned to a
reduction of Pt-oxide species and/or to a reduction of oxychlorplatinum surface complex \([\text{PtO}_x\text{Cl}_y]\). The small peak at 707 K could be assigned to a reduction of dispersed Pt in isolated patches PtO, on alumina [26].

The TPR profiles of Pt samples supported over CeO\textsubscript{2}\textendash Al\textsubscript{2}O\textsubscript{3} oxides with different CeO\textsubscript{2} loading and calcined at low temperature (773 K) are shown in Fig. 3(curves c\textendash g). The TPR profiles of these samples show main peaks at \(\approx 560\) and 700 K, with high and small intensity, respectively. The intensity of the peak at 560 K increases clearly with rising of CeO\textsubscript{2} loading and becomes asymmetric. The main species like CeAlO\textsubscript{3} precursor, presented in CeO\textsubscript{2}\textendash Al\textsubscript{2}O\textsubscript{3} support with 6 wt.% CeO\textsubscript{2}, is not observed in the TPR profile of Pt/6CeO\textsubscript{2}\textendash Al\textsubscript{2}O\textsubscript{3} sample. This supports the initial idea, that these peaks can be attributed to both, the reduction of Pt and different superficial species, like CeAlO\textsubscript{3} precursor and nanoparticles of CeO\textsubscript{2}. The peak at 700 K can be associated with PtO\textsubscript{2}\textendash Al\textsubscript{2}O\textsubscript{3} interactive species similar to that observed for Pt/Al\textsubscript{2}O\textsubscript{3} sample. The increase of the temperature treatment of the supports from 773 to 1173 K results in decreasing of the intensity of the peak at 700 K (Fig. 3 curve e)). The TPR profiles of Pt/CeO\textsubscript{2}\textendash Al\textsubscript{2}O\textsubscript{3} samples, calcined at 1173 K, depend on the amount of CeO\textsubscript{2}. For the Pt/CeO\textsubscript{2}\textendash Al\textsubscript{2}O\textsubscript{3} samples with CeO\textsubscript{2} loading \(\geq 12\) wt.% the peaks at high temperatures, corresponding to the presence of species like CeAlO\textsubscript{3} precursor and CeO\textsubscript{2}, become more pronounced with increasing of the treatment temperature of the support from 773 to 1173 K. The main TPR peaks for Pt catalysts supported on CeO\textsubscript{2}\textendash Al\textsubscript{2}O\textsubscript{3} carriers, previously calcined at 1173 K, occur in lower temperature region of 483\textendash 653 K. A duplet at around 600 K is observed in the TPR profile of Pt/20CeO\textsubscript{2}\textendash Al\textsubscript{2}O\textsubscript{3} sample, similar to that previously described by Yao and Yao [21]. This is presumed to the interaction between PtO\textsubscript{2} and CeO\textsubscript{2} with various states of aggregation. The OSC results of the catalysts are listed in Table 2. In terms of \(\mu\text{mol/g cat}\) the OSC of Pt/CeO\textsubscript{2}\textendash Al\textsubscript{2}O\textsubscript{3} samples increase with CeO\textsubscript{2} loading, independent from the fact that the values are very small compared to that of CeO\textsubscript{2}. The lower efficiency of the ceria in contact with alumina, may be, is due to its lower surface area in the Pt/CeO\textsubscript{2}\textendash Al\textsubscript{2}O\textsubscript{3} or the intimate PT/ceria contact is partially hindered by the presence of alumina [27].

Table 2. Oxygen storage capacity (OSC), energy activation of dehydrogenation of cycle hexane (\(E\)), dispersion of Pt and TOF for the conversion of CH\textsubscript{4} on Pt/Al\textsubscript{2}O\textsubscript{3}, Pt/CeO\textsubscript{2}\textendash Al\textsubscript{2}O\textsubscript{3} and Pt/CeO\textsubscript{2} catalysts at 773 K

