

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

Francisco González, Antonio Gómez-Cortés, Jesús Arenas-Alatorre and Gabriela Díaz*
Instituto de Física, UNAM, A. P. 20-364 México D. F. 01000 México.
*diaz@fisica.unam.mx

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 ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$) and carbon monoxide disproportionation ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$). 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. Figure 2 shows a typical HRTEM image of the spent Pt/CeO₂ (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 maintenance 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.

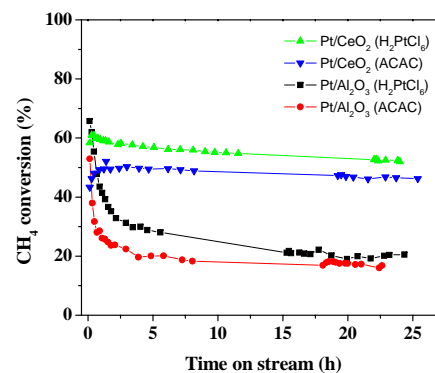


Figure 1. CH₄ conversion as a function of time on stream at 800 °C. CH₄/CO₂ = 1, GSHV = 450,000 h⁻¹.

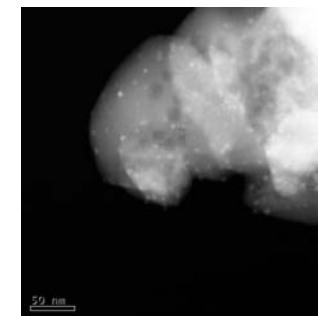


Figure 2. Z-contrast typical TEM image of Pt/CeO₂ spent catalyst.

Acknowledgements

To M. Aguilar for the XRD determinations and L. Rendón of LCMIF for HREM images. Also to CONACYT, project 42666F for funding.

References

1. Bradford, M. C. J. and Vannice, M. A., *Catal. Rev. Sci. Eng.*, 41,1(1999)
2. Hegarty, M.E.S., O'Connor, A.M., Ross, J.R.H., *Catal Today* 42, 225(1998).
3. S.T. Ashcroft, A.K. Cheetham, M.L.H. Green and P.D.F. Vernon, *Nature* 352, 225 (1991).
4. V.A. Tsipouriari, A.M. Estathiou, Z.L. Zhang and X.E. Verykios, *Catal. Today* 21, 579 (1994).
5. K. Nagaoka, K. Seshan, K. Aika and J.A. Lercher, *J. Catal.*, 197 (1), 34 (2001).
6. Lercher, J.A., Bitter, J.H., Hally, W., Niessen, W. Seshan, K. *Stud. Surf. Sci. Catal.* 101, 463 (1996).