Review of Kinetic Models of Oxidative Coupling of Methane and Methane DehydroAromatization

Muhammad Umar Jamil, and Ma'moun Al-Rawashdeh* (mamoun.al-rawashdeh@qatar.tamu.edu)

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Introduction

- OCM and MDA reactions are very **promising but not yet commercial**
- **Complex** reaction schemes with many **gas phase and catalytic surface** intermediate components
- Require **special considerations** to obtain **reliable kinetic experimental data**

Mathematical modeling across the scales from micro to macro is essential to overcome technical challenges

Target Reactions

Oxidative Coupling of Methane (OCM)

Ethylene: $2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$

Challenges

- Requires good heat management
- Low C2+ selectivity
- COx formation

Methane DehydroAromatization (MDA)

Benzene: $6CH_4 \rightarrow C_6H_6 + 9H_2$

Challenges

- Requires high temperature
- Fast catalyst deactivation
- Low conversion – thermodynamic limitation

This Work Objectives

- **Compiling** a list for **all kinetic models** for OCM and MDA reactions
- **Historical development of OCM technology** is studied by tracing development of kinetic and reactor models
- An effort is made to **replicate some empirical kinetic models** leading to the **identification of major pitfalls** in reporting and formulation of these kinetic models

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Year	Author	OCM catalysts and kinetic models	
1988	V. T. Amorebieta	7% Li-MgO	Empirical
1988	J. M. Deboy	1 wt% Sr/La203	Empirical
1989	E. Iwamatsu	15% Na+-MgO	Microkinetic
1989	J. A. Roos	2.8 wt.% Li / 8.2 wt.% CO2	Microkinetic
1990	E. E. Miro	0.5, 5.4, 7.6, 9.7, 13.8% Li/NiTiO3 1.6, 8.7, 14, 22, 32% Na/NiTiO3	Microkinetic
1991	Y. Feng	1% Sr/La203	Microkinetic
1992	L. Lehmann	11 mol% NaOH/CaO	Empirical
1995	S. Cheng	34 wt% PbO/ r-alumina	Empirical
1995	W. Wang	3 % Li/MgO	Empirical
1996	U. Pannek	La2O3/CaO	Empirical
1996	M. Sohrab	CaTiO3	Empirical
1997	Z. Stansch	La2O3 (27 at. %)/CaO	Empirical
1998	Yu. I. Pyatnitsky	10% La2O3/MgO	Empirical
1998	M. Traykova	TiSi2 and CoSi2 /MgO	Microkinetic
2006	N. S. Matin	Na/BaTiO3/MgO	Microkinetic
2006	J. A. Langille	2 wt% Mn/ 5 wt% Na2WO4/SiO2	Empirical
2008	J. Sun	Li/MgO and Sn/Li/MgO	Microkinetic
2008	N. Yaghobi	SnBaTiO3	Empirical
2009	M. Daneshpayeh	4 wt.% Mn-5 wt.% Na2WO4	Empirical
2009	K.Takanabe	La0.6/Sr0.4/Co0.8/Fe0.2/O3-d	Empirical
2009	Z. Taheri	2wt%Mn and 5wt%Na2WO4/SiO2	Microkinetic
2010	N. R. Farooji	SnBaTiO3	Empirical
2011	A. Farsi	La(0.6)-Sr(0.4)-Co(0.8)-Fe(0.2)-O(3−δ)	Empirical
2013	V. I. Lomonosova	2 wt% Mn/1.2 wt% Na/2.7 wt% W/SiO2	Microkinetic
2013	A. Valadkhani	1% La/MgO & NaWMn/SiO2	Microkinetic
2013	J. S. Ahari	Mn/Na2WO4/SiO2	Microkinetic
2014	A. Vatani	3.3 wt.% Li/MgO	Empirical
2019	D. Li	-	Microkinetic

Complied OCM and MDA Kinetic Models

- All kinds of kinetic models have been reported, from simple power law to more detailed mechanistic ones.
- Total number of found kinetic models are 30 for OCM and 12 for MDA in the period of 1988 to 2020
- Most OCM kinetic models are for Li/MgO and Mn/Na2WO4/SiO2 catalyst
- Most MDA kinetic models are for Mo/HZSM-5 catalyst