<table>
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<tr>
<th>Sample</th>
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<th>OCS ((\mu\text{mol/g CeO}_2))</th>
<th>(E) (kcal/mol)</th>
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<td>Pt/6CeO\textsubscript{2}\textendash Al\textsubscript{2}O\textsubscript{3}</td>
<td>–</td>
<td>–</td>
<td>30.6</td>
<td>0.69</td>
<td>5.70</td>
<td>1.96</td>
</tr>
<tr>
<td>Pt/12CeO\textsubscript{2}\textendash Al\textsubscript{2}O\textsubscript{3}</td>
<td>115</td>
<td>1204</td>
<td>26.0</td>
<td>0.54</td>
<td>6.99</td>
<td>2.99</td>
</tr>
<tr>
<td>Pt/20CeO\textsubscript{2}\textendash Al\textsubscript{2}O\textsubscript{3}</td>
<td>112.9</td>
<td>677</td>
<td>29.8</td>
<td>0.51</td>
<td>8.17</td>
<td>2.92</td>
</tr>
<tr>
<td>Pt/3CeO\textsubscript{2}\textendash Al\textsubscript{2}O\textsubscript{3}\textsuperscript{a}</td>
<td>–</td>
<td>–</td>
<td>25.4</td>
<td>0.84</td>
<td>4.69</td>
<td>1.52</td>
</tr>
<tr>
<td>Pt/12CeO\textsubscript{2}\textendash Al\textsubscript{2}O\textsubscript{3}\textsuperscript{a}</td>
<td>74.8</td>
<td>701</td>
<td>23.0</td>
<td>0.69</td>
<td>6.63</td>
<td>2.78</td>
</tr>
<tr>
<td>Pt/20CeO\textsubscript{2}\textendash Al\textsubscript{2}O\textsubscript{3}\textsuperscript{a}</td>
<td>110.20</td>
<td>661</td>
<td>25.1</td>
<td>0.69</td>
<td>6.63</td>
<td>2.78</td>
</tr>
</tbody>
</table>
It has been shown [28], [29], [30], [31], [32] and [33] that the determination of metal dispersion by chemisorption's techniques is difficult because the support is able to chemisorb the most usual probe molecules like H\textsubscript{2} and CO. Is the case of redox supports such ceria the likely occurrence of spillover phenomena represents a major drawback because the intensity of hydrogen spillover should be very sensitive to the ceria surface area and chlorine from the metal precursor H\textsubscript{2}PtCl\textsubscript{6} [28] and [32]. The dehydrogenation of cyclohexane is classified like structure-insensitive reaction [34]. For Pt based catalysts this reaction is very selective with formation of benzene and it is an indirect measure of the dispersion of Pt. Therefore, the Pt dispersion of Pt/CeO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} catalysts can be estimated by the rate of cyclohexane dehydrogenation. The values of Pt dispersion are summarized in Table 2.

From Table 2 it is observed that the dispersion of Pt (PtD) on the surface of Pt/Al\textsubscript{2}O\textsubscript{3} is higher than that of Pt/CeO\textsubscript{2}. The values of Pt dispersion of Pt/CeO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} catalysts calcined at 773 K increase with increasing of CeO\textsubscript{2} loading up to 6 wt.%, after that the dispersion decreases. However, when the supports are calcined at higher temperature (1173 K), the supported Pt samples with CeO\textsubscript{2} ≥ 12 wt.% show higher dispersion.

The XPS results [16] showed that Pt/Ce ratios of Pt/CeO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} samples are significantly higher than those of Pt/Al, suggesting a more intimate contact between Pt and Ce. The Pt/Ce ratios decreased with increasing of CeO\textsubscript{2} loading. The lowest Pt dispersion was observed for Pt/CeO\textsubscript{2} sample, most probably, caused by the very low surface area of the CeO\textsubscript{2} support. Pt/Al ratios decrease with increasing of CeO\textsubscript{2} loading up to 6 wt.%; after that, the Pt/Al increases significantly at 12 wt.% CeO\textsubscript{2} due to the agglomeration of CeO\textsubscript{2} crystallites and the surface of alumina becomes free [16]. It has been shown that Pt interacts preferentially with Ce even in the presence of a much larger Al\textsubscript{2}O\textsubscript{3} surface [22].

