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Partial oxidation of methane in Pd-supported catalysts on $Ce_xZr_{1-x}O_2/SiO_2$: Effect of continuous reaction cycles

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Abstract

Six Pd catalysts supported on CeO_2/SiO_2, ZrO_2/SiO_2 and $CexZr_{1-x}O_2/SiO_2$ (x= 0; 0.3;0.7 and 1 in terms of molar composition) were prepared and submitted to several reaction cycles of the partial oxidation of methane up to 700 °C, under stoichiometric feeding conditions (CH_4/O_2=2). The catalysts were characterized by Temperature Programmed Reduction (TPR) before and after the reaction. TPR results indicated that Zr addition displaced the reducibility of cerium oxide at lower temperature and the formation of the β-PdH_x phase after three reaction cycles, suggesting the presence of PdO agglomerates. 1%Pd catalysts were more active, with the possible restructuring of the PdO particles caused by the repeated reduction and oxidation steps. $Pd/Ce_xZr_{1-x}O_2/SiO_2$ catalysts exhibited higher catalytic activities than $Pd/ZrO_2/SiO_2$ and $Pd/CeO_2/SiO_2$ references samples with Pd loading of 0,5%. Although the CH_4 conversion decreased during the reaction cycles between 4 and 49% depending on the support, 1%$Pd/Ce_{0,7}Zr_{0,3}O_x/SiO_2$ catalyst was the most active (~40% CH_4 conversion) and high stability at 600 °C (60% CH_4 conversion), keeping the syngas selectivity (H_2/CO=1.5).

Keywords: β-PdH_x; phase; CeZr mixed oxide; partial oxidation of methane; Pd; TPR.

Oxidación parcial de metano en catalizadores de Pd soportados sobre $Ce_xZr_{1-x}O_2/SiO_2$: Efecto de los ciclos continuos de reacción

Resumen

Se prepararon catalizadores de Pd soportados sobre $Ce_xZr_{1-x}O_2/SiO_2$ (x=0; 0,3; 0,7 y 1 en términos de relación molar), los cuales se sometieron a varios ciclos continuos de la reacción de oxidación parcial de metano hasta 700 °C en condiciones de alimentación estequiométricas (CH_4/O_2=2). Los catalizadores fueron caracterizados mediante Reducción a Temperatura Programada (RTP) antes y después de reacción. Los resultados de RTP indicaron que la adición de Zr desplazó la reducibilidad del óxido de cerio a más baja temperatura y la formación de la fase β-PdH_x después tres ciclos de reacción, sugiriendo la presencia de aglomerados de PdO. Los catalizadores con 1% de Pd fueron los más activos, ocurriendo posiblemente una reestructuración de las partículas de PdO causado por los pasos de reducción y oxidación repetidos. Los catalizadores de $Pd/Ce_xZr_{1-x}O_2/SiO_2$ exhibieron actividades catalíticas más altas que los usados como referencia ($Pd/ZrO_2/SiO_2$ y $Pd/CeO_2/SiO_2$) con carga de Pd de 0,5%. Aunque la conversión de CH_4 disminuyó durante los ciclos de reacción entre un 4 y 49% dependiendo del tipo de soporte, el catalizador 1%$Pd/Ce_{0,7}Zr_{0,3}O_2/SiO_2$ fue el más activo (~40% conversión de CH_4) y con mayor estabilidad a 600 °C (60% conversión de CH_4), manteniendo la selectividad a gas de síntesis (H_2/CO=1,5).

Palabras clave: fase β-PdH; óxido mixto CeZr; oxidación parcial de metano; Pd; RTP.

Introduction

Methane conversion reaction to valuable chemicals such as methanol, formaldehyde, ethane, ethylene and synthesis gas is of great industrial interest due to the high abundance of methane in gas fields [1,2]. Natural gas, which contains more than 90% of methane, is an increasingly available resource. Additionally, the world's natural gas reserves are constantly increasing, with more than 193 trillion cubic meters in 2018 [3,4].

