

Partial oxidation of methane using Pt/CeZrO₂/Al₂O₃ catalyst—Effect of the thermal treatment of the support

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Abstract

In this work, the effect of the thermal treatment temperature of the support on the behavior of Pt/CeZrO₂/Al₂O₃ catalysts on the methane partial oxidation was evaluated. BET surface area, metal dispersion and oxygen storage capacities and hydrogen consumption during TPR decreased with the increase of the thermal aging temperature. During the reaction of partial oxidation of methane, Pt/CeZrO₂/Al₂O₃ aged at 1073 and 1173 K presented the best performance. This result was attributed to the higher reducibility of the support and to the larger metal dispersion presented by these materials. These properties favor the carbon removal mechanism from the metal surface, avoiding deactivation.

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1. Introduction

Natural gas presents a great potential to supply the energy needs for the XXI century. One of the most promising approaches to convert this raw material into more desirable products involves the so-called gas-to-liquid (GTL) technology. In this process, methane, which is the main component of natural gas, is transformed into syngas (a mixture of CO and H₂). Then, syngas is used to produce higher molecular weight hydrocarbons through the Fischer Tropsch synthesis. Nowadays, the reduction of the costs of the syngas generation process seems to be one of the biggest problems yet to be solved [1,2].

Today, syngas is largely produced by steam methane reforming (SMR). However, its high energy demand has served as a motivation to the development of other technologies. As the energy needs of POM reaction are much smaller than the ones required for steam reforming, a lot of attention has been given

to this process. In addition, POM reaction coupled to a ceramic membrane into a single reactor may reduce significantly the capital cost of the synthesis gas production [3].

Since methane is a very stable molecule, its transformation to syngas has to be done at very high temperatures (usually above 1100 K) in order to achieve a good yield. The main reaction products usually are CO, H₂, CO₂ and H₂O, although some undesirable reactions can also occur, producing carbon deposits. For instance, the decomposition of CH₄ on the surface and the reaction of CO disproportionation leading to C and CO₂ may happen, causing the catalyst deactivation.

In the search of a catalyst that could be both active, selective to syngas formation and stable under such severe reaction conditions, researchers from around the globe are reporting studies using metals such as Ni, Rh, Pt and Ru [4–9]. Several authors [6,8,10–14] reported that the support has an important role on the stability of catalysts on partial oxidation of methane. In particular, the addition of CeO₂ to supported Pt catalysts improved their performance on partial oxidation of methane. Ceria is a very interesting catalytic material because of its redox properties (switching rapidly between +3 and +4 oxidation states) and the large O²⁻ mobility in the ceria lattice. Due to the

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automotive industry researchers, during the last decade of the last century, it was discovered that the addition of zirconia to the ceria lattice can improve its thermal stability and increase the O^{2-} mobility.

The suggestion that ceria could be a good material for methane partial oxidation was first reported in 1997 [15]. Recently, our group has been researching Pt catalysts supported over ceria and ceria–zirconia-based materials [11–14] and we could verify that the catalysts supported on ceria–zirconia mixed oxides present very high activity and stability for the POM reaction.

This improved performance depends not only on the amount of oxygen vacancies of the ceria–zirconia support but also on the metal particle size. The higher reducibility and oxygen storage/release capacity of Pt/Ce_xZr_{1-x}O₂ catalysts promotes the mechanism of continuous removal of carbonaceous deposits from the active sites, which takes place at the metal–support interfacial perimeter. On the other hand, the increase of metal particle size decreases the metal–support interfacial area, reducing the effectiveness of the cleaning mechanism of metal particle.

Although ceria–zirconia supports exhibit high reducibility, their surface areas are very low, which provide poor metal dispersion. In order to improve metal dispersion, the deposition of ceria–zirconia over an oxide with high surface area has been proposed [16,17].

We have previously reported [13,14] that the use of alumina in the composition of Pt/Ce_xZr_{1-x}O₂ catalysts increased platinum dispersion. Among all the catalysts studied, Pt/Ce_{0.50}Zr_{0.50}O₂/Al₂O₃ catalyst presented the higher activity and stability on partial oxidation of methane.

However, it is well known that the exposure of any catalytic material to high temperatures such as the ones used for POM reaction cause severe deactivation, due to sintering. Therefore, the objective of the present study was to elucidate the effects of the thermal treatment temperature of the supports on the Pt/Ce_{0.50}Zr_{0.50}O₂/Al₂O₃ catalysts properties such as oxygen storage capacity, metallic phase dispersion, surface area and mainly in the activity, selectivity and stability of the catalysts for POM reaction.

2. Experimental

2.1. Catalyst preparation

CeZrO₂/Al₂O₃ supports were prepared following the sequence: first, the Al₂O₃ was precalcined at 1073, 1173 and 1273 K, under oxygen flow for 6 h. After that, CeZrO₂/Al₂O₃ supports were obtained by incipient wetness impregnation method with an aqueous solution of cerium (IV) ammonium nitrate (Aldrich) and zirconium nitrate (MEL Chemicals) so as to obtain a 14 wt.% of Ce_{0.50}Zr_{0.50}O₂. Finally, the supports were aged in a muffle furnace for 4 h at 1073, 1173 and 1273 K.

