

# Selectivity of Product Formation in Catalytic Radiant Burners: Thermodynamic and Kinetic Aspects

Oksana V. Shapovalova, Vladimir S. Arutyunov, Mikhail Yu. Sinev\* and Kirill Ya. Troshin  
Semenov Institute of Chemical Physics, R.A.S., Moscow, 119991, Russia  
\*e-mail address of corresponding author: sinev@chph.ras.ru

## Introduction

Volumetric radiant burners are known to be efficient for heat production, when fuel-poor mixtures are utilized, due to a high degree of energy recuperation inside the combustion cavity [1,2]. Recently it was suggested to use such devices for production of various chemical products, which form in the conditions of high-temperature oxidative transformations of light alkanes [3]. In the latter case, the process is conducted in fuel-rich conditions, usually close to or even out of the upper combustion limit of alkane. The use of catalysts in such burners allows one not only to widen the combustion limits but as well fuel conversion and, thus, to improve further the overall process efficiency. This study is devoted to the analysis of the ruling factors that control the formation of target products, i.e. process selectivity in (a) partial oxidation of methane to syngas (POM) and (b) oxidative cracking of  $C_{3+}$  alkanes (OCA) to light olefins.

## Experimental

The experimental equipment (various types of radiant burners) used in this work is described in detail elsewhere [3]. Several types of catalysts that allow one to stimulate the combustion and to vary product selectivities were tested. Among them, highly active Pt supported on La-stabilized alumina, alkaline-earth metal aluminates, and typical alkane oxidative cracking/dehydrogenation catalysts (mixed oxides containing rare-earth elements).

The effect of thermodynamic factors onto product selectivities was analyzed using calculations of adiabatic temperature and equilibrium composition based on standard procedures and thermodynamic properties of reaction components (reactants and products).

## Results/Discussion

The major thermodynamic factors ruling the product distribution in both POM and OCA processes are temperature and initial alkane-to-oxygen ratio. Among the two, the latter is more important for obtaining high selectivity to target products. Fig.1 demonstrates the results of

thermodynamic calculation that shows that despite the decrease of adiabatic temperature, selectivities to CO and  $H_2$  are increasing along with the initial  $CH_4:O_2$  ratio;  $H_2:CO$  ratio also increases approaching the optimal value '2'.

The experimental data obtained on 1-dimensional (axial) burner demonstrate that the use of active Pt/(La)Al<sub>2</sub>O<sub>3</sub> catalyst allows one to widen the combustion limits towards the more fuel-rich side and, thus, significantly improve the syngas formation efficiency.

Among the kinetic factors controlling product distributions, the gas velocity and the efficiency of catalyst should be considered. Their optimisation allows one to keep the balance between the stability of combustion and relatively low heat evolution if partial (like  $C_2-C_3$  olefins in OCA process) instead of total oxidation products are formed. If the activity of the catalyst is low, a partial consumption of oxygen is taking place; as a result, the tightening of combustion limits is observed. And vice versa, in the presence of the most active catalysts (among studied here), total oxidation becomes predominant.

The optimal catalysts are able to stimulate the process via the partial pre-flame conversion and injection of highly reactive species (oxygenates, free radicals, etc.) into the combustion zone and, thus, to maintain the stability of combustion and optimal product distributions.

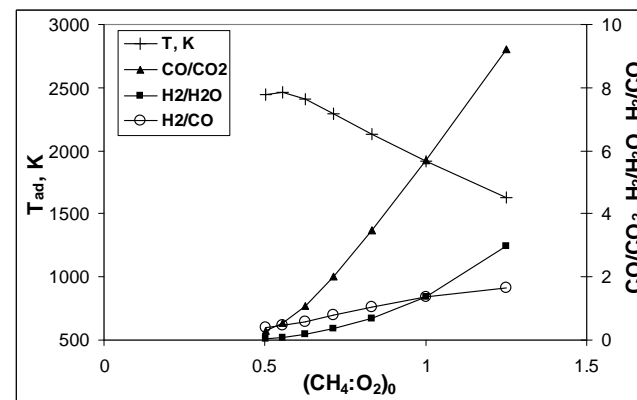


Figure 1. Adiabatic temperature and product distributions vs.  $CH_4:O_2$  ratio;  $T_0 = 773$  K.

## References.

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