During the last years, there has been an increasing interest in the partial oxidation of methane, considering it as one of the most promising processes to produce synthesis gas, with extremely high efficiency. Synthesis gas is produced industrially through processes such as steam, dry and autothermal reforming [5]. Catalytic partial oxidation of methane is a good option to produce synthesis gas at low energy cost since it allows a 10-15% reduction in energy requirement and a 25-30% less capital investment compared to typical steam reforming processes. Furthermore, the synthesis gas produced with a H_2/CO=2 ratio is suitable for the synthesis of methanol, ammonia and Fischer Tropsch [6,7].

It has been reported that to obtain high CH_4 conversions, as well as good selectivities towards H_2 and CO, catalysts containing transition metals (Ni, Co, Cu and Fe) [8], metal oxides [9] and noble metals (Pt, Pd, Rh, Ru and Ir) [10] have been used. Noble metals have been extensively studied in the catalytic partial oxidation reaction because, despite its high cost, they show higher activity than cheaper Ni-based catalysts. Pd catalysts are known to be active for the CH_4 combustion; however, the limited stability of the catalysts at elevated temperatures makes them unsuitable for the catalytic partial oxidation reaction. This barrier can be overcome by adding rare earth and/or alkaline earth oxides to the catalyst formulations [6]. CeO_2 and CeO_2-ZrO_2 are suitable redox promoters for this kind of reaction due to their redox properties and high oxygen storage capacity, which play an important role to improve the catalytic activity under reducing and oxidizing conditions. In this sense, special attention must be considered to the selection and preparation of the redox promoter to obtain the best catalyst performance [3]. Furthermore, silica has been widely used as a support for many heterogeneous catalysts due to its good thermal stability and inert character, which could prevent loss of redox promoter avoiding interactions with the support [11]. An increasing number of publications related to the alteration produced by surface reconstruction phenomena on catalyst performance have been reported [12,13]. Likewise, activation periods have been detected to cause a repeated reduction and oxidation cycles under reaction conditions [3].

Considering the previously described, in this investigation, the partial oxidation of CH_4 in Pd catalysts supported on $Ce_{0.3}Zr_{0.7}O_2/SiO_2$ and $Ce_{0.7}Zr_{0.3}O_2/SiO_2$ was studied, analyzing the effects of reaction cycles on reducibility and activity catalytic of samples. Catalystswere characterized, before and after reaction, usingthe programmed temperature reduction technique (TPR), and the surface area and chemical composition were determined for the fresh samples. The catalytic activity was evaluated by the partial oxidation of CH_4, under stoichiometric feeding conditions (CH_4/O2=2), from room temperature up to 700 °C.

Experimental

Catalysts

SiO_2 (Acros Organics, 60-200 mesh) support was firstly calcined at 700 °C for 4 h, with a heating rate of 10 °C min^{-1}. SiO_2 was impregnated (incipient wetness impregnation) with a mixture of $Ce(NO_3)_2.6H_2O$ (Acros Organics, 99.50%) and $Zr(NO_3)_3.H_2O$ (Acros Organics, 99.5%)solutions in appropriate proportions to obtain a molar ratio of Ce/Zr=3/7 andCe/Zr=7/3 and a mixed oxide composition of 16.7 wt.%. Subsequently, the impregnated silica was calcined at 700 °C for 4 h to obtain the $Ce_{0.3}Zr_{0.7}O_2/SiO_2$ ($Ce_{0.3}Zr_{0.7}$/Si) and $Ce_{0.7}Zr_{0.3}O_2/SiO_2$($Ce_{0.7}Zr_{0.3}$/Si) supports. The catalysts were prepared following the previously described method, impregnating the supports with a $Pd(NO_3)_2.2H_2O$ (AcrosOrganics, 99.9%) solution in adequateamountstoobtain 0.5wt.%and 1wt.%ofPd. After impregnation, samples were calcined at 500 °C for 2 h to obtain 0.5%Pd/$Ce_xZr_{1-x}O_2/SiO_2$ (x=0; 0.3; 0.7 and 1) and 1%Pd/$Ce_xZr_{1-x}O_2/SiO_2$ (x=0.3 and 0.7) catalysts.

