Mn-Na_2WO_4/SiO_2 KINETICS FOR OXIDATIVE COUPLING OF METHANE; INFLUENCE OF SECONDARY REACTIONS

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Introduction

The oxidative coupling of methane (OCM) is a direct route for the production of hydrocarbons (C_{2+}) from methane.

$$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O \qquad \Delta H < 0$$

The OCM yield is hampered by the parallel oxidation reactions and the consecutive ones (reforming and combustion of C_2's).

These undesired reactions impede the achievement of the at least 30% C_{2+} yield is widely believed to be required to make the process economically

Experimental and results

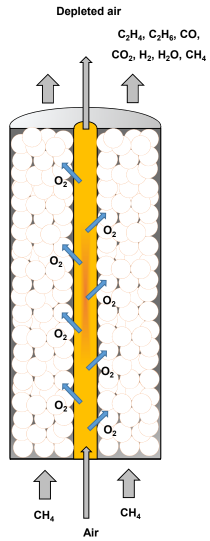
- The understanding of the catalyst behavior can help to improve the OCM reactor design, thus securing higher performances.
- Mn-Na_2WO_4/SiO_2 catalyst, one of the most promising OCM catalysts, has been chosen to perform individual sets of experiments (of primary and secondary OCM reactions) in a micro fixed bed reactor at 800 ˚C and 2 bar.

Set of experiments	Type of reaction	Reactions considered	Influence of catalyst	Selectivity towards C_2
$CH_4 + O_2$	Primary	$2\,CH_4 + 0.5\,O_2 \rightarrow C_2H_6 + H_2O$ $CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$ $CH_4 + O_2 \rightarrow CO + H_2$	No C_2 formation found without catalyst	<60 %
$C_2H_6 + O_2$	Secondary	$C_2H_6 \rightarrow C_2H_4 + H_2$ $C_2H_6 + 0.5\,O_2 \rightarrow C_2H_4 + H_2O$ $C_2H_6 + O_2 \rightarrow 2\,CO + 3\,H_2$ $C_2H_6 + 3.5\,O_2 \rightarrow 2\,CO_2 + 3\,H_2O$	Makes reactions faster	85-95 %
$C_2H_6 + H_2O$	Secondary	$C_2H_6 \rightarrow C_2H_4 + H_2$ $C_2H_6 + 2\,H_2O \rightarrow 2\,CO + 5\,H_2$	No reforming reaction occurs without catalyst	>70 %
$C_2H_4 + O_2$	Secondary	$C_2H_4 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O$ $C_2H_4 + O_2 \rightarrow 2\,CO + 2\,H_2$	Makes reactions faster	-
$C_2H_4 + H_2O$	Secondary	$C_2H_4 + 2\,H_2O \rightarrow 2\,CO + 4\,H_2$	No reforming reaction occurs without catalyst	-

(*) Oxygen independent reaction

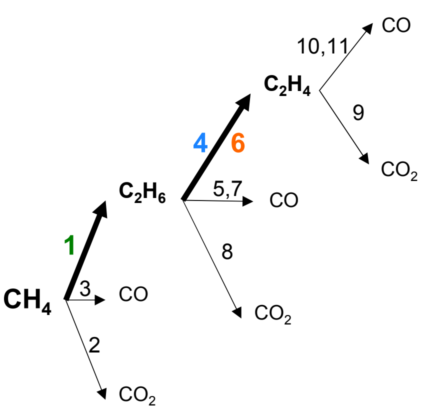
Primary reactions CONCLUSIONS

A distributed O_2 feeding (with a **MEMBRANE REACTOR**) increases the C_2 selectivity, thus providing higher C_2 yield to the OCM process.



Secondary reactions CONCLUSIONS

An OCM kinetic model has been built out of the performed experiments:



Step	Reaction	Kinetic expression $[\frac{\mu mol}{g.solid*s*KPa^{-(m+n)}}]$
1	$2\,CH_4 + 0.5\,O_2 \rightarrow C_2H_6 + H_2O$	$r = 0.0053 * P_{CH_4}^{1,14} * P_{O_2}^{0,32}$
2	$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$	$r = 0.096 * P_{CH_4}^{0,50} * P_{O_2}^{0,51}$
3	$CH_4 + 0.5\,O_2 \rightarrow CO + 2\,H_2$	$r = 0.0074 * P_{CH_4}^{0,84} * P_{O_2}^{0,59}$
4	$C_2H_6 \rightarrow C_2H_4 + H_2$	$r = 0.116 * P_{C_2H_6}^{1,66}$
5	$C_2H_6 + 2\,H_2O \rightarrow 2\,CO + 5\,H_2$	$r = \frac{5.658 * P_{C_2H_6}^{0,59}}{(1 + (0.055 * P_{H_2O}^{1,5}))^2}$
6	$C_2H_6 + 0.5\,O_2 \rightarrow C_2H_4 + H_2O$	$r = \frac{0.0577 * P_{C_2H_6}^{1,38} * P_{O_2}^{1,05}}{(1 + (0.0166 * P_{O_2}^{7}))^2}$
7	$C_2H_6 + O_2 \rightarrow 2\,CO + 3\,H_2$	$r = 1.5605 * P_{C_2H_6}^{0,08} * P_{O_2}^{1,13}$
8	$C_2H_6 + 3.5\,O_2 \rightarrow 2\,CO_2 + 3\,H_2O$	$r = 0.0039 * P_{C_2H_6}^{1,35} * P_{O_2}^{0,74}$
9	$C_2H_4 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O$	$r = 2.1677 * P_{C_2H_4}^{0,18} * P_{O_2}^{0,6}$
10	$C_2H_4 + O_2 \rightarrow 2\,CO + 2\,H_2$	$r = 1.0829 * P_{C_2H_4}^{0,33} * P_{O_2}^{0,8}$
11	$C_2H_4 + 2\,H_2O \rightarrow 2\,CO + 4\,H_2$	$r = 0.0051 * P_{C_2H_4}^{1,11} * P_{H_2O}^{0,83}$

(*) Gas-phase reaction

$C_2H_6 \rightarrow C_2H_4 + H_2$ main route for the C_2H_4 production.

$C_2H_4 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O$
$C_2H_4 + O_2 \rightarrow 2\,CO + 2\,H_2$
Minimization of these fast reactions is important.

Use of catalyst increase the velocity of the 2^{ary} reactions, thus faster consuming the C_2.

Conclusions

- An OCM kinetic model for the Mn-Na_2WO_4/SiO_2 has been developed, consisting of 11 desired and undesired reactions.
- 2^{ary} reactions can consume the C_2 formed in previous steps, thus becoming critical for an OCM proper reactor design.

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