Support effects on the performance of Pt/CeO₂ and Pt/Al₂O₃ catalysts for the dry reforming of methane.

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Introduction
The dry reforming of methane as a source of carbon monoxide and hydrogen is a major issue in heterogeneous catalysis [1]. Noble metals are well known as catalysts for this reaction; however, a major problem linked with this reaction is the catalyst deactivation. There are two causes for catalyst deactivation, i.e., carbon deposition and sintering of the metal particles [2-5]. Carbon originates mainly from two reactions, methane decomposition (CH₄ → C + 2H₂) and carbon monoxide disproportionation (2CO → C + CO₂). Catalytic stability seems to depend on the nature of the support and its interaction with the metallic phase. It has been shown that ZrO₂ as support for Pt and Ni minimizes coke deposition for this reaction [6]. In this work Pt supported on CeO₂ and Al₂O₃ was prepared and characterized focusing on the effect of the support on the stability of the catalyst for the CO₂ reforming of CH₄.

Materials and Methods
Catalysts were prepared by classical impregnation using H₂PtCl₆ and Pt(ACAC)₂ as Pt precursors. Metal loading was fixed at 1.5 wt.%. Supports (Al₂O₃, Rhone Poulanc and CeO₂ obtained from precipitation of Ce(NO₃)₃·6H₂O) were calcined at 800 °C prior to impregnation. After impregnation the catalysts were dried at 60 °C for 12 h, then calcined in air for 2 h at 500 °C and finally reduced in H₂ for 4 h at 600 °C. Several techniques were used to characterize the physicochemical properties of the catalysts: N₂ adsorption, DRX, HRTEM, TPR and TPO-MS. The catalytic properties were studied in a flow reactor system working under atmospheric pressure. The catalytic reactivity as a function of reaction temperature and time on stream was evaluated using high GHSV values and a CO₂/CH₄ ratio of 1. Before any catalytic run the catalysts were reactivated in H₂ flow for 1h at 600 °C. The exit gases were analyzed using online GC (TCD) and a 4 m column packed with Carboxen 1000.

Results and Discussion
Stability of the catalysts under stream for a period of 25 h is shown in Figure 1. It is clear that the Pt/CeO₂ catalysts, independently of the Pt precursor, are much more stable towards deactivation than the Pt/Al₂O₃ catalysts. Taking into account the causes for catalyst deactivation (carbon deposition and/or sintering of the metal particles) the fresh and spent catalysts were characterized by HRTEM. Mean Pt particle size of the fresh catalysts determined by HRTEM was about the same (~ 3.0 nm), however, particle size distribution was significantly different as a function of the support. After reaction, particle size increased to about 6 nm in the case of the Pt/CeO₂ for both Pt precursors and to 13 nm in the case of Pt/Al₂O₃ (H₂PtCl₆) catalyst. A strongest metal-support interaction in the case of the CeO₂ support is developed which diminishes the sintering of Pt particles. An epitaxial growth of Pt particles on CeO₂ crystals is suggested by HRTEM. In order to characterize the carbon residues present on the surface of the catalysts after 25 h under stream at 800 °C, TPO experiments were done following the signal of CO₂ (m/e= 44). The Pt/Al₂O₃ catalyst showed a peak at 450 °C while practically no CO₂ was observed in the case of the Pt/CeO₂ catalyst. HRTEM observation of the spent catalysts confirmed this result. The higher stability observed for the Pt/CeO₂ catalyst is a combination of two factors. On one hand the inhibition of a strong Pt particle growth which allows the main tenance of a high metal-support interfacial area which is important for an efficient cleaning of the metal particle, and on the other, a high oxygen transfer and CO₂ dissociation attributable to the CeO₂ support.

Significance
Contribution to the development of stable and active Pt-based catalysts for dry reforming of methane.

Materials and Methods

Figure 1. CH₄ conversion as a function of time on stream at 800 °C. CH₄/CO₂ = 1, GHSV = 450,000 h⁻¹.

Figure 2. Z-contrast typical TEM image of Pt/CeO₂ spent catalyst.

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References