Nitrogen adsorption

N_2 adsorption isotherms were determined at -196 °C using a Micromeritics ASAP 2020 equipment. The isotherm was determined by injecting N_2 gas to the sample at small pressure intervals until reachs the N_2 saturation pressure (P/Po= 1). The specific surface values were determined using the BET method.

X-ray fluoresecence (XRF)

To determine the chemical composition of samples, a Shimadzu EDX-700HS spectrometer was used, equipped with a Rh radiation source that operated at 50 kV and 30 mA.

Temperature-programmed reduction (TPR)

TPR tests were carried out on a stainless-steel line coupled to a Thermal Conductivity Detector (TCD), using 50 mg of sample. The samples (fresh and the one from the third reaction cycle) were dried in an Ar flow (30 mL min^{-1}) at 120 °C for 1 h with a heating rate of 10 °C min^{-1}, then cooled to room temperature, except for those containing Pd which were cooled down up to -10 °C, using brine. Subsequently, the flow was switched to 30 mL min^{-1} of 5% H_2/Ar and the brine was removed, starting H_2 consumption register in a first stage of free heating (-10 °C to room temperature) and then heating the sample from roomtemperature up to 850 °C using a heating program of 10 °Cmin^{-1}.

Catalytic activity

50 mg of sample were mixed with 500 mg of quartz glass to improve the heating transfer in the reactor. The catalyst was dried in Ar flow at 30 ml min^{-1} at 120 °C for 1 h (heating rate of 10 °C min^{-1}). Subsequently, the partial oxidation of CH_4 was carried out in a fixed-bed micro-reactor, using a reaction mixture consisting of CH_4 and O_2(10%)/He, in a stoichiometric ratio of $CH_4/O_2=2$, with a total feed flow of 30 ml min^{-1} (5 ml min^{-1} of CH_4 and 25 ml min^{-1} of O_2/He), and a space velocity of 669 h^{-1}. At the reactor outlet, the composition of CH_4, H_2 and CO was analyzed by a Perkin Elmer Clarus 500 gas chromatograph, using a TCD and a 5Å molecular sieve capillary column. This test was carried out in three consecutive reaction cycles, with a controlled heating (10 ° C min^{-1}) from room temperature up to 700 °C, registering the conversion at each temperature. The analysis of reactor effluent was performed 10 min after reach the selected temperature. After reaction at the maximum evaluated temperature, it was cooled down freely to room temperature, waiting 30 min before starting the new reaction cycle. The isothermal reaction was also carried out at 600 °C (heating from room temperature up to 600 °C with controlled heating of 10 °C min^{-1}), evaluating the CH_4 conversion for 180 min after reaching the reaction temperature, to study the catalytic stability of samples. Tests were carried out with a blank (reactor containing only quartz glass) and no catalytic activity or reduction signals were recorded.

Discussion and results

Nitrogen adsorption

The values of the specific surface of samples (S_{BET}) are reported in Table 1. The surface of the $Ce_xZr_{1-x}O_2/SiO_2$ samples is not greatly affected by the impregnation with Ce, Zr and/or Pd salts, reporting areas close to 360 m^2 g^{-1}. The decrease in area of samples compared to the SiO_2 support is produced by the diminishing in pore volume due to deposition of oxides in the cavities of samples during the impregnation and calcination process [14].

Table 1. Chemical composition (wt.%), specific surface area (S_{BET}) and CH_4 conversion (X_{CH4}) at 700 °C of samples.