### 3.2. Reaction data

The TOF\textsubscript{obs} for conversion of methane at 773 K are summarized in Table 2. Considering the fact that the TOF\textsubscript{obs} is obtained at 773 K and the consumption of oxygen is extremely fast, the TOF\textsubscript{obs} is a result of the coupling of total oxidation and H\textsubscript{2}O and CO\textsubscript{2}–CH\textsubscript{4} reforming. Consequently, the TOF for reforming reaction (TOF\textsubscript{ref}) could be approximately represented by: TOF\textsubscript{ref} = TOF\textsubscript{obs} − TOF\textsubscript{ox}, where TOF\textsubscript{ox} is the turnover frequency of the consumption of oxygen for total oxidation. Interestingly, the activity of Pt/CeO\textsubscript{2} catalyst in the reforming reaction (TOF\textsubscript{CH\textsubscript{4}}=2.28 s\textsuperscript{-1}) is higher than that of Pt/Al\textsubscript{2}O\textsubscript{3} (TOF\textsubscript{CH\textsubscript{4}}=0.16 s\textsuperscript{-1}). The values of TOF for Pt/CeO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} samples are between the values of TOF for Pt/CeO\textsubscript{2} and Pt/Al\textsubscript{2}O\textsubscript{3} and depend on the amount of CeO\textsubscript{2}. The TOF for the sample with low CeO\textsubscript{2} loading (1 wt.%) is similar to that observed for Pt/Al\textsubscript{2}O\textsubscript{3}. The high CeO\textsubscript{2}-loaded samples (≥12 wt.% CeO\textsubscript{2}) are the most active catalysts and their TOF increase with increasing of CeO\textsubscript{2} loading (Table 2).

The results of stability test with time on stream for Pt catalysts supported on CeO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} carriers, previously calcined at 773 and 1173 K, are shown in Fig. 4. Interestingly, similar to the activity, the stability depends on the amount of CeO\textsubscript{2}. The low CeO\textsubscript{2}-loaded catalysts (≤6 wt.%) strongly deactivate with the time on stream, whereas the high CeO\textsubscript{2}-loaded catalysts (≥12 wt.%) are quite stable. The curves of the selectivity to H\textsubscript{2} follow the same trend of the results of methane conversion (Fig. 4).
Fig. 4. CH$_4$ conversion and selectivity to H$_2$, CO and CO$_2$ over Pt/Al (▲) and Pt/CeO$_2$–Al$_2$O$_3$ catalysts with different CeO$_2$ loading calcined at 773 K 3 wt.% (▼), 12 wt.% (●), 20 wt.% (■) and 1173 K 3 wt.% (♦) and 12 wt.% CeO$_2$ (♦).

The selectivity to CO and CO$_2$ of the catalysts in the reaction of partial oxidation of methane are shown in Fig. 4. The selectivity to CO and CO$_2$ of Pt/CeO$_2$–Al$_2$O$_3$ catalysts with 12 and 20 wt.% CeO$_2$, practically, did not change during the reaction. On other hand, the formation of CO strongly decreases for Pt/Al$_2$O$_3$, Pt/3CeO$_2$–Al$_2$O$_3$ and Pt/6CeO$_2$–Al$_2$O$_3$ catalyst, while the production of CO$_2$ increases with time on stream.

4. Discussion

4.1. Effect of CeO$_2$ loading on the characteristics of Pt/CeO$_2$–Al$_2$O$_3$ catalysts

In the previous our work [16] it was observed by XPS and FTIR of CO adsorbed on Pt, that the identity of the support (Al$_2$O$_3$, CeO$_2$ and CeO$_2$–Al$_2$O$_3$) influence in different ways on the crystal surface structure of Pt, as well as on the interaction between Pt and the support. The XPS results [16] showed that Pt supported on CeO$_2$ has δ character in comparison with Pt supported on Al$_2$O$_3$.