Year	Author	MDA catalysts and kinetic models	
1990	A. M. Dean	-	Microkinetic
2001	O. Rival	-	Microkinetic
2001	L. Li	0.5% Ru-3% Mo/HZSM-5	Empirical
2002	L. Li	Mo/HZSM-5	Empirical
2003	M. C. Iliuta	0.5% Ru-3% Mo/HZSM-5	Empirical
2008	B. Yao	modified Mo/HZSM-5	Empirical
2012	K. S. Wong	5.3 wt.%Mo/HMCM-22, Si/Al ratio of 15.5	Microkinetic
2015	C. Karakaya	Mo2C/HZSM-5	Microkinetic
2016	C. Karakaya	6 wt % Mo/HZSM-5	Microkinetic
2017	N. I. Fayzullaev	(MoO3)x·(ZrO2)y·(ZnO2)z/bentonite	Empirical
2018	Y. Zhu	6 wt% Mo/HZSM-5	Empirical
2020	J. Jeong	5.94% Mo/HZSM-5	Empirical

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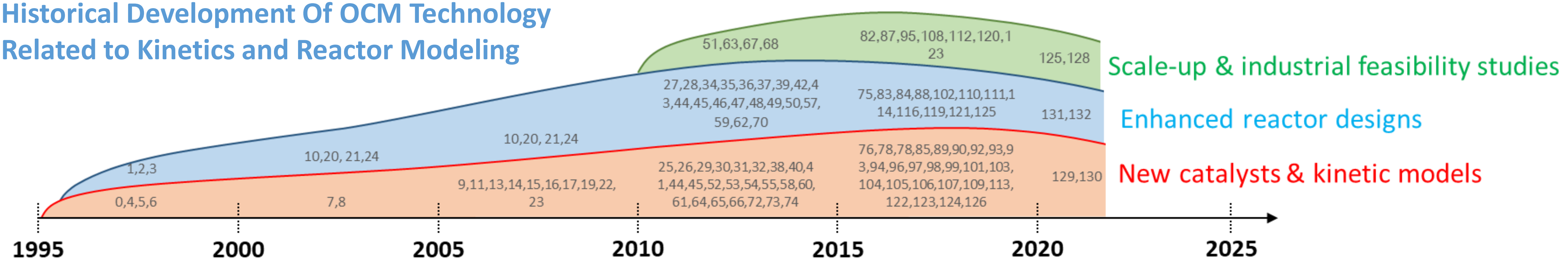
Historical Development Of OCM Technology Related to Kinetics and Reactor Modeling



Key Findings

- OCM technology has matured from new catalysts towards industrial reactor designs, scale-up and feasibility studies from 1997 based on Stansch model till 2021
- Over 132 follow up research works were analyzed on how OCM kinetic model and developments took place using a categorization matrix
- The matrix was formed by these combinations: experiment, kinetic modeling, reactor modeling, new catalysts, new reaction scheme and new reactor type
- Langmuir-Hinshelwood mechanism and $Mn/Na_2WO_4/SiO_2$ catalyst is widely used for OCM
- Majority of work (83 publications) are related to reactor modeling studies
- Around 30 different reactor designs are proposed
- Until recently, techno-economic studies and scale-up of autothermal operation of OCM is of key interest

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Replication of Kinetic Models

Efforts to replicate some empirical kinetic models lead to identifying major pitfalls in reporting and formulation of these kinetic models

Missing or Inconsistent Information

- Example of a mass balance: bulk density, porosity, superficial velocity are needed

Mass balance: $-u_s \frac{dC_j}{dz} - \rho_b r_{c,j} + \varepsilon_b r_{g,j} = 0$

- Example of kinetic parameters units and design equation

Rate constant k_1: *gmol/gcat h. bar*^{2}

- Examples of definition of kinetic parameters and incomplete kinetic expressions; shown either w.r.t. reactions, and not components or vice versa

$C_2H_6 + 0.5O_2 \rightarrow C_2H_4 + H_2O$

$$r_j = \frac{k_{0j} e^{-E_a/RT} p_C^{m_j} p_{O_2}^{n_j}}{(1 + K_{j,CO_2} e^{-\Delta H_{ad,CO_2,j}/RT} p_{CO_2})^n}$$