Sample	S_{BET} (m^2 g^{-1})	Pd	CeO_2	ZrO_2	SiO_2	X_{CH4} 1st cycle(%)	X_{CH4} 3rd cycle(%)
SiO_2	420	-	-	-	-	-	-
ZrO_2/SiO_2	n.c.o	-	-	12.11	87.89	-	-
CeO_2/SiO_2	n.c.o	-	17.85	-	82.15	-	-
$Ce_{0.3}Zr_{0.7}$/Si	364	-	7.27	7.70	85.03	-	-
$Ce_{0.7}Zr_{0.3}$/Si	367	-	12.57	3.01	84.42	-	-
0.5Pd/ZrO_2/SiO_2	n.c.o	0.42	-	8.54	91.04	28	3
0.5Pd/CeO_2/SiO_2	n.c.o	0.48	17.74	-	81.78	57	7
0.5Pd/$Ce_{0.3}Zr_{0.7}$/Si	n.c.o	0.49	7.20	7.91	8440	22	12
0.5Pd/$Ce_{0.7}Zr_{0.3}$/Si	n.c.o	0.47	14.41	2.66	82.46	24	10
1Pd/$Ce_{0.3}Zr_{0.7}$/Si	365	1.02	6.38	6.57	86.03	31	27
1Pd/$Ce_{0.7}Zr_{0.3}$/Si	358	0.89	15.10	2.32	81.69	54	38

n.c.o: test not carried out

XRF

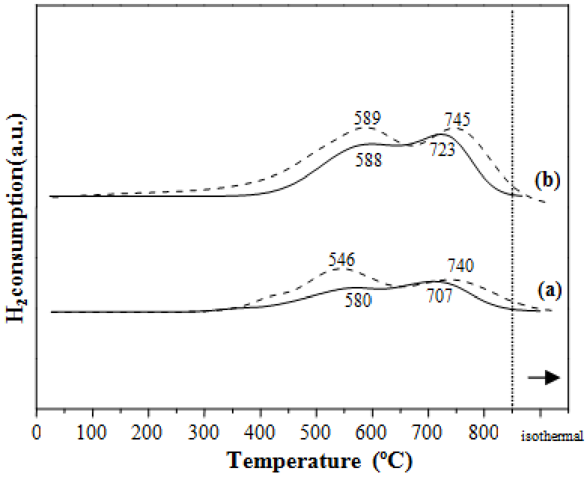
For samples containing Ce, Zr and CeZr, the compositions of the respective oxides were between 12-17 wt.% (Table 1); very close to the nominal value formulated during the preparation (16.7 wt.%). Regarding the Pd content, the reported value was very similar to the nominal load established for all catalysts.

TPR

Figure 1 shows the H_2 consumption profiles for the supports. For the $Ce_{0.3}Zr_{0.7}$/Si fresh sample (Figure 1a), the reduction starts at 400 °C, registering two intense signals, the first one with a maximum at 580 °C and the second one at 707 °C. Thus, the profile recorded for $Ce_{0.7}Zr_{0.3}$/Si sample (Figure 1b) also includes these two signals, but slightly displaced towards higher temperature (588 and 723 °C). As observed, the relative intensity of peaks strongly depends on CeO_2 content [15]. The reduction signals observed around 580 and 700 °C correspond to the reduction of surface and bulk cerium oxide, respectively [16,17]. The introduction of ZrO_2 into the CeO_2 network has been reported to affect the reduction characteristics of ceria. This occurs through modifications of ceria fluorite-like structure because of the substitution of Ce^{4+} (ionic radius 0.97 Å) by Zr^{4+} (ionic radius 0.84 Å). The effect of this substitution causes a decrease in activation energy for diffusion of oxygen ions into the cell, favoring the reduction [15]. Although supports did not register catalytic activity, the changes in reducibility of the species after the chemical reaction were evident. This aspect will be discussed later.

H_2 consumption profiles for catalysts with 0.5% and 1%Pd are shown in Figure 2. With the Pd addition to $Ce_{0.3}Zr_{0.7}$/Si and $Ce_{0.7}Zr_{0.3}$/Si supports, the reduction behavior is drastically modified. The reduction signal at room temperature could be attributed to reduction of large Pd oxide particles [18]. The negative signal around 52-84 °C could be caused by decomposition of the β-PdH_x phase [19]. The variety of reduction signals observed below 100 °C corresponds to reduction of PdO particles of different sizes [20]. Above 100 °C, it would be reducing highly dispersed crystalline PdO particles that strongly interact with the support [19], along with the simultaneous reduction of surface cerium oxide promoted by the presence of Pd, since the noble metal addition effectively promotes the reduction of CeO_2 via H_2 spillover [15]. The peaks observed at 693 and 710 °C for samples that contain Ce (0.5Pd/Ce/Si and 0.5Pd/$Ce_{0.7}Zr_{0.3}$/Si), correspondto reduction of bulk CeO_2 [15], which starts to reduce above 600 °C. On the other hand, the 0.5Pd/Zr/Si sample registered a very low hydrogen consumption, only recording the negative signal at 70 °C, which would be associated with the β-PdH_x phase decomposition. The presence of this phase was related to a low Pd dispersion [21].

