Catalytic Combustion of Methane over PdO-CeO$_2$/Al$_2$O$_3$ and PdO-CeO$_2$/ZrO$_2$ catalysts

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1. Introduction

Hydrocarbon combustion is one of the most important processes for heat and energy generation; however, it results in polluting emissions of nitrogen oxides and carbon monoxide. Methane is one of the most commonly used fuel, and the development of more efficient and less pollutant processes of its combustion (complete combustion at lower temperatures) is a priority. In this context catalytic combustion appears to offer an alternative to flame combustion due to its ability to promote combustion at lower temperatures than conventional flame combustion, thus reducing residual emissions of NOx, CO and unburned hydrocarbons (1). Noble metal catalysts are considered extremely active for the total oxidation of hydrocarbons and palladium is described in literature as the most active for methane combustion. The active phase of noble metal catalysts is usually dispersed on supports such as SiO$_2$, Al$_2$O$_3$, ZrO$_2$, TiO$_2$ and zeolites (2-8). Alumina is the most commonly used because of its high surface area while zirconia presents high thermal stability due its oxygen rich surface (9). This later is very interesting for palladium based catalysts because it promotes PdO thermal stability, which is the active phase for methane combustion. This work describes the preparation, characterization and activity tests in methane combustion using palladium and cerium supported on alumina and zirconia catalysts.

2. Experimental

PdO/Al_2O_3, PdO/ZrO_2, PdO-CeO_2/ZrO_2, PdO-CeO_2/Al_2O_3 and PdO/Al_2O_3/ZrO_2 were prepared using wet impregnation method. CeO_2 modified supports were prepared with zirconia and alumina impregnation with a cerium nitrate solution for 24 hours. After impregation, the materials were dried at 110°C for 24 hours and calcined at 600°C for 10 hours. PdO-CeO_2/ZrO_2, PdO-CeO_2/Al_2O_3 were prepared by impregnation of the modified ceria supports with palladium acetylacetonate solution in toluene for 24 hours. After impregnation the materials were dried at 110°C for 24 hours and calcined at 600°C for 10 hours.

Alumina (Pural SB) and zirconia were used as supports. Palladium acetylacetonate (Achros Organics) and cerium nitrate (Fluka) were used in amounts to result in 1% w/w of Pd and 6% w/w of Ce in the catalysts. All the samples were calcined at 600°C for 10 hours under air flow and characterized by X-ray diffraction (XRD), O_2 temperature programmed desorption (TPD), specific surface area (BET) and X-ray fluorescence (XRF).

The X-ray diffraction measurements were carried out on a Shimadzu apparatus (XRD-6000). The Cu Kα radiation (λ = 1.5418 Å) and the following experimental conditions were used: 2θ range = 10-80°, step size = 0.02^o and time per step = 4.80 s. The powder samples were analyzed without further treatment.

The palladium content in the samples was obtained by X-ray fluorescence on a Shimadzu WDS (XRF-1800) apparatus.

The reduction-oxidation properties of the catalysts were studied by temperature programmed desorption (TPD) of oxygen in a flow system. 1000 mg of the catalyst was loaded in a quartz reactor and heated at a rate of 5°C.min^{-1} from room temperature to 1000°C, under helium flow. Oxygen in the reactor outlet was detected by using a quadrupole mass spectrometer, Balzers QMS-200. The mass-to-charge ratio (m/e) = 32 was used to monitor the oxygen concentration.

Catalytic properties were evaluated using temperature programmed surface reaction (TPSR) feeding a mixture containing 0.5% of CH_4, 2% of O_2 and 97.5% of N_2. Transient flow microreactor measurements were performed in a quartz reactor fixed with 100 mg of catalyst diluted in 100 mg of quartz granules. The samples were heated to 600°C at a rate of 10°C.min^{-1}, under a flow of 100 mL.min^{-1} of the gas mixture. The reactant gases were fed to the reactor by means of electronic mass flow meter controller MKS 247. The effluent gases were detected by using quadrupole mass spectrometer, Balzers QMS-200, connected in the reactor outlet. The following mass-to-charge ratios (m/e) were used to monitor the concentrations of the products and reactants: 15 and 16 (CH_4), 18 (H_2O), 28 (CO), 32 (O_2), 44 (CO_2).

