

## New Approach of Kinetic Modelling and Analysis of Catalytic Cycle: Evolution of Production and Catalyst Composition in Ethylene Oxychlorination

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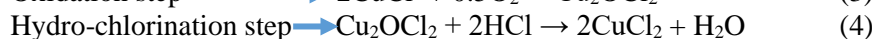
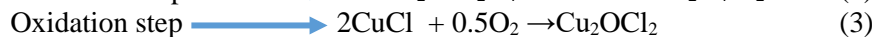
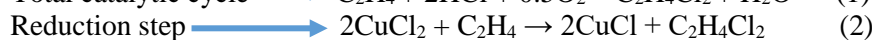
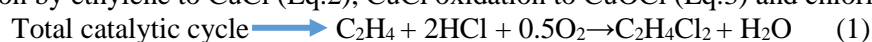
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### Highlights

- Kinetics of reduction- and oxidation steps was modeled separately.
- Kinetics of catalytic cycle of redox reaction was obtained by steady-state approach.
- Kinetic responses of gas phase composition and catalyst oxidation state were described.
- Kinetics was applied for rational catalysts design to achieve better catalysts.

### 1. Introduction

Vinyl chloride monomer (VCM) is the raw material for production of polyvinyl chloride (PVC), most massively produced in the worldwide, since it's extensively use in the thermoplastics industry. A commercial way of producing VCM is to crack 1, 2 dichloroethane (EDC)[1]. A gaseous mixture of ethylene, HCl and air on a CuCl<sub>2</sub> based catalyst via oxychlorination (Eq.1), in turn, produces EDC. The ethylene oxychlorination reaction occurs in the catalytic cycle with three sequential reactions steps such as CuCl<sub>2</sub> reduction by ethylene to CuCl (Eq.2), CuCl oxidation to CuOCl (Eq.3) and chlorination of CuOCl (Eq.4)[2]:



Cu<sup>2+</sup> is recognized as the active sites and Cu<sup>1+</sup> is not active but volatile[1]. The catalytic system suffers from volatilization of cuprous copper and catalyst particle agglomeration, abated by alkali, alkali earth and/or La promotion[3]. The active site is highly dynamic inside the catalytic cycle. The distribution of Cu<sup>2+</sup> and Cu<sup>1+</sup> at the steady-state conditions depends on the kinetic balance of above three reaction steps (Eq.2-4)[4]. Catalyst properties and operation conditions can influence the rate of each step in the catalytic cycle, thus the Cu<sup>2+</sup> and Cu<sup>1+</sup> distribution. The prediction and strategy to control the Cu<sup>2+</sup> and Cu<sup>1+</sup> distribution is thus highly desired[3-5]. The Langmuir-Hinshelwood and Mars van Krevelen kinetic approach have been widely applied in kinetic modeling. The key assumption for these approaches is the constant number of active sites and often a rate-determining step existing. Owing to the dynamic nature of the active site, a new kinetic approach is highly desired to describe the kinetics of total catalytic cycle (Eq.1) including the metal oxidation state changes.

For the first time, the present work deals with a new approach of kinetic modelling by modeling of individual reaction steps following a steady-state approach gain a kinetic model of the catalytic cycle at the steady-state conditions. The kinetic model are applied for rational catalysts design to achieve the high content of Cu<sup>2+</sup>, as well as reactor simulation to predict not only the concentration and temperature profile but also Cu<sup>2+</sup> and Cu<sup>1+</sup> profile. The results from our group confirms that that the methodology developed here paves the way for a general method for catalyst design of heterogeneous catalysts where the catalyst undergoes oxidation state changes, in particular in redox reactions (catalytic combustion of methane).

### 2. Methods

The operando setup is described in detail elsewhere[3]. Catalysts were impregnated via the incipient wetness method. The catalyst contained 5wt% Cu with a 45-100 μm particle size. The kinetic model developed in this study was fitted to experimental data by minimizing the objective function for the sum of the squared residuals for each temperature.

### 3. Results and discussion

Supported by Rout et al. [3], the reduction step (Eq. 2) and the oxidation step (Eq. 3) were assumed to be rate determining. The reduction reaction rate (Fig. 1a) curve is split into two parts,  $r_{1,I}$  and  $r_{1,II}$  by deconvolution using Gaussian multiple peak, such that  $r_1 = r_{1,I} + r_{1,II}$ . In the beginning of the reaction, at high concentrations of removable Cl, the first active site (denoted by part I) is dominating. In the last part of the reaction, at low removable Cl concentrations, the second active site (denoted by part II) is dominating. For Cl concentrations lower than  $C_{Cl^{**}}$ , the rate representing the first active site,  $r_{1,I}$ , is zero. For Cl concentrations higher than  $C_{Cl^{**}}$ , the rate representing the second active site,  $r_{1,II}$  is zero. Since the catalytic activity change is difficult to account for through elementary steps, the power law was used as a baseline for the derivation of  $r_{1,I}$  and  $r_{1,II}$ . The reduction rate is given by;  $r_1 = r_{1,I} + r_{1,II}$ ;  $r_{1,I} = k_{1,I} P_{C_2H_4} (C_{Cl} - C_{Cl^{**}})^2$ ;  $r_{1,II} = k_{1,II} P_{C_2H_4} (C_{Cl^{**}} - C_{Cl}) C_{Cl}$ . Similarly, the oxidation rate (Fig. 1b) derived from the power law is given by;  $r_2 = r_{2,I} + r_{2,II}$ ;  $r_{2,I} = \frac{k_{2,I} P_{O_2} (C_{CuCl} - C_{CuCl^*})^2}{1 + K_{eq} P_{O_2}}$ ;  $r_{2,II} = \frac{k_{2,II} P_{O_2} (C_{CuCl^{**}} - C_{CuCl}) C_{CuCl}}{1 + K_{eq} P_{O_2}}$ . The transient behaviour of the  $Cu^{2+}$  concentration was then derived from the derived expressions for the reduction and oxidation;