After reaction, the presence of PdO available for reduction is strongly affected, registering only the decomposition of β-PdH_x phase in all the samples (Figure 2). This decrease in the PdO reducibility could be attributed to the low dispersion of PdO, CeO_2 or mixed oxide species, which could be affected by aging process [18,22], where PdO could be overlapped by CeO_2 or CeZr mixed oxide.



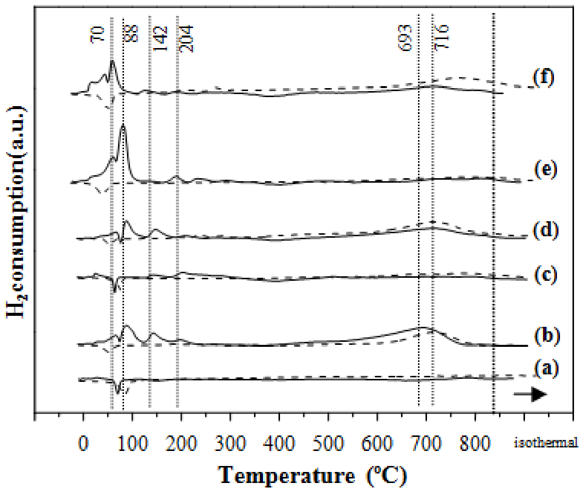


Figure 2. TPR profiles for simples (a) 0.5Pd/Zr/Si; (b) 0.5Pd/Ce/Si; (c) 0.5Pd/$Ce_{0.3}Zr_{0.7}$/Si, (d) 0.5Pd/$Ce_{0.7}Zr_{0.3}$/Si, (e) 1Pd/$Ce_{0.3}Zr_{0.7}$/Si, (f) 1Pd/$Ce_{0.7}Zr_{0.3}$/Si. (–) Fresh, (--) Spent.

It should be noted that for samples with a higher Ce content, the decomposition signal of β-PdH_x phase is displaced at a lower temperature, while for samples with a lower content, it is displaced at a higher temperature. The apparent change in the decomposition temperature was reported on Pd/SiO_2 catalysts by Bonarowska et al. [23], indicating that this occurs when Pd is sintered to very large crystals and suggest that the position, shape and intensity of a palladium hydride decomposition peak depend on the Pd dispersion, the type of support and the modifying additives used. This result suggests that changes in the interaction of Pd with the support have occurred in these catalysts because of exposing the sample to reaction cycles.

For samples containing Ce, after the reaction cycles (Figure 2), it was qualitatively registered that H_2 consumption in the 35-300 °C zone is much lower than its fresh counterpart, regardless of ceria and Pd content. This result could be expected if CeO_2 is coating these PdO particles, which would avoid its reduction [24]. The partial oxidation reaction of CH_4 under the specified conditions greatly modified the Pd phases formed, suggesting the formation of PdO agglomerates that further favor the formation of β-PdH_x phases, possibly caused by exposing the catalysts to a repeatedly changing atmosphere from reducing to oxidizing in activity tests.

Catalytic activity

The curves of methane conversion for catalysts after the first reaction cycle are shown in Figure 3. Supports did not report any catalytic activity,but noticeable changes in their reducibility were observed. In general, the reduction profiles of supports change after three reaction cycles, resulting in more intense signals than those obtained for fresh supports, increasing the intensity of the reduction signal for the first peak. A hypothesis that could explain this behavior is that after reaction, a redispersion of the mixed oxide occurs, although it is not ruled out that in the reduction profiles of spent supports there is an important contribution of carbonated species, generated during the reaction. Bychkov et al. [25], using thermogravimetric analysis combined with mass spectrometry of the effluent gas mixture and oxidation experiments at programmed temperature demonstrated the significant variation of carbon content in Pd catalysts that occurs during methane oxidation. These researchers found that hundreds of carbon layers could periodically accumulate in Pd catalyst during the reaction. Although the analyzed supports do not contain Pd, the apparent carbon deposition in these samples could be the reason of inactivity[26], which, despite not being quantified, a change in color of support from light yellow to black after the reaction was observed.