Platinum was added to the supports by incipient wetness impregnation method, using an aqueous solution of H₂PtCl₆ (Aldrich). After the impregnation with 1.5 wt.% of platinum,

the samples were dried at 373 K, and calcined under air (50 ml/min) at 673 K for 2 h.

2.2. BET surface area

The texture of all samples was characterized by nitrogen adsorption, using a Quantasorb Jr. (Quantachrome) equipment endowed with a thermal conductivity detector. The catalyst was dried under N₂ flow at 423 K for 16 h. The adsorption isotherms by nitrogen adsorption were determined at 77 K.

2.3. X-ray diffraction

The catalysts were analyzed by powder X-ray diffraction (Philips PW3710), using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). XRD patterns were collected in the range of 2θ from 20° to 80°, at 0.04°/step with integration times of 1 s/step and 2θ from 27° to 32°, at 0.02°/step with integration times of 10 s/step. Crystallite sizes were estimated using the Scherrer equation.

2.4. CO₂ infrared spectroscopy

Infrared spectra of adsorbed CO₂ experiments were conducted using a Magna 560—Nicolet equipment. The wafers containing around 20 mg of support were first preheated under high vacuum at 773 K for 1 h. After this, and still maintaining the sample at 773 K, the sample was oxidized under air flow (30 ml/min) and then submitted to vacuum during 30 min. Then, the sample was cooled to room temperature and a first spectrum was obtained (reference). Following this pretreatment, 10 Torr of CO₂ was allowed into the chamber for 1 h. The sample was then submitted to high vacuum at room temperature for 1 h and a CO₂ adsorbed spectrum was recorded.

2.5. Oxygen storage capacity

Oxygen storage capacity measurements were carried out in a multipurpose unit connected to a quadrupole mass spectrometer (Balzers Omnistar). The samples were reduced under H₂ at 773 K for 1 h and heated to 1073 K in flowing He. Then, the samples were cooled to 723 K and a 5% O₂/He mixture was passed through the catalyst until the oxygen uptake was finished. The reactor was purged with He and the dead volume was obtained by switching the gas to the 5% O₂/He mixture. Finally, the amount of oxygen consumed on the catalysts was calculated taking into account a previous calibration of the mass spectrometer.

2.6. Temperature programmed reduction

TPR measures were carried out in the same apparatus previously described for OSC experiments. The samples (300 mg) were dehydrated at 423 K for 30 min in a He flow prior to reduction. After cooling to room temperature under He, a mixture of 2% H₂ in Ar flowed through the sample at 30 ml/min, raising the temperature at a heating rate of 10 K/min up to

1273 K. The hydrogen consumption was monitored by a quadrupole mass spectrometer.

2.7. Cyclohexane dehydrogenation

Platinum dispersion was determined through cyclohexane dehydrogenation reaction, since more traditional techniques such as H₂ or CO chemisorption are not recommended for these catalysts due to the possibility of adsorption of both gases on ceria [18,19]. Recently, we successfully used the cyclohexane dehydrogenation as a structure insensitive reaction to obtain Pt dispersions of Pt/CeZrO₂/Al₂O₃ catalysts. Initially, the dispersions of different Pt/Al₂O₃ samples were determined by H₂ chemisorption and the rate of cyclohexane dehydrogenation was also measured for each one. Such correlation was used to estimate the catalyst dispersion values in this work.

The reaction was performed at 10⁵ Pa in a flow micro-reactor. The sample (10 mg) was previously dried in situ under N₂ flow (30 ml/min) at 393 K during 30 min. Then, the sample was cooled to room temperature and heated in pure hydrogen flow to 733 K at a heating rate of 10 K/min. This temperature was held for 1 h. The sample was then cooled in hydrogen flow to 543 K. The reaction mixture was obtained by bubbling hydrogen through a saturator containing cyclohexane (99.9%) at 285 K (H₂/C₆H₁₂ = 13.2). The space velocity was (WHSV) 170 h⁻¹ and the reaction temperatures varied from 520 to 570 K. At these conditions, no mass transfer or equilibrium limitations were observed. The conversions were kept below 10%. The composition of effluent gas phase was measured by online gas chromatograph (Shimadzu GC 17-A) equipped with a thermal conductivity detector and a Chrompack CP-WAX 57 CB column.

2.8. Partial oxidation of methane

Partial oxidation of methane was performed in a quartz reactor at atmospheric pressure. In order to avoid temperature gradients, catalyst samples (20 mg) were diluted with inert SiC (36 mg). The transfer lines were kept at 423 K to avoid condensation. Prior to the reaction, the catalyst was reduced under H₂ at 773 K for 1 h and then heated to 1073 K under N₂. The reaction was carried out at 1073 K and a WHSV = 260 h⁻¹. The WHSV is defined by total flow rate (g/h)/weight of catalyst (g) ratio. A reactant mixture with CH₄:O₂ ratio of 2:1 and a flow rate of 100 ml/min was used. We did not use any inert gases since we wanted to evaluate the performance of the catalysts in a condition that facilitated the deactivation. The exit gases were analyzed using a gas chromatograph (Agilent 6890) equipped with a thermal conductivity detector and a Carboxen 1010 column (Supelco).

