Kinetics study of a $Mn/Na_2WO_4/SiO_2$ catalyst for its application in an OCM membrane reactor

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Highlights

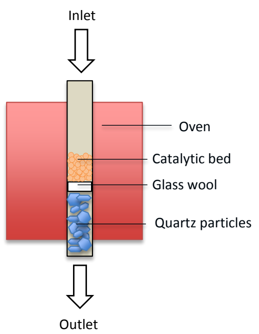
- 50% C_2 selectivity is reached with the $Mn/Na_2WO_4/SiO_2$ catalyst.
- Addition of H_2O has a positive influence into the OCM performance.
- C_2 consecutive reactions can limit the overall C_2 selectivity in an OCM membrane reactor.

1. Introduction

The oxidative coupling of methane (OCM) is a promising process to obtain high-value hydrocarbons from natural gas. The industrial exploitation of this reaction system is, however, hampered by low yields due to mainly parallel combustion reactions. Novel membrane reactors, which integrate the oxygen separation in the system, can improve the C_2H_4 yield because a low O_2 concentration can be maintained along the reactor, thus favoring the OCM reaction over the total combustion. The performance and stability of a $Mn/Na_2WO_4/SiO_2$ catalyst, which is one of the most promising OCM catalysts, has been studied under membrane reactor conditions, i.e. at very low oxygen concentrations. Special attention is paid to the C_2 consecutive reactions, which can have a strong impact on the overall performance of the process.

2. Methods

Kinetic experiments have been performed in a 6 mm diameter fixed bed tubular reactor. The length of the bed is kept between 1 and 2 cm to limit axial temperature profiles. A $Mn/Na_2WO_4/SiO_2$ catalyst is 50% diluted with quartz to reduce the amount of reactions, which can easily create hotspots because of their exothermicity. The quartz has been also placed in the post-catalytic zone, thus minimizing the void space that would lead to an increase of the undesired gas-phase reactions. To assure differential conditions, a relatively high flow rate of 360 mL/min is used with 70% N_2 dilution. The experiments have been carried out at typical OCM operating conditions, namely 800 °C and 2 bar, and the outlet stream has been analyzed using an Agilent microGC. A scheme of the setup can be seen in Figure 1.



Setup description	
Reactor length [mm]	15
Reactor diameter [mm]	6
Amount of catalyst [mg]	150
Particle size [µm]	250-355
Total flow rate [mL/min]	360

Figure 1. Scheme of the setup used to perform the kinetic experiments (right) and its description (left).

3. Results and discussion

Gas-phase (in the presence of inert material) and catalytic experiments were carried out at the same conditions in order to distinguish the effect of the catalyst on the OCM reaction rates. Some typical results are shown in Figure 2.

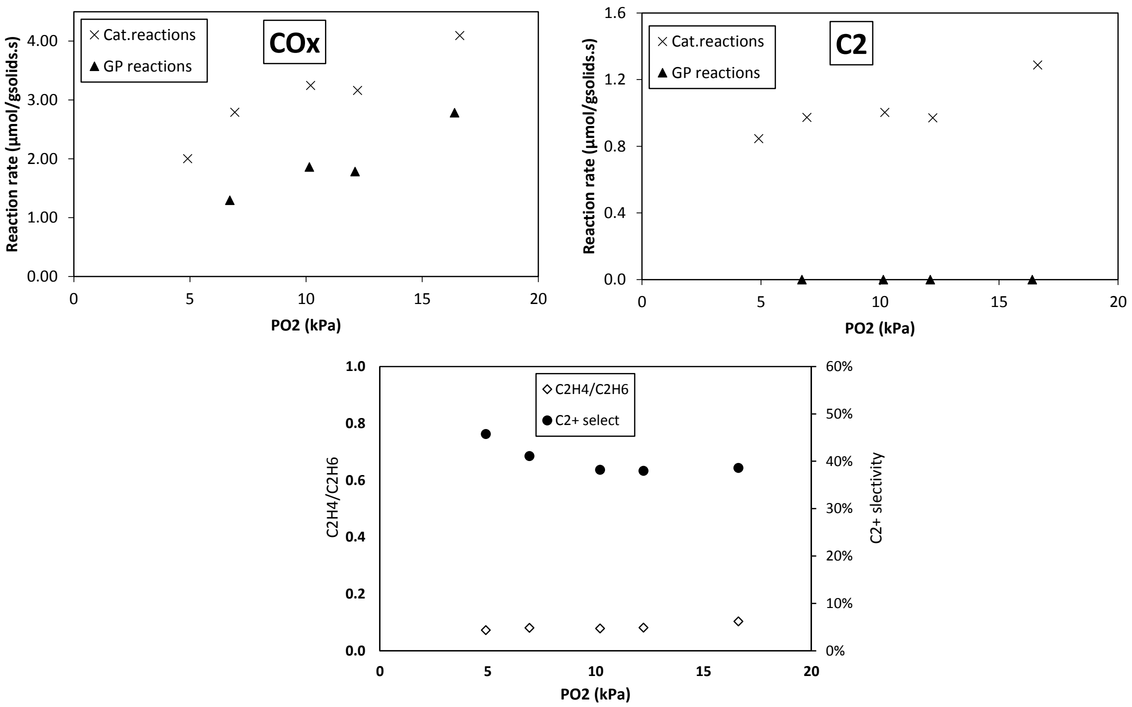


Figure 2. Production rates of CO_x (top left) and C_2 (top right) while changing P_{O2}. C_2H_4/C_2H_6 ratio and C_2 selectivity (bottom) obtained in the same experiment. Conditions of the experiment: P_{CH4}=70 KPa, Total Pressure=200 KPa, Temperature=800 °C.

The results show that the introduction of the catalyst enhances the production of C_2's, reaching a selectivity of around 50% when a high CH_4/O_2 ratio is applied, which is in agreement with literature [1]. It was also noticed in another set of experiments that the addition of steam improves the desired reactions, leading to higher selectivities towards C_2's. On the other side, the addition of CO_2 did not affect the OCM reaction rates. In addition, the combustion and reforming rates of both C_2H_4 and C_2H_6 have been investigated and quantified. It has been found that these reactions play an important role at the end of the OCM membrane reactor, where the amount of desired products will be relatively high. These reactions prevail both at the catalyst and in the gas phase, although it has been found that their importance is higher when the catalyst is introduced.

4. Conclusions

It has been shown that the catalyst strongly improves the OCM selectivity, especially at high CH_4/O_2 ratios, as present in an OCM membrane reactor. The kinetic rate expressions have been determined including consecutive oxidation and reforming reactions, since they can negatively affect the OCM membrane reactor performance. The kinetic rate model can subsequently be used to optimize the operating conditions and the design of an OCM membrane reactor.

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References

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Keywords

"Kinetics" "$Mn/Na_2WO_4/SiO_2$ catalyst" "membrane reactor" "oxidative coupling of methane"