Regarding the activity of Pd samples, it started to be active near 300 °C, except for 1Pd/$Ce_{0.7}Zr_{0.3}$/Si catalyst, which was observed at 200 °C. The maximum conversions at 700 °C for 0.5Pd/Ce/Si and 1Pd/$Ce_{0.7}Zr_{0.3}$/Si catalysts were 57 and 54%, respectively (Table 1). It is noteworthy the low activity of 0.5Pd/$Ce_{0.7}Zr_{0.3}$/Si catalyst. It has been reported that the causes of deactivation may be restructuring, redispersion and/or changes in the oxidation state of the catalyst under reaction conditions [27]. From TPR analyzes, changes in the reducibility of surface species after reaction were observed, which agree with the possible causes of deactivation before mentioned. PdO to Pd reduction has an important effect on catalytic activity [28]. It has been proposed that small and well dispersed PdO particles are not active while large PdO particles are the active sites for methane oxidation [29]. For this reason, we could consider the PdO phase as active for the partial oxidation of methane and the fully oxidized Pd species as promoter of a better activity.

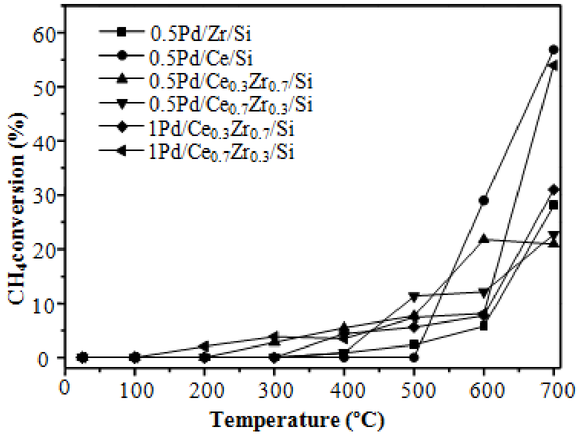


Figure 3. Conversion vs. temperature curves for partial oxidation of methane for the fresh catalysts during 1st activity cycle.

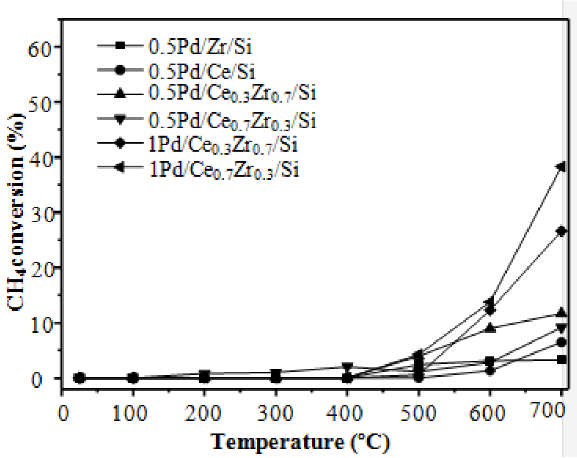


Figure 4. Conversion vs. temperature curves for partial oxidation of methane for the catalysts during the 3rd activity cycle.