3. Results and discussion

3.1. Characterization

Table 1 presents BET surface area results of alumina and Pt/CeZrO₂/Al₂O₃ catalysts calcined at 1073, 1173 and 1273 K. As

Table 1

BET surface area and CeO₂ average particle sizes (*D*_{DRX}) values obtained for Pt/CeZrO₂/Al₂O₃ catalysts aged at 1073, 1173 and 1273 K

<i>T</i> _{aging} (K)	<i>S</i> _{BET} (m ² g ⁻¹) (Al ₂ O ₃)	<i>S</i> _{BET} (m ² g ⁻¹) (Pt/CeZrO ₂ /Al ₂ O ₃)	<i>D</i> _{DRX} (nm)
1073	96	85	8
1173	67	70	9
1273	38	37	12

expected, an increase of aging temperature caused a decrease of BET surface area and this effect was more significant after the exposure to 1273 K. These results are in agreement with literature data, that show the occurrence of sintering processes of CeO₂- and CeZrO₂-based catalysts, when they were submitted to high temperatures [20,21].

Fig. 1 presents XRD patterns of alumina calcined at 1073, 1173 and 1273 K. The results showed that the increase of calcination temperature produced changes in the phases of alumina. The sample aged at 1073 K showed just the presence of γ-Al₂O₃. However, after the exposure to 1173 K, different phases of alumina were detected (θ-, δ- and γ-Al₂O₃). When the temperature was increased to 1273 K, a mixture composed of α-Al₂O₃, θ-Al₂O₃ and small quantities of δ-Al₂O₃ was observed. These phase changes are well known in the literature [22,23].

XRD patterns of Pt/CeZrO₂/Al₂O₃ catalysts are presented in Fig. 2. Besides the lines characteristic of the respective alumina phases, all catalysts exhibit peaks with positions close to ceria cubic phase. It is important to stress that no diffraction peaks related to zirconia phases were detected. Furthermore, a shift of all the peaks related to the ceria phase to higher 2θ positions is observed. This displacement is an indication that probably ceria and zirconia form a solid solution on the Al₂O₃ surface [13,14].

In order to verify better the shape and positions of the peaks, data collection with a slow scanning speed was done for all the samples between 2θ positions of 27° and 32° and the results are shown in Fig. 3. The peak characteristic of ceria cubic phase (JCPDS-4-0593) shifted from the usual position of 28.6° to

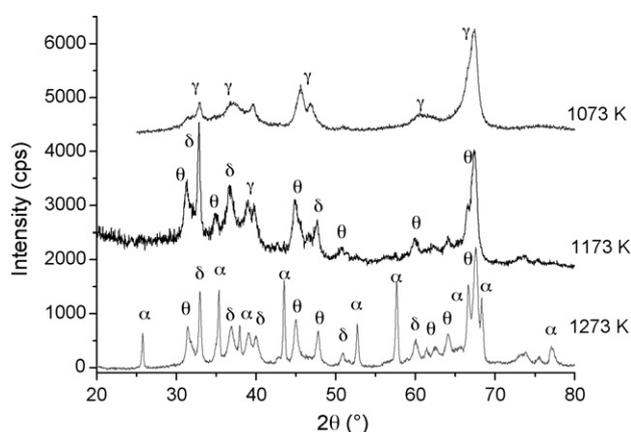


Fig. 1. X-ray diffraction patterns showing the phases present in the alumina aged at 1073, 1173 and 1273 K.

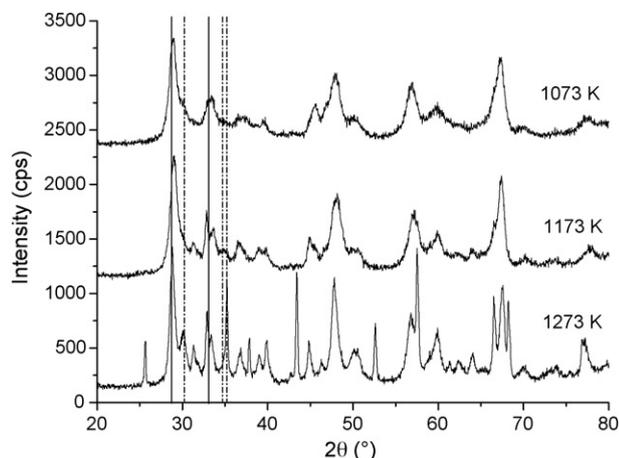


Fig. 2. X-ray diffraction patterns of Pt/CeZrO₂/Al₂O₃ catalysts aged at 1073, 1173 and 1273 K. The solid vertical lines marks the characteristic positions of the main cubic ceria peaks and the broken vertical lines of the tetragonal zirconia ones. Data collected at 0.04°/step between 2θ = 20° and 80°.

