

Partial Oxidation of Methane over Ni, Pd and Pt Catalysts - Mechanism Investigation

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Introduction

Due to the great abundance of natural gas industries have shown a growing interest in the conversion of methane to more useful and easily transportable chemicals (liquids). The most common route to convert natural gas in these products is via synthesis gas [1, 2, 3]. Partial oxidation of methane (POM) has been described as an interesting alternative for syngas production and its mechanism has been widely reported in literature. Some authors suggest that the reaction occurs in one step with directly and selective formation of CO and H₂, while other research suggests that the mechanism occurs in two distinct steps: Total oxidation of methane, producing CO₂ and H₂O, followed by the methane reforming with these products to generate syngas[4, 5]. In this work Ni/Al₂O₃, Pd/Al₂O₃ and Pt/Al₂O₃ were prepared in order to investigate the POM mechanism and the nature of active phase for this reaction.

Materials and Methods

The samples were prepared by alumina impregnation with solutions of Ni(NO₃)₂, Pd(C₅H₇OO)₂ and H₄[PtCl₆]. The materials were dried at 110°C and calcined at 600°C for 10 h. The samples obtained from nickel, palladium and platinum were labeled NIA, PDA and PTA and were prepared to result in a loading of 10%, 1% and 1% of Ni, Pd and Pt, respectively. The catalysts were characterized by XRD, XRF, BET, XPS, H₂ TPR and CH₄ TPR. Unsteady-state partial methane oxidation was carried out by temperature-programmed surface reaction (TPSR).

Results and Discussion

In order to investigate the active phase for methane adsorption in each catalyst CH₄ TPR experiments were carried on the reduced and oxidized samples. On the reduced samples the main product was H₂, which confirms that adsorption of methane on metallic sites is dissociative, generating C and H adsorbed on the surface. Adsorbed H atoms combine leading to the formation of H₂ [2, 5]. The results also showed that activation of C-H bonds occurs at lower temperatures on Ni sites followed by Pd and Pt. On the oxidized samples adsorption of methane originated H₂ and small amounts of CO, CO₂ and H₂O. According to literature [2], adsorption of methane over an oxidized surface leads to the formation of OH groups which condense generating H₂O. Besides this, CO and CO₂ are formed as a result of the adsorbed carbon oxidation. The results also showed that for the oxidized samples the activation of C-H bonds occurs at lower temperatures on Pt sites followed by Pd and Ni. It can be concluded that for Ni and Pd the active site to activate C-H bond is metallic, while for Pt a partially oxidized surface would be better.

TPSR results are shown in Figure 1 and they indicate a POM mechanism in which total oxidation of methane takes place. It can be observed that O₂ adsorption is more favored over Ni and Pd than over Pt as it occurs at lower temperatures on Ni and Pd. Therefore, the

difference in catalytic behavior of these sites can be attributed to the fact that the platinum surface covered with adsorbed oxygen (Pt^{δ+}-O^{δ-}) does not activate as easily C-H bonding as the ions Ni²⁺O²⁻ and Pd²⁺O²⁻ [2, 6]. Furthermore, the mechanism of C-H bond activation in the case of the Pt is homolytic, a typical CH₄ adsorption assisted by oxygen, while for Ni and Pd the presence of the ionic pair (M²⁺O²⁻) promotes a heterolytic mechanism of C-H bond activation.

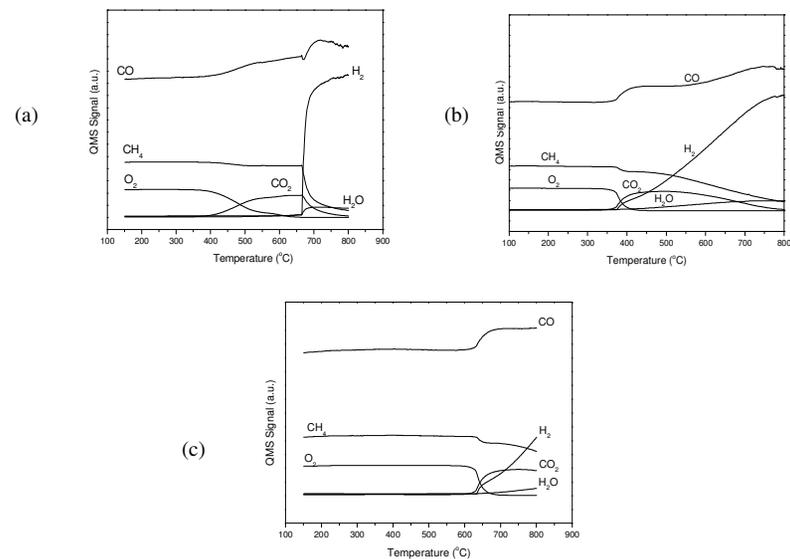


Figure 1. TPSR profiles of the catalysts NIA (a), PDA (b) and PTA (c).

Significance

This work describes an investigation of POM mechanism over different catalysts in order to understand how it is influenced by the kind of catalyst and nature of active phase.

References

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