3. Results and Discussion

XRD patterns of all catalysts (Figure 1) presented the characteristic peaks of the active phase, PdO, in $2\theta = 33.8$ and 60°. PdO/Al_2O_3 and $PdO-CeO_2/Al_2O_3$ patterns presented peaks in $2\theta = 19, 36, 39, 45, 60$ and 67° confirming the presence of the γ-alumina phase of the support.

For PdO/ZrO_2 and $PdO-CeO_2/ZrO_2$ catalysts, the characteristic peaks of the zirconia monoclinic phase in $2\theta = 17, 24, 28, 31, 34, 50$ and 55° were observed and another peak at $2\theta = 30^{\circ}$, which is characteristic of the tetragonal phase. According to literature, the calcination temperature, 600°C, used here makes the coexistence of these two zirconia phases possible (10). All phases described elsewhere were also found in the $PdO/Al_2O_3/ZrO_2$ catalyst. As well as the tetragonal form of PdO, XRD patterns of $PdO-CeO_2/ZrO_2$ and $PdO-CeO_2/Al_2O_3$ catalysts, the presence of cubic CeO_2, with reflection peaks at $2\theta = 28^{\circ}$ and 56° was detected.
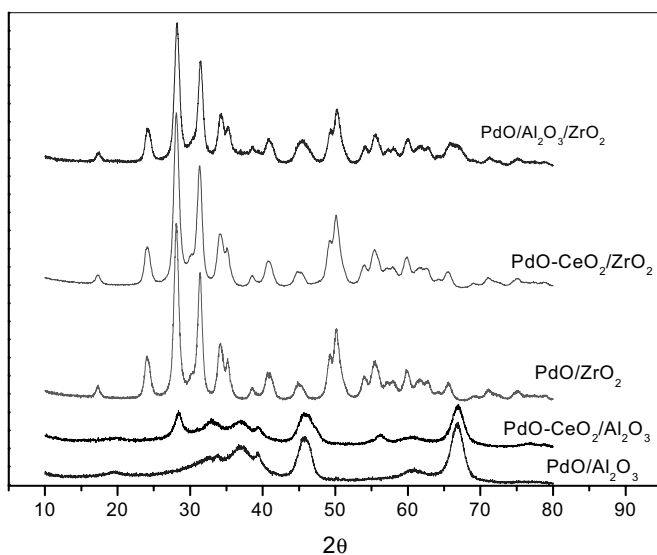

Figure 1. XRD patterns of the catalysts

BET and XRF results analysis are presented in Table 1. The XRF indicated that Pd concentrations are approximately 1% w/w. BET analysis indicated that the

catalysts supported on alumina have higher specific surface areas than the zirconia supported catalysts.

Table 1. Palladium content and specific surface area of the catalysts.

Catalysts	Pd (%)	Specific surface area ($m^2.g^{-1}$)
PdO/Al_2O_3	1.00	178.6
PdO/ZrO_2	0.85	67.8
$PdO-CeO_2/Al_2O_3$	0.84	158.9
$PdO-CeO_2/ZrO_2$	0.96	68.3
$PdO/Al_2O_3/ZrO_2$	0.91	128.8

TPD analysis (Figure 2) showed that on catalysts containing ZrO_2, PdO decomposition temperatures were higher than those supported on alumina.

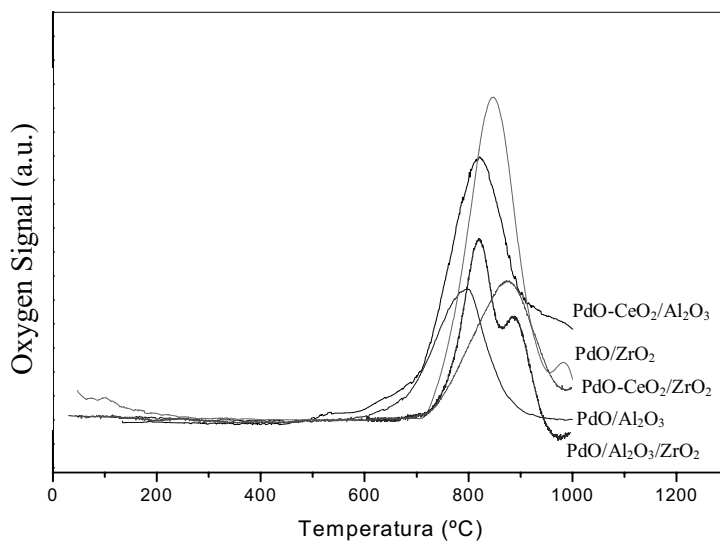Figure 2. TPD profiles of the catalysts.