2θ = 28.8° (aging at 1073 K) and 28.97° (aging at 1173 K). According to the literature [16,20], this shift is an indication that Zr was introduced into the cerium lattice. The compositions of these solid solutions were calculated using the procedure described by Kozlov et al. [16]. The authors proposed an estimate of the solid solution real composition from the corresponding position of the Ce(1 1 1) diffraction and JCPDS data. According to the results, around 25% and 46% of zirconium were incorporated into the cerium oxide lattice for the samples treated at 1073 and 1173 K, respectively. Silva et al. [13,14] and Koslov et al. [16] also observed that zirconium was not fully incorporated to ceria lattice of ceria–zirconia samples. These results indicate the formation of a solid solution between the ceria and zirconia with the following compositions: Ce_{0.875}Zr_{0.125}O₂ (2θ = 28.8°) and Ce_{0.77}Zr_{0.23}O₂ (2θ = 28.97°). In addition, these results reveal a large deviation from the nominal composition on both samples (Ce_{0.50}Zr_{0.50}O₂).

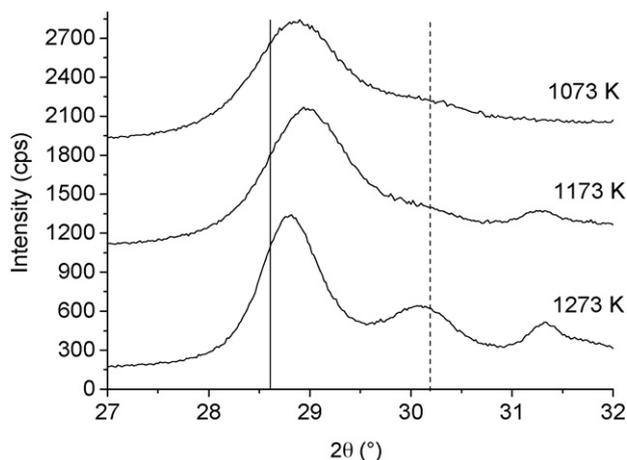


Fig. 3. X-ray diffraction patterns of Pt/CeZrO₂/Al₂O₃ catalysts thermally aged at 1073, 1173 and 1273 K. The solid vertical line marks the characteristic position of cubic ceria peak and the broken vertical line of tetragonal zirconia one. Data collected at 0.02°/step between 2θ = 27° and 32°.

Fig. 3 also shows the existence of a small shoulder around 2θ = 30°, for the samples aged at 1073 and 1173 K. For the catalyst aged at 1273 K, the presence of a peak at 2θ = 30° is more evident. These results indicate the presence of a zirconia-rich phase, besides the ceria-rich one. The catalyst treated at 1273 K presented two peaks with maxima at 2θ = 28.8° and 30°. This behavior indicates the formation of a solid solution between the ceria and zirconia with heterogeneous composition: Ce_{0.875}Zr_{0.125}O₂ (2θ = 28.8°) and Ce_{0.125}Zr_{0.725}O₂ (2θ = 30°). Similar results were obtained by Yao et al. [21]. They observed the formation of solid solutions with heterogeneous composition for samples aged at 1273 K with zirconia loadings larger than 10%. According to XRD data, they did not obtain ceria–zirconia phases with the nominal zirconia loadings. This implied the existence of a finely dispersed zirconia phase on the surface of the alumina. After steam aging, there was the appearance of a zirconia-rich phase probably due to the sintering of the highly dispersed zirconia that was on the surface.

Table 1 also presents average particle sizes for ceria calculated through the Scherrer equation using Ce(1 1 1) reflection. As the aging temperature of the supports was raised, an increase of ceria particle size was observed. Iglesias-Juez et al. [17] studied the effects of thermal aging on Pd/CeZrO₂/Al₂O₃ catalysts. These researchers also observed an increase on ceria–zirconia particle sizes after exposure to 1273 K. The authors suggested that the integrity of the ceria–zirconia material is maintained during the thermal treatment at 1273 K for 12 h, although a certain degree of heterogeneity was observed.

Table 2 presents the values of the optical density of the band at 1235 cm⁻¹ per gram of alumina calculated through adsorbed CO₂ infrared data. Frety et al. [24], while studying ceria-based samples supported on alumina with different loadings, observed that the optical density of this band may be used as a quantitative measurement of the surface of the alumina that is not covered by ceria. Silva et al. [13,14] also used successfully this procedure for ceria–zirconia samples supported on alumina. In this present study, the alumina was calcined at three different temperatures and therefore the optical density of each of them had to be measured. Unfortunately, it was not possible to measure the adsorption of CO₂ for the sample treated at 1273 K. At this high calcination temperature, the presence of α-Al₂O₃ was detected in our DRX experiments (Fig. 1), and then most of hydroxyl groups were probably removed. According to Frety et al. [24], the band at 1235 cm⁻¹ is related to the interaction of CO₂ with

