

Methane Partial Oxidation Mechanism over Pt-Ru Catalysts

Roberto Lanza^{1*}, Sven Järås¹ and Paolo Canu²

¹KTH - Royal Institute of Technology, Department of Chemical Engineering and Technology, Chemical Technology, SE-100 44 Stockholm (Sweden)

²Università di Padova, Dipartimento di Principi e Impianti di Ingegneria Chimica, Via Marzolo 9, IT-35131 Padova, (Italy)

*roberto.lanza@gmail.com

Introduction

During the last decades the research on partial oxidation of methane (CPO) has received a big impulse both for environmental and economic reasons. Notwithstanding the big number of studies, the mechanism that leads to the formation of CO and H₂ is not fully clarified, yet. There are two different reaction mechanisms proposed: one is the direct pathway in which CH₄ and O₂ adsorb on the catalyst and then give CO and H₂ [1]; the second one is the so called “combustion and reforming mechanism” (CRM) [2]. According to this one, CH₄ and O₂ first form CO₂ and water following a complete combustion pathway; afterwards steam (SR) and dry reforming (DR) occur forming CO and H₂.

Materials and Methods

Activity tests have been carried out in a continuous flow reactor. It consists of a quartz tube, where the catalyst was located. The reactor is centered inside an electrically heated furnace, governed by a programmable controller. Reaction products and residual reactants were detected by a non-dispersive infrared detector (NDIR) for CH₄, CO and CO₂; hydrogen was detected by a TCD and O₂ by a paramagnetic detector. Water was calculated from mass balances. During the CPO activity tests run with this catalyst, a CH₄/O₂/N₂ mixture (3.4/1.7/94.9 % by vol.) was fed (stoichiometric according to the CPO reaction) at different gas space velocity (GHSV) and temperature (T). Results are reported in terms of % variations between inlet and outlet concentration scaled with the inlet methane concentration, $\Delta C_i^* = |C_i^{IN} - C_i^{OUT}| / C_{CH_4}^{IN} \times 100$, where C_i is the concentration (% vol) of species i and $C_{CH_4}^{IN}$ is that of methane at the reactor inlet. ΔC_i^* allows to easily analyze the stoichiometry of the results. When applied to methane $\Delta C_{CH_4}^*$ is the standard % conversion. The catalyst was Pt and Ru (50:50 by weight) supported on alumina added with a mixture of ceria and zirconia. The total metal load was 1 % in weight.

Results and Discussion

In a recent work [3], we presented the results on partial oxidation of methane of a bimetallic catalyst, which showed both good activity high selectivity towards CO and H₂. With the present work we try both to identify the reactions occurring and to quantify their contribution to the final products composition.

The presence of H₂O and CO₂ detected during the CPO tests suggested a complete combustion step after which CO and H₂ were formed mainly by dry and steam reforming, but other reactions (probably WGS both direct and reverse) are involved. This is coherent with the combustion and reforming mechanism and to provide evidences of that we run some dry and steam reforming (DR and SR) tests and also verified the activity of the catalyst in the water gas shift reaction (WGSR, both direct and reverse).

Figure 1 (left) shows CH₄ and CO₂ ΔC^* , detected feeding them in a 1:1 ratio. The catalyst shows to be active for DR and the products detected were CO and H₂ but also small amounts of water were produced suggesting that other reactions were involved.

According to the CRM, steam reforming is a reaction that contributes to the conversion of methane after the first step of complete combustion. Feeding a mixture of CH₄ and H₂O allowed verifying that the reaction is actually catalyzed. The reaction gives the highest conversions at the lowest GHSV, that is at the longer residence time, confirming that the H₂O formed from the first complete combustion step leads to CPO products if enough reacting time is allowed for steam reforming to occur (see Figure 1, right). All the tests run in different conditions (varying the species fed, the gas space velocity and the temperature) provided evidences that the global partial oxidation reaction goes through the combustion and reforming mechanism. CO₂ and water, indeed, reached the maximum concentration possible with the CH₄/O₂ ratio fed during the CPO tests and the catalyst showed to be active both for dry and steam reforming. Both these reactions gave conversions of the reactants inversely proportional to the space velocity set, also explaining the higher methane conversion detected at low GHSVs during the CPO tests previously run. Direct and reverse water gas shift reaction tests were run (results not shown here). The concentration of the species fed were chosen after and analysis of the $\Delta C_i / \Delta C_y$ ($i = H_2$ and CO and $y = CO, CO_2$ and H₂O). The catalyst was active and both the reactions approached the predicted equilibrium.

Significance

The work distinguish and quantifies the contribution of the reactions occurring in the partial oxidation of methane, being this is extremely important to know because in the industrial process serious heat management problems have to be solved if the indirect mechanism is the one followed by the partial oxidation reaction.

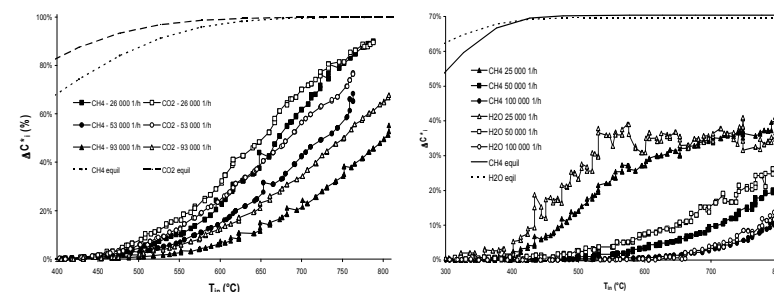


Figure 1. DR (left) and SR (right) results obtained during activity tests.

References

- Elmasides, C. and Verykios, X. *J. Catal.* 203, 477 (2001).
- Weng, W. Z., Chen, M. S., Yan, Q. G., Wu, T. H., Chao, Z. S., Liao, Y. Y. and Wan, H. L. *Catal. Today*, 63, 317 (2000).
- Lanza, R., Canu, P. and Järås, S.G. *Appl. Catal. A: General* 348, 2, 221 (2008).