Figure 4 shows the conversion vs. temperature curves for catalysts during the third activity cycle. The conversion increased between 500 and 600 °C, with a maximum methane conversion of 38% at 700 °C (Table 1). With the increase in the Pd load, the activity of catalysts on both mixed supports is favored, which has been previously reported [26]. The 0.5Pd/Ce/Si catalyst showed the lowest activity in all catalysts that contain ceria, while the 0.5Pd/Zr/Si catalyst is the least active. It is noteworthy that 0.5Pd/Ce/Sisample, despite registering the highest conversion in the first cycle (56.8%), changes its behavior after successive cycles, showing the lowest conversion (6.5%) at 700 °C for the third cycle. The decrease in activity of Pd/Ce/Si catalyst could be explained considering the effect of support; a poor textural stability against thermal treatments has been reported [30], which would affect its catalytic activity. Additionally, coke deposition may be another factor that affects the activity. In this sense, Fangli et al. [26] studying the amount and nature of carbon deposits by thermogravimetric analysis (TG-DTA) and Raman, found that carbon deposition was the main reason for the deactivation of 3%Pd/α-Al_2O_3 and 3%Pd/CeO_2-ZrO_2 catalysts after 24 h of reaction. In Pd samples that we prepared, the change of color from brown to black was observed after reaction, suggesting the presence of carbon deposits in the exhausted catalysts.

Considering the CO chemisorption results at 500 °C reported by Espina et al. [31] for fresh samples here studied, the CO/Pd ratio values were low (between 0.03 and 0.18), indicative of a low dispersion, which after three continuous cyclic treatments could have been affected and decreased further. In this way, the presence of larger PdO particles it is been promoted, suggested by the presence of the β-PdH_x phase [21]. On the other hand, in the TPR profile for Pd-supported on cerium oxide and mixed oxide samples (Figure 2), a decrease was detected in all reduction signals (except for the one reported at T>

650 °C), which could indicate that the active phase was encapsulated by the support and/or the formation of Pd-O-Ce species during the reaction [32].

Table 2 reports the H_2 and CO selectivities of the prepared catalysts. In the case of $Ce_{0.3}Zr_{0.7}$/Si, $Ce_{0.7}Zr_{0.3}$/Si, 0.5Pd/Zr/Si, 0.5Pd/$Ce_{0.3}Zr_{0.7}$/Si and 0.5Pd/$Ce_{0.7}Zr_{0.3}$/Si samples, the formation of H_2 or CO was not detected. For other catalysts, a variation in H_2 selectivity between 20 and 34% was observed.

As previously mentioned, PdO is the active phase for the partial oxidation of methane reaction, however, the absence of H_2 and CO in catalysts with 0.5% Pd (except for 0.5Pd/Ce/Si), can be due to the low Pd loading [26,29,33]. In this sense, Briot and Primet [33] observed that the presence of PdO agglomerates favors high methane conversions at 600 °C for 1.95%Pd/Al_2O_3 catalyst. The higher activity and selectivity of the PdO agglomerates are consistent with the results obtained for 1% Pd catalysts. This suggests that PdO agglomerates may be present in these samples after three reaction cycles (presence of β-PdH_x phase in TPR tests), which could lead to methane conversion and selectivity towards synthesis gas higher than catalysts with 0.5% Pd load. Likewise, the ability of catalysts to dissociate C-H bonds and adsorb oxygen species (in which the redox promoter participates) are important factors that influence the efficiency of synthesis gas production, with Pd being effective in activating C-H bonds in CH_4 [34].

Table 2. H_2 and CO selectivities (%) at 700 °C and H_2/CO molar ratio for the reaction cycles in the selected catalysts.

Sample	Reaction cycles								
	I			II			III		
	S_{CO}	S_{H2}	H_2/CO	S_{CO}	S_{H2}	H_2/CO	S_{CO}	S_{H2}	H_2/CO
0.5Pd/CeO_2/Si	22	29	1.32	53	34	0.64	3	-	0
1Pd/$Ce_{0.3}Zr_{0.7}$/Si	25	27	1.08	26	29	1.11	28	22	0.78
1Pd/$Ce_{0.7}Zr_{0.3}$/Si	21	16	0.76	13	21	1.61	17	26	1.53

Previous studies have shown that reaction conditions can influence catalytic activity and product distribution [8,9]. In general, with stoichiometric reagent mixtures (CH_4:O_2=2:1), high temperatures (up to 925 °C) are often required to achieve high conversion and selectivity to partial oxidation products, due to limited balance thermodynamic of the reforming reaction at low temperatures [35].