Table 2
Optical density of band 1235 cm⁻¹ obtained from CO₂ adsorbed infrared

Sample	Optical density/g _{alumina}	Degree of coverage (%)
Al ₂ O ₃ T _{aging} 1073 K	31.20	–
CeZrO ₂ /Al ₂ O ₃ T _{aging} 1073 K	6.01	80.7
Al ₂ O ₃ T _{aging} 1173 K	23.53	–
CeZrO ₂ /Al ₂ O ₃ T _{aging} 1173 K	7.96	66.2

the hydroxyl groups of the alumina. Consequently, for the sample calcined at 1273 K, the absence of, at least part of the hydroxyl groups makes this measurement inaccurate. Therefore, only the data for the alumina and CeZrO₂/Al₂O₃ supports treated at 1073 and 1173 K are reported. It may be observed that the optical density decreases for both samples as ceria–zirconia oxide was added to the alumina surface. This result is consistent with the ones obtained by Frety et al. [24] and Silva et al. [14]. In fact, Silva et al. [14] obtained a degree of coverage of the alumina around 62% for a Ce_{0.5}Zr_{0.5}O₂/Al₂O₃ when the alumina was calcined at 1173 K. Comparing the degree of coverage obtained in this study, a decrease can be observed on the alumina coverage by the ceria-based oxide when the aging temperature is increased. This is consistent with XRD data that indicated a larger ceria average particle size for this sample.

Fig. 4 presents temperature programmed reduction profiles of Pt/CeZrO₂/Al₂O₃ samples. Reduction peaks were observed around 440–480 K and a small hydrogen consumption at higher temperatures (>1200 K) for all the samples. Besides, the sample submitted to 1173 K also presented small hydrogen consumption at 636 K. The reduction peaks at lower temperatures (<873 K) may be attributed to platinum reduction and the CeZrO₂ mixed oxide reduction promoted by the metal [13,25]. The hydrogen consumption verified at higher temperatures (>873 K) is usually related to the CeZrO₂ bulk reduction [13]. H₂ consumptions during TPR analysis are also presented in Table 3. The increase of aging temperature of the support caused a decrease in H₂ consumption, indicating probably the occurrence of a sintering process when the supports were submitted to higher temperatures. The same tendency was observed during oxygen storage capacity measurements and the results are shown also in Table 3. The decrease on the samples reducibility when the temperature of thermal aging was increased can be attributed to the sintering of ceria–zirconia particles which makes harder to remove bulk oxygen from the inside of the ceria particles. In addition, the larger ceria–zirconia average particle sizes decreased the contact between Pt and CeZrO₂, causing lower reducibilities. These results are in agreement with those presented by Cuif

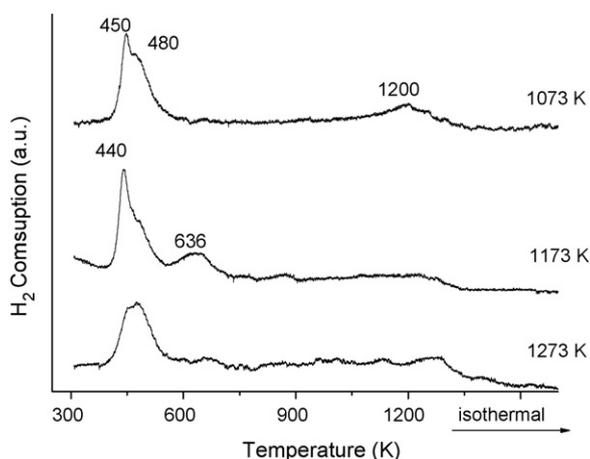


Fig. 4. Temperature programmed reduction profiles of Pt/CeZrO₂/Al₂O₃ catalysts treated at 1073, 1173 and 1273 K.

Table 3

Oxygen storage capacity (OSC), hydrogen consumption during temperature programmed reduction (TPR) and metallic dispersions calculated from the cyclohexane dehydrogenation of Pt/CeZrO₂/Al₂O₃ catalysts aged at 1073, 1173 and 1273 K

T_{aging} (K)	OSC ($\mu\text{mol O}_2/\text{gcat}$)	TPR ($\mu\text{mol H}_2/\text{gcat}$)	Pt dispersion (%)
1073	558	700	47
1173	344	564	41
1273	279	421	39

et al. [26] and Hori et al. [27] while studying the effects of sintering on the reducibility and on the oxygen storage capacities of Pt/CeZrO₂ samples. It is usually proposed that when ceria particles are very large, the oxygen release process becomes limited by oxygen diffusion from the bulk to the surface of these particles.

Pt dispersion values, obtained through the dehydrogenation of cyclohexane as a structure insensitive reaction, are also presented in Table 3. The metallic dispersion dropped from 47% for the sample treated at 1073 K to 39% for the one submitted to 1273 K. These values are in the same range than the ones obtained in previous studies [13,14]. The higher dispersion obtained for the sample treated at lower temperature is consistent with the higher value of BET surface area observed for this catalyst. When the aging temperature of the support was increased, there was a small decrease of the metallic dispersion.