$2CH_4 + 0.5O_2 \rightarrow C_2H_6 + H_2O$

$$r_2 = \frac{k_{0,2} e^{-E_{a,2}/RT} (K_{0O_2} e^{-\Delta H_{ad,O_2}/RT} p_{O_2})^{n_2} p_{CH_4}}{[1 + (K_{0,O_2} e^{-\Delta H_{ad,O_2}/RT} p_{O_2})^n + K_{j,CO_2} e^{-\Delta H_{ad,O_2}/RT} p_{O_2}]^2}$$

$$R_{CH_4} = 5.375443 e^{\frac{-1049527}{RT}} P_{CH_4}^{0.39563} P_{O_2}^{0.72761}$$

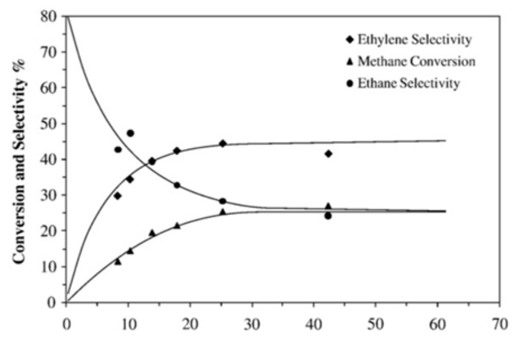
- Examples of definitions of reactor performances e.g., selectivity w.r.t. which component

$$S_1 = \frac{2r_2}{2r_2 + 2r_{16}}$$

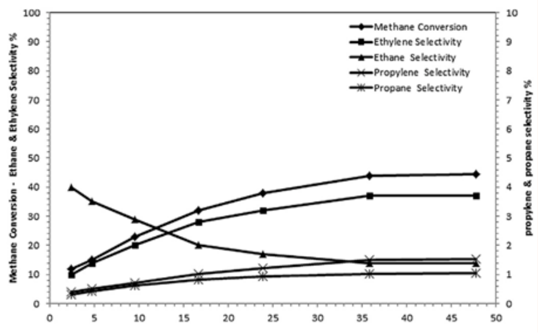
$2R_{C_2}/(2R_{C_2} + R_{CO_2} + R_{CO})$

$S_{C2H4} = 2F_{C2H4}/(F_{CH4_0} - F_{CH4})$

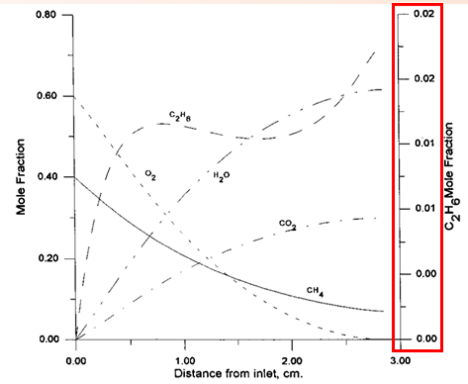
Typing Errors



Space time (kg.s.m-3)



Space velocity (hr-1)



Other Challenges

- **Different or missing statistical tests** for defining a kinetic model's accuracy, hence comparing models becomes difficult
- **Limited validation of kinetic models** done for specific reaction conditions for simulation purpose, but not mentioned

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Compiling OCM and MDA Kinetic Models

- This work compiled and analyzed the literature for OCM and MDA kinetic models and found 30 and 12, respectively.
- Among the many MDA kinetic models, only 1 kinetic model accounts for the catalyst deactivation, without which the process understanding remains incomplete.

Historical Development of OCM Technology

- Analysis of 132 research articles related to kinetic modeling and their utilization was performed for OCM technology
- Following the development of the OCM Stansch kinetic model, a view is showcased on how a kinetic model is developed, upgraded, and utilized towards developing new promising technology from lab toward commercial scale.

Replicating the Kinetic Models and Pitfalls in Models Reporting

- Several challenges are faced while attempting to replicate some of the kinetic models in the literature, most important of these are missing or wrong information and typing errors.
- This work draws attention towards reconsidering how kinetic models and experimental data are exchanged in the scientific community.
- With the rapid advancements of the digital era, sharing data in the right format can lead to higher quality research work and efficient advancement of needed technologies of the future as OCM and MDA