Although the Pt/Al$_2$O$_3$ catalyst show a high Pt dispersion (PtD = 0.66), our FTIR results of the CO adsorbed on similar Pt/Al$_2$O$_3$ catalyst [16] revealed a main band at 2049 cm$^{-1}$ with a clearly resolved shoulder at 2070 cm$^{-1}$ and a broad band at 1816 cm$^{-1}$. It was suggested [16] the presence of at least two
phase of Pt on Pt/Al₂O₃, one high dispersed with higher electron density and a crystalline. Similar results have been established in several studies [35] and [36]. Pt/CeO₂ catalyst shows the lowest Pt dispersion (PID = 0.28, Table 2). The IR results of CO adsorbed on Pt/CeO₂ [16] revealed the Pt surface with the lowest electron density, expressed by two not well-resolved bands at 2087 and 2070 cm⁻¹, that has been related to the interaction of Pt with CeO₂ support fluorite structure and to the different morphology of Pt relative to that for Pt/Al₂O₃. Interestingly, the Pt/CeO₂–Al₂O₃ catalyst with CeO₂ loading of 3 and 6 wt.% show high Pt dispersion of 0.72 and 0.69 (Table 2), respectively, although it was expected Pt surface with lower electron density caused by the highly unsaturated Pt [16]. The main CO bands for these samples were observed at 2063–2065 cm⁻¹ with shoulder at about 2077 cm⁻¹ and no band of CO was observed at about 1840 cm⁻¹ [16]. It should be noted that the frequencies of CO bands of Pt/3CeO₂–Al₂O₃ and Pt/6CeO₂–Al₂O₃ samples are higher than those of Pt/Al₂O₃ with lower Pt dispersion. The high Pt dispersion (Table 2) and the absence of the band at about 1840 cm⁻¹ for CeO₂-containing catalysts with low CeO₂ loading (≤6 wt.%) suggests that the addition of CeO₂ into Al₂O₃ avoids the possible agglomeration of PtO₂ during calcination. This leads to a high Pt dispersion and to a more uniform size distribution of Pt with lower electron density relative to that for Pt/Al₂O₃. Consequently, it is reasonable to suppose that the low electron density of Pt atoms can be caused by the interaction between PtO₂ and the support like CeAlO₂, which can promote the change in the Pt morphology relative to that for Pt/Al₂O₃. It cannot be excluded the possibility that the residual chlorine in the catalysts changes the interaction between the support and Pt. Similar results have been observed by Hicks et al. [37] for highly dispersed Pt on ZrO₂. The Pt dispersion of Pt/CeO₂–Al₂O₃ samples decreases to about 0.54 with increasing of CeO₂ loading (≥12 wt.%) (Table 2). This can be supported by the XRD results which show a pronounced among of CeO₂ fluorite structure (Fig. 1). The IR spectra of adsorbed CO showed the band at lower frequency (1835 cm⁻¹) [16], which was connected with the decreasing of Pt dispersion on the samples with high CeO₂ loading (≥12 wt.%).

The TPR results for Pt/CeO₂–Al₂O₃ catalysts with low CeO₂ loading (≤6 wt.%) show that almost all the Ce(IV) is reduced to Ce(III) in the low temperature reduction region (773 K), while a higher temperature is necessary to reduce the Ce(IV) in the catalysts with high CeO₂ loading (≥12 wt.%) and Pt/CeO₂. These results are consistent with the previous XPS results [16] for Pt/CeO₂–Al₂O₃ catalysts, which showed that the v¹ peak characteristic of cerium in the oxidation state of IV increased with increasing of CeO₂ loading in the supports. For samples with lower CeO₂ loading (≤3 wt.%) the higher contribution of Ce(III) was observed [16].

4.2. Effect of CeO₂ loading on the activity and stability of Pt/CeO₂–Al₂O₃ catalysts

It is clear from Table 2 and Fig. 4 that the activity and stability of Pt/CeO₂–Al₂O₃ catalysts depend on the CeO₂ loading. Recently, we reported that the support plays an important role on the mechanism of the reaction of partial oxidation of methane [13]. According to this mechanism, the partial oxidation of methane on supported platinum catalysts proceeds through a two-step route. In the first step, combustion of methane takes place, producing CO₂ and H₂O. In the second one, synthesis gas is produced via carbon dioxide and steam reforming reaction of un-reacted methane. Although Hicks et al. [37] have demonstrated that the methane oxidation over platinum is a structure-sensitive reaction; the first step of the oxygen adsorption on Pt is extremely fast. Since the consumption of oxygen is very fast on the catalyst at 773 K, the activity of the catalysts were compared in TOF for H₂O–CH₄ and CO₂–CH₄ reforming reactions (TOFref). Many authors [38], [39], [40], [41] and [42] have described that the activity of metal supported catalysts in the reaction of CO₂ reforming of CH₄ is strongly depends on the nature of the support. Nevertheless, Wei and Iglesia [15] and [43] have demonstrated that the TOF for H₂O–CH₄ and CO₂–CH₄ reforming reactions not depend on the identity of the supports as ZrO₂, γ-Al₂O₃ and ZrO₂–CeO₂. These authors [43] and [44] considered the following conclusions: (i) The forward CH₄ turnover rates of H₂O–CH₄ and CO₂–CH₄ reforming reactions increase with increasing of Pt, Rh, Ir and Ru dispersion on ZrO₂, γ-Al₂O₃ and ZrO₂–CeO₂. (ii) The increase of forward TOF with increasing of Pt dispersion is connected with the presence of coordinative unsaturated surface Pt atoms that are more reactive for C–H bond activation than Pt atoms in a low-index surface. From these conclusions and the results of Pt dispersion (Table 2), XPS and FTIR of CO adsorbed on Pt supported on Al₂O₃ and CeO₂ [16] it is
reasonable to suppose that Pt/Al2O3 catalyst will show higher activity in the reactions of H2O–CH4 and CO2–CH4 reforming. However, comparing the activity of Pt/CeO2 and Pt/Al2O3 catalysts, which have different Pt dispersion of 0.28 and 0.66, respectively, it is observed that Pt/CeO2 shows higher activity (TOF_ref = 2.28 s⁻¹, Table 2). Although the Pt/Al2O3 shows Pt surface with higher electron density than that of Pt/CeO2 [16], its activity in the reforming reaction is lower (TOF_ref = 0.16 s⁻¹, Table 2). It is surprisingly that the TOF_ref of CeO2-containing catalysts, which showed higher uniformity of Pt particle size relative to that of Pt/Al2O3 [16], increase with decreasing of Pt dispersion at higher CeO2 loading (Table 2). To understand these behaviors of the catalysts we should consider the results obtained by Wei and Iglesia [44], related to the isotopic studies and forward rate measurements of nickel catalysts in the reactions of H2O–CH4 and CO2–CH4 reforming. It was proposed that CH4 decomposes to chemisorbed carbon (C*) via sequential elementary H-abstraction step. The carbon species is removed using H2O or CO2. The first H-abstraction step in CH4 decomposition is the limiting reaction rate. From these results it is reasonable to suppose that the activity and stability of the catalysts should be correlated with the relative ratio between the first H-abstraction step in CH4 decomposition and the step of removing of C*. Therefore for the active and stable catalysts, which have no partial blocked metal sites by carbon, the rates of activation of CH4 and of carbon removing should be equilibrated.