3.2. Methane partial oxidation

Fig. 5 shows methane conversion values as a function of time on stream (TOS) for Pt/CeZrO₂/Al₂O₃ catalysts treated at three different temperatures. The catalysts thermally aged at 1073, 1173 and 1273 K presented similar initial conversions. The behavior of the samples submitted to 1073 and 1173 K during the reaction was very similar, and, in both cases, there was a slight deactivation along the reaction time. However, for the catalyst treated at 1273 K, a strong deactivation was observed

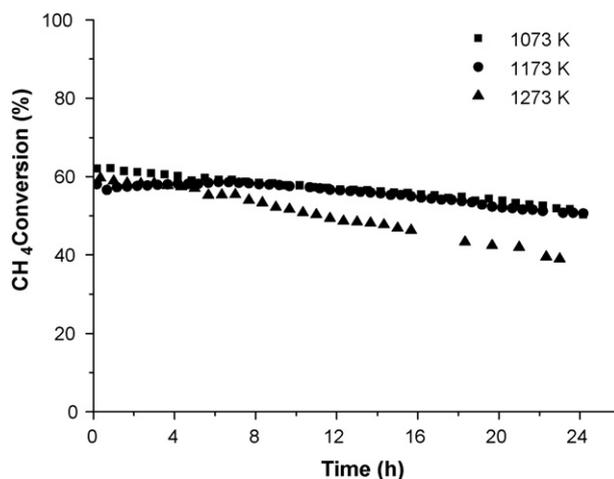


Fig. 5. CH₄ conversion during 24 h of methane partial oxidation of Pt/CeZrO₂/Al₂O₃ catalysts aged at 1073, 1173 and 1273 K ($T_{\text{reaction}} = 1073$ K, WHSV = 260 h⁻¹ and CH₄/O₂ = 2).

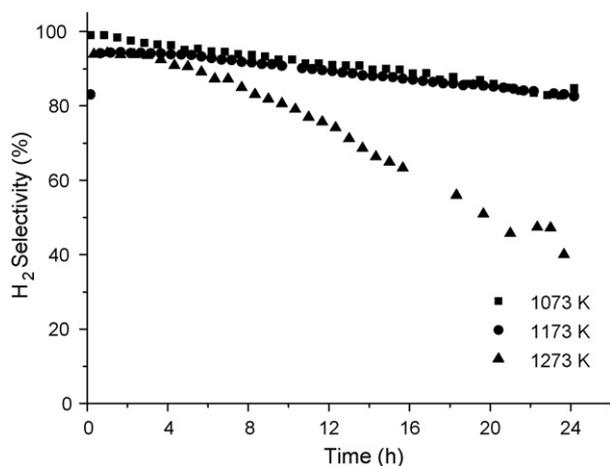


Fig. 6. H₂ selectivity during 24 h of methane partial oxidation of Pt/CeZrO₂/Al₂O₃ catalysts aged at 1073, 1173 and 1273 K ($T_{\text{reaction}} = 1073$ K, WHSV = 260 h⁻¹ and CH₄/O₂ = 2).

after 24 h of reaction. Although there was some deactivation for the three samples, all the oxygen was consumed. However, the carbon balance indicated carbon deposition during the catalytic tests. In average, the carbon balances closed within 10%.

Fig. 6 presents the selectivity to H₂ as a function of TOS for Pt/CeZrO₂/Al₂O₃ catalysts on the methane partial oxidation. The results showed that the H₂ selectivities follow the same tendency observed for methane conversion. For catalysts aged at 1073 and 1173 K, the H₂ selectivity decreased smoothly during the reaction, while, the catalyst treated at 1273 K presented a strong decrease in the H₂ formation.

CO and CO₂ selectivities for Pt/CeZrO₂/Al₂O₃ catalysts are shown in Fig. 7. For all the samples, CO selectivity decreased and CO₂ production increased during the reaction. However, this effect was more accentuated on the sample submitted to higher temperature.

The results obtained in this work may be explained by the mechanism of the methane partial oxidation reaction, as suggested by Mattos et al. [11]. In the first step of the reaction process, methane is completely burned to H₂O and CO₂ (Eq. (1)). In the second stage, there is the synthesis gas (mixture of H₂ and CO) formation through the CO₂ and steam reform

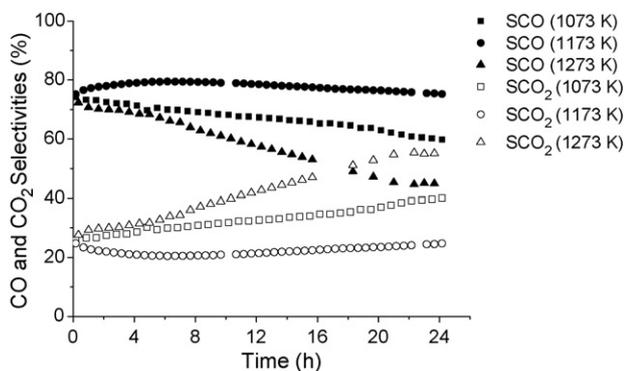


Fig. 7. CO (SCO) and CO₂ (SCO₂) selectivities during 24 h of methane partial oxidation of Pt/CeZrO₂/Al₂O₃ catalysts aged at 1073, 1173 and 1273 K ($T_{\text{reaction}} = 1073$ K, WHSV = 260 h⁻¹ and CH₄/O₂ = 2).

reactions of methane unreacted in the first stage of the process (Eqs. (2) and (3)).