For the 0.5Pd/Ce/Si catalyst, the selectivity towards H_2 increased from 29% during the first cycle of activity up to 34% during the second cycle and finally not detecting H_2 formation during the third cycle of activity. This behavior can be related to low textural stability due to the continuous cyclic treatments. This poor performance for the third cycle (Figure 4) was also observed in the methane conversion value and can be explained by the reduction of cerium oxide according to reactions (1) and (2). Both reactions are endothermic and, therefore, are favored at high temperatures. In addition to reactions (1) and (2), the reverse water-gas shift reaction could also be occurring, catalyzed by cerium oxide, consuming H_2 and CO_2 and producing CO and H_2O [3]. This reason could explain why a higher CO production than H_2 was obtained.

$$2CeO_2 + CO \leftrightarrow Ce_2O_3 + CO_2 \tag{1}$$

$$2CeO_2 + H_2 \leftrightarrow Ce_2O_3 + H_2O \tag{2}$$

For 1%Pd catalysts supported on Ce_xZr_{1-x}/Si, there are changes in the H_2/CO ratio, indicating that the reaction cycles are modifying the stability of surface catalytic species. The catalytic performance of the catalyst supported on the mixed oxides is higher than the catalyst supported on Ce/Si. This behavior can be attributed to a high capacity of reduction and oxygen transfer, which could decrease carbon deposition or promote the removal of carbon from the surface of metal [26] and explain why the sample with the highest Ce/Zr ratio was the one that maintained high H_2/CO ratio.

Figure 5 shows the methane conversion vs. time under isothermal conditions (600 °C) for fresh catalysts. After 15 min of reaction, all samples kept a stable methane conversion. Only 0.5Pd/Ce/Si and 0.5Pd/$Ce_{0.7}Zr_{0.3}$/Si samples showed a slight decrease in conversion. In general, an activation period for catalysts is observed, requiring approximately the same time to reach the steady state. Furthermore, the 1Pd/$Ce_{0.7}Zr_{0.3}$/Si catalyst has the highest activity andthe best stability, which could be explained by the higher Pd content together with the ease of oxygen migration to the CeO_2-ZrO_2 lattice [26].

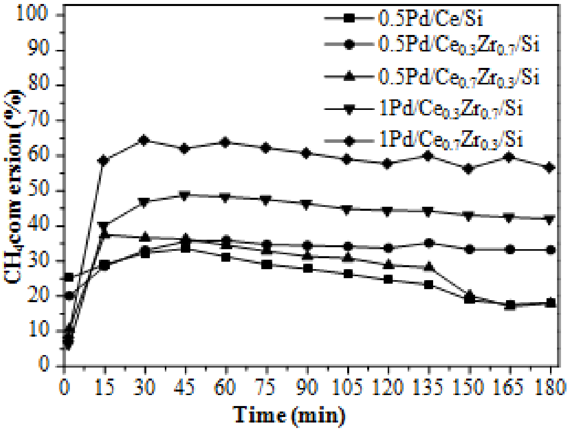


Figure 5. Conversion vs. time curves for the partial oxidation of methane for the catalysts (CH_4/O_2=2, T=600 °C).

Conclusions

Pd catalysts supported on Ce_xZr_{1-x}/Si were prepared and their reducibility and catalytic activity were evaluated for three reaction cycles. The appearance of the β-PdH_x phase observed in the TPR profiles after reaction cycles indicated the formation of PdO agglomerates considered the active phase for the methane oxidation, and that interacts with CeO_2 or Ce_xZr_{1-x} mixed oxide. The reaction cycles could promote the encapsulation of active phase of Pd by CeO_2 or mixed oxide, together with the presence of carbon deposits that caused a decrease inactivity. The catalysts with the highest Pd content reported the best catalytic behavior, being 1Pd/$Ce_{0.7}Zr_{0.3}$/Si the catalyst with the highest final conversion and stability at 600 °C, as well as the highest selectivity to synthesis gas, even for three reaction cycles. This result was due to the higher Pd content that promoted the formation of PdO agglomerates and the presence of the redox promoter with a higher Ce/Zr ratio, which facilitated the oxygen mobility in the CeO_2-ZrO_2 lattice.

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