$$\frac{dC_{Cu^{2+}}}{dt} = r_2 - r_1 \quad (5)$$

A steady-state kinetic model incorporating the dynamics of the catalyst has been developed based on the kinetic models obtained for the transient reduction and oxidation process. The oxygen adsorption term was included for the roxidation and the final steady-state reaction rate expression becomes:

$$r = \frac{k_{2,I} C_{Cl,max}^2 P_{C_2H_4}^2 P_{O_2}}{(P_{C_2H_4} + k_{2,I} / k_{1,II} P_{O_2})^2 (1 + K_{eq} P_{O_2})} \quad (6)$$

There is an excellent match between the predicted (Eq.6) and experimental steady-state reaction rate. Figure 1c) shows the  $Cu^{2+}$  concentration during TOS for total catalytic cycle (Eq.1) by the model (Eq.5) and experiment. Spent catalyst after 40 min of total catalytic cycle is analyzed by XPS and it shows that  $Cu^{1+}$  is dominating, which further validates the developed kinetic model (Eq.5). The above reaction rate (Eq.5 and 6) is used to simulate industrial reactor in order to find out not only gas phase composition and temperature profile but also the distribution of  $Cu^{2+}$  in the reactor.

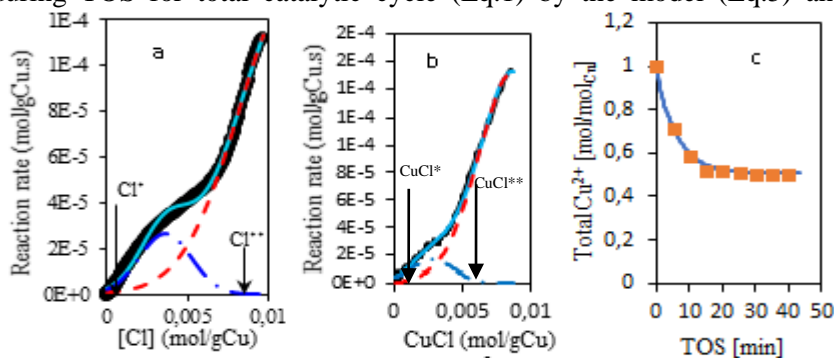


Fig. 1. Dependence of reduction a) and oxidation b) reaction rate on the removable chlorine concentration. Experimental reaction rate (●) fitted reaction rate,  $r_{1,I}$  and  $r_{2,I}$  (---); fitted reaction rate,  $r_{1,II}$  and  $r_{2,II}$  (- · - ·). c)  $Cu^{2+}$  with time on stream (TOS), experimental (—), kinetic model (■),  $C_2H_4:O_2:HCl = 1:1:2$

### 4. Conclusions

The kinetic model developed here predicts product distribution and catalyst composition, can be applied for rational catalysts design, as well as reactor simulation to predict the concentration and temperature profile, and  $Cu^{2+}$  distribution.

### References

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- [3] Rout, KR et. al. J. Catal. 2017, 352: 218-228.
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- [5] Baidoo, MF et. al., Catal. Today, 2017, <http://dx.doi.org/10.1016/j.cattod.2017.06.040>

### Keywords

Redox catalysis, Reaction kinetics, Catalyst design, Descriptor

## Curriculum Vitae

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**Name:** Kumar Ranjan Rout  
**Born:** 1981-05-25  
**Nationality:** Norwegian  
**Present position:** Research Scientist (since September 2016)  
Kinetics and Catalysis Research Group, SINTEF Materials and  
Chemistry, SINTEF, Trondheim, Norway.

**Degree:** PhD (Dr. ing.), Dept. of Chemical Engineering, Norwegian University of  
Science and Technology (NTNU), December 2012.

### Work Experience:

December 2012-September 2016: Post-doctoral Research Fellow, Catalysis and Reactor  
Technology, Dept. of Chemical Engineering, NTNU.

August 2008-December 2012: PhD Fellowship, Catalysis and Reactor Technology, Dept. of  
Chemical Engineering, NTNU.

### Research Areas

- 1) Synthesis and applications of nanomaterials including metal and oxide nanoparticles with controlled shape, size, morphology (core-shell) and surface compositions as catalysts and sorbents.
- 2) Kinetic study and modeling of gas-solid reactions by a highly integrated theoretical and experimental approach (in-situ study) focusing on different catalytic processes, i.e., steam methane reforming, dry reforming, CO<sub>2</sub> capture by solid sorbent, oxy-chlorination of ethylene, desulfurization from bio-syngas, catalytic aldol condensation and hydrodeoxygenation of biomass pyrolysis vapours.
- 3) Development of kinetic models based on catalytic/non-catalytic gas-solid reaction mechanism.
- 4) Steady-state- and dynamic multiphase reactor modelling for moving bed, fixed bed and circulating fluidized bed reactors to understand coupling between multi-phase flow phenomena and chemical kinetics, and mass- and heat transfer process in chemical reactors.
- 5) Design, build and operation of innovative reactors, applicable to