First step:



Second step:



The increase of CO₂ production during the reaction indicates that the CO₂ reforming of methane (second step) is being inhibited. In this work, the inhibition of this stage was more significant for the catalyst calcined at 1273 K, since the increase in the CO₂ formation was more accentuated for this sample.

Stagg-Williams et al. [28] proposed a two step mechanism for methane reforming with CO₂, in which the support participates in the CO₂ dissociative adsorption close to the metallic particle. According to them, the first reaction path comprehends the decomposition of CH₄ on the metal particle, resulting in the formation of carbon and hydrogen. Carbon formed can partially reduce the support near the metal particles. The second path is the dissociation of CO₂ on the support followed by the formation of CO and O, which can reoxidize the support. The support supplies oxygen for the metallic surface, promoting the removal of the carbon deposited in the metal. When the support does not present that capacity to supply oxygen, there is excessive coke formation, inhibiting the CO₂ dissociation and, consequently, the second stage of the mechanism of methane partial oxidation.

In spite of the sample treated at 1073 K presenting an oxygen storage capacity larger than that submitted to 1173 K, the performance of these materials for the methane partial oxidation was similar. The oxygen consumption obtained in the OSC analyses is related to the vacancies depletion in the surface and inside the support. However, the oxygen that participates in the carbon removal mechanism is that placed in the metallic particle proximities. Therefore, for this mechanism to be efficient it is necessary a certain OSC value that corresponds to the amount related to the vacancies next to the metallic particles. Very high OSC values do not necessarily lead to better catalytic performance.

Comparing the results obtained for the Pt/CeZrO₂/Al₂O₃ catalysts aged at 1173 and 1273 K, it was observed that, although both materials present similar values of OSC and metallic dispersions, the catalyst submitted to 1273 K was much less stable. Silva et al. [13] studied the behavior of Pt/CeZrO₂/Al₂O₃ catalysts prepared by different methods in the methane partial oxidation reaction. They showed that the catalysts with larger degree of coverage of the alumina by the CeZrO₂ oxide presented larger stability in the reaction. This result was attributed to the best interaction of the metal with the mixed oxide, promoting the carbon removal mechanism of the metallic surface. Therefore, in this work, one may suggest that the smallest stability of the catalyst submitted to 1273 K could be related to a low degree of

coverage of the alumina by the mixed oxide. Although it was impossible to measure the degree of coverage of the alumina for this sample by FTIR, the XRD analysis show that the increase of the aging temperature caused sintering of the CeZrO₂ particles. Also, it could be observed that an increase on the treatment temperature from 1073 to 1173 K caused a decrease on the degree of coverage of the alumina. When the support was submitted to 1273 K, there was an increase on the average particle size of the ceria-based oxide and with this, probably, a decrease on the contact between platinum particles and this mixed oxide on the surface of alumina. Recently, it was shown that a Pt/Al₂O₃ catalyst suffers a strong deactivation in the methane partial oxidation, due to the absence of the metallic particle cleaning mechanism [11]. In order to make sure that coke deposition also played an important role on the deactivation of Pt/CeZrO₂/Al₂O₃ samples, we performed a temperature programmed oxidation (TPO) with a sample used during 24 h of reaction. For this experiment the used sample was heated in a 5% O₂/He flow with a heating rate of 10 K/min from room temperature to 1273 K. The effluent was analyzed using a mass spectrometer. There was the release of 48 mg of CO₂/gcat during the TPO analysis, indicating the accumulation of carbon on the catalyst surface during the partial oxidation of methane reaction. Therefore, we can conclude that the coke removal mechanism of the metallic particles in the Pt/CeZrO₂/Al₂O₃ catalyst treated at 1273 K is not favored, causing the catalyst deactivation.

4. Conclusions

XRD results showed the formation a solid solution between ceria and zirconia for all the catalysts. However, from the peak position there is an indication that for all the samples submitted to different pretreatment temperatures not all the zirconia was incorporated into the lattice of ceria. In addition, for the catalyst aged at 1273 K, the formation of heterogeneous solid solutions was observed. Regarding the average ceria particle sizes; the increase of aging temperature from 1073 to 1173 K caused a small increase on the value. However, when the sample was treated at 1273 K, there was a strong increase on ceria's average particle size, probably due to sintering.

The increase of aging temperature of the supports caused a decrease of BET surface area, degree of coverage of the surface of the alumina by the ceria-based oxide, metallic dispersion, oxygen storage capacities and hydrogen consumption during TPR.

In the methane partial oxidation reaction, the Pt/CeZrO₂/Al₂O₃ catalysts aged at 1073 and 1173 K presented larger stability and selectivity for H₂ and CO formation. This behavior can be attributed to appropriate balance between the support reducibility and the metallic dispersion presented by these materials. The high reducibility of the Pt/CeZrO₂/Al₂O₃ catalysts aged at 1073 and 1173 K favors a high oxygen concentration on catalytic surface, while the good metallic dispersion promotes the interaction metal/support.