The PdO/ZrO$_2$ catalyst, for example, presented a peak of O$_2$ desorption at 847ºC, while the PdO/Al$_2$O$_3$ presented it at 797ºC. This behavior is confirmed by comparing catalysts PdO-CeO$_2$/Al$_2$O$_3$ and PdO-CeO$_2$/ZrO$_2$ and indicates that at high temperatures zirconia increases PdO stability, which can be attributed to the oxygen storage capacity of zirconia (9).

The cerium effect on PdO decomposition temperatures was also observed. TPD of PdO-CeO$_2$/Al$_2$O$_3$ and PdO-CeO$_2$/ZrO$_2$ presented O$_2$ desorption peaks which shifted to higher temperatures than PdO/Al$_2$O$_3$ and PdO/ZrO$_2$. This indicates that cerium promotes PdO stabilization. This stabilization can be attributed to CeO$_2$ ability to shift easily between reduced and oxidized state (Ce^{+4}/Ce^{+3}), which provides O$_2$. This ability and the high mobility of oxygen species contributes to the stabilization of palladium oxide phase.

Figure 3 illustrates the profiles of methane conversion as a function of temperature. The results indicated that all catalysts are active for methane combustion. As can be observed, alumina catalysts were the most active presenting the lowest ignition temperatures.
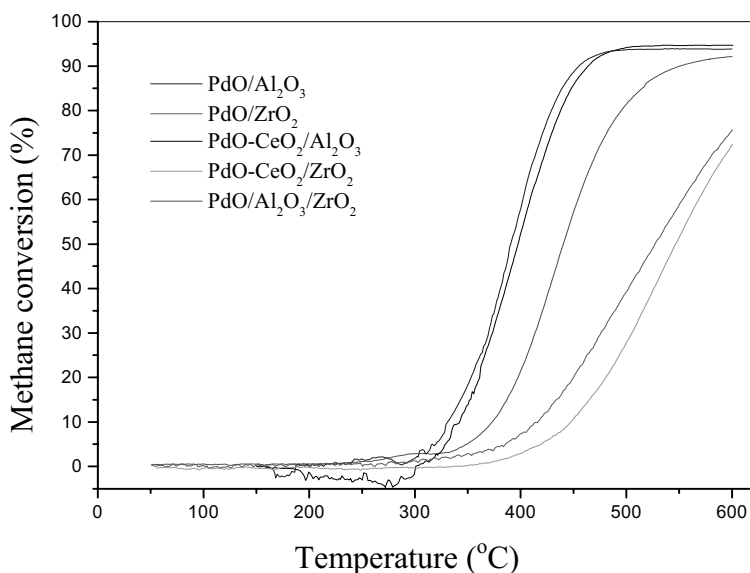

Figure 3. TPSR profiles of the catalysts

Catalysts supported on ZrO$_2$ were less active, showing the highest ignition temperatures. On the other hand, the catalyst containing zirconia and alumina at a ratio of 1:1 presented an ignition temperature of 372ºC, indicating that the presence of alumina promotes methane ignition at lower temperatures. As

regards the lower activity, PdO phase on zirconia catalysts are more stable, which suggests that these catalysts are better suited to catalytic combustion of methane at higher temperatures.

4. Conclusion

The results obtained in this work indicated that the catalysts prepared in this work showed to be very active for methane combustion. PdO/Al_2O_3 and $PdO-CeO_2/Al_2O_3$ were the most active ones. Besides its lower activity in this temperature range, zirconia catalysts are promising for high temperature combustion due to its high thermal stability. Combining alumina and zirconia supports can be an alternative to improve activity and PdO thermal stability. The later can also be promoted by the addition of CeO_2 in the catalyst formulation.

5. References

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