The XRD results of CeO2-containing catalysts show that the size of the crystallites of CeO2 fluorite structure increases with increasing of CeO2 loading (Table 1). It was shown by Yao and Yao [21] that for CeO2/Al2O3 support, previously reduced at high temperature, the oxygen partially restores by reoxidation at around 773 K, corresponding to a species reducible in the low temperature region. It means that the CO2 and H2O can be partially activated on CeO2 species reducible at low temperature on Pt/CeO2–Al2O3. Otsuka et al. [2] have demonstrated that the reactions: (i) CeO2-x + xCO2 → CeO2 + xCO and (ii) CeO2-x + xH2O → CeO2 + xH2 are thermodynamically favorable at temperature lower than 973 K. Zafiris and Gorte [45] have shown that the oxygen migration from CO2 to Rh has an important role in the enhancement of catalytic activity of Rh/CeO2 catalyst for CO oxidation. Consequently, the CeO2 sites on Pt/CeO2–Al2O3 catalysts could be restored by the oxygen migration from the CeO2 to Pt surface, which reacts with adsorbed C* species. This can result in an increase of catalytic activity of the catalysts with increasing of CeO2 loading in the reforming reactions. Although the electron density of Pt surface decreases from Pt/Al2O3 to Pt/CeO2 and a decrease in the CH4 activation is expected, the presence of CeO2 can result in a more efficiency of removing of C from the metal surface. Consequently, the opposite effect of CeO2 loading on TOF is observed with decreasing of C* surface and more Pt sites are available for reforming reaction with rising of CeO2 content.