These factors favor the occurrence of the carbon removal mechanism from the metallic surface, avoiding the deactivation. The thermal aging at 1273 K reduced catalyst stability probably due to the low degree of coverage of the alumina that causes a decrease of the contact between Pt and CeZrO₂ mixed oxide particles. Then, the redox mechanism responsible for the cleaning of the metallic surface was not very effective.

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References

- [1] I. Dybkjaer, *Fuel Process. Technol.* 42 (1995) 85.
- [2] P.K. Bakkerud, *Catal. Today* 106 (2005) 30.
- [3] C.M. Chen, D.L. Bennett, M.F. Carolan, E.P. Foster, W.L. Schinski, D.M. Taylor, *Stud. Surf. Sci. Catal.* 147 (2004) 55.
- [4] M.A. Pena, J.P. Gomez, J.L.G. Fierro, *Appl. Catal. A* 144 (1996) 7.
- [5] E. Ruckenstein, H.Y. Wang, *Appl. Catal. A* 198 (2000) 33.
- [6] E. Ruckenstein, H.Y. Wang, *J. Catal.* 187 (1999) 151.
- [7] Q.G. Yan, T.H. Wu, W.Z. Weng, H. Toghiani, R.K. Toghiani, H.L. Wan, C.U. Pittman Jr., *J. Catal.* 226 (2004) 247.
- [8] L. Pino, A. Vita, M. Cordaro, V. Recupero, M.S. Hegde, *Appl. Catal. A* 243 (2003) 135.
- [9] T.G. Kuznetsova, V.A. Sadykov, S.A. Veniaminov, G.M. Alikina, E.M. Moroz, V.A. Rogov, O.N. Martyanov, V.F. Yudanov, I.S. Abornev, S. Neophytides, *Catal. Today* 91–92 (2004) 161.
- [10] M.M.V.M. Souza, M. Schmal, *Catal. Lett.* 91 (2003) 11.
- [11] L.V. Mattos, E.R. Oliveira, P.D. Resende, F.B. Noronha, F.B. Passos, *Catal. Today* 77 (2002) 245.
- [12] L.V. Mattos, E. Rodino, E. Resasco, F.B. Passos, F.B. Noronha, *Fuel Process. Technol.* 83 (2003) 147.
- [13] P.P. Silva, F.A. Silva, H.P. Souza, A.G. Lobo, L.V. Mattos, F.B. Noronha, C.E. Hori, *Catal. Today* 101 (2005) 31.
- [14] P.P. Silva, F.A. Silva, L.S. Portela, L.V. Mattos, F.B. Noronha, C.E. Hori, *Catal. Today* 107–108 (2005) 734.
- [15] K. Otsuka, E. Sunada, T. Ushiyama, I. Yamanaka, *Stud. Surf. Sci. Catal.* 107 (1997) 531.
- [16] A.I. Kozlov, D.H. Kim, A. Yezerets, P. Andersen, H.H. Kung, M.C. Kung, *J. Catal.* 209 (2002) 417.
- [17] A. Iglesias-Juez, A. Martínez-Arias, M. Fernández-García, *J. Catal.* 221 (2004) 148.
- [18] E. Rogemond, N. Essayem, R. Fréty, V. Perrichon, M. Primet, F. Mathis, *J. Catal.* 166 (1997) 229.
- [19] P. Pantu, G. Gavalas, *Appl. Catal. A: Gen.* 223 (2002) 253.
- [20] C.E. Hori, H. Permana, K.Y.S. Ng, A. Brener, K. More, K.M. Rahmoeller, D. Belton, *Appl. Catal. B: Environ.* 16 (1998) 105.
- [21] M.H. Yao, R.J. Baird, F.W. Kunz, T.E. Hoost, *J. Catal.* 166 (1997) 67.
- [22] M.A. Fraga, E.S. Souza, F. Villain, L.G. Appel, *Appl. Catal. A: Gen.* 259 (2004) 57.
- [23] P. Burtin, J.P. Brunelle, M. Pijolat, M. Soustelle, *Appl. Catal. A: Gen.* 34 (1987) 225.
- [24] R. Frety, P.J. Lévy, V. Perrichon, V. Pitchon, M.M. Chevrier, C. Gauthier, F. Mathis, *Stud. Surf. Sci. Catal.* 96 (1995) 405.
- [25] H.C. Yao, Y.F. Yao, *J. Catal.* 86 (1984) 256.
- [26] J.P. Cuiff, G. Blanchard, O. Touret, A. Seigneurin, M. Marcz, E. Quéméré, SAE paper 970463, 1996.
- [27] C.E. Hori, K.Y.S. Ng, K.M. Rahmoeller, D. Belton, *Brazil. J. Chem. Eng.* 18 (1) (2001) 23.
- [28] S.M. Stagg-Williams, F.B. Noronha, G. Fendley, D.E. Resasco, *J. Catal.* 194 (2000) 240.