Fig. 4 demonstrates that the stability of Pt/CeO2–Al2O3 catalysts depends strongly on the CeO2 loading. Pt/CeO2–Al2O3 catalysts with low CeO2 loading; there is a strong deactivation at high temperature of reaction similar to that for Pt/Al2O3 catalyst (Fig. 4). The strong deactivation should be related to the sintering of metal particles and to the formation of carbon on the surface of metal particles. The deactivation of Pt/Al2O3 catalyst in the reaction of partial oxidation of methane can be mainly attributed to the increase of the number of carbon deposits around the metal particles, as it was reported in the previous work [13]. The carbon formation at high temperature may occur by the decomposition of methane through successive steps of dissociation of CH4 giving C* species (CH4 → C* + 2H2) and disproportionation of CO at low temperature (2CO → C* + CO2) [49]. Therefore, the different mechanisms of removing of C from the metal surface in the reactions of CO2 and steam reforming of methane should be contributed to the stability of the catalysts in the partial oxidation of methane. Bengaard et al. [46] have shown by density functional theory calculation of the steam reforming process that the atomic carbon (C*) species over stepped Ni(2 1 1) surface show lower energy than over terrace sites like Ni(1 1 1). Therefore C* has much higher stability on the step sites than on terrace sites. This means that the nucleation of carbon should be start at step sites. The defect step sites are very reactive for activation of methane, CO and water. Tripa et al. [47] have shown that N2 only binds to the defect step sites of Pt. As expected the increase in the activity of the activation of methane and CO would result in an increase of C* on the surface, while the activation of water and CO2 has the opposite effect on the catalyst stability. By analogy with the results for the reactivity of the reactants and stability of C* on the surface of Ni we can presume that the different stability of
Pt/CeO$_2$–Al$_2$O$_3$ catalysts should be influenced by the different surface structure of Pt. Although the FTIR results of CO adsorbed on Pt/CeO$_2$–Al$_2$O$_3$ suggested [16] an increasing of Pt coordination with increasing of CeO$_2$ loading, the higher stability is observed for Pt/CeO$_2$–Al$_2$O$_3$ catalyst with high CeO$_2$ loading (Fig. 4). It is seen from Fig. 4 that the catalysts with high CeO$_2$ loading (≥12 wt.%) and, consequently, with high amount of CeO$_2$ fluorite structure are stable. In these samples part of Ce(IV) is reduced in the low temperature region (500–750 K), but a higher temperature (≥1000 K) is necessary to reduce almost all the Ce(IV) (Fig. 3). According to the literature data [48] the relative abstraction of oxygen from the surface and bulk ceria depends on the size of CeO$_2$ crystallites. Considering the fact that the tests of stability were performed at high temperature (1073 K) and at high methane conversion with main products of H$_2$ and CO, we may conclude that these conditions correspond to the higher reducing conditions relative to those for the test reaction of catalytic activity. The stability of Pt/CeO$_2$–Al$_2$O$_3$ catalyst with low CeO$_2$ loading is lower compared to that of other catalysts, due to the predominance of Ce in Ce(III)$_3$ form. Consequently, the equilibrium of the reaction 2Ce(IV)$_3$ + O$_2$ $\rightleftharpoons$ 2Ce(III)$_3$ + V$_{5s}$ + O$_2^2$ is not favored for a possible oxygen transfer from the ceria surface to Pt surface [49] through the activation of H$_2$O and CO$_2$. On other hand, Pt/CeO$_2$–Al$_2$O$_3$ sample with high CeO$_2$ loading, where CeO$_2$ is in a bulk form (Ce)$_3$, and is reducible at high temperature, the temperature of reduction of ceria is similar to that of stability test. It means, that the equilibrium of reaction 2Ce(IV)$_3$ + O$_2$ $\rightleftharpoons$ 2Ce(III)$_3$ + V$_{5s}$ + O$_2^2$ in these conditions can favor the oxygen transfer from ceria to Pt surface and the lattice oxygen is replaced by oxygen from the CO$_2$ dissociation and by diffusion mechanism [49]. Although the superficial structure of Pt does not play determinant role for the high stability of the catalyst, the different superficial structures of Pt can show different rates of methane activation and the C$^+$ species should be removed in part via the mechanism of oxygen transfer from the ceria support. Furthermore, the oxygen exchange capacity of cerium oxide is associated with the ability of cerium to act as an oxygen buffer by storing/releasing O$_2$ due to the Ce$^{4+}$/Ce$^{3+}$ redox couple [31] and [50]. Then, the high amount of cerium aluminate and CeO$_2$–Al$_2$O$_3$ species on the surface of low ceria loaded catalysts can also contribute to the deactivation process since the Ce$^{3+}$ ions remain in the same oxidation state and do not take place in the redox couple at high temperature. It is necessary to maintain the equilibrium between the rates of methane activation and of oxygen transfer at high temperature in reducing atmosphere. This leads to obtain resistant catalysts to carbon deposition that is observed for Pt/CeO$_2$–Al$_2$O$_3$ catalysts with high CeO$_2$ loading.

5. Conclusions

The increase in the treatment temperature of the support from 773 to 1173 K leads to the change in the textural properties; decrease in the S$_{BET}$ and V$_p$ corresponding to formation of micropores. The dispersion of Pt increases with increasing of the pretreatment temperature of the support from 773 to 1173 K. The catalytic activity and stability of Pt/CeO$_2$–Al$_2$O$_3$ catalysts depend strongly on the CeO$_2$ content. The catalysts with high CeO$_2$ loading (≥12 wt.%) show higher catalytic activity and stability in the reaction of partial oxidation of methane. Therefore the support identity is crucial to obtain catalysts resistant to carbon deposition.

The high catalytic activity and stability of the catalysts is attributed to the combination of different properties: (i) the presence of CeO$_2$ fluorite structure, which show higher OSC and reducibility (ii) the high Pt dispersion, which increases the Pt–CeO$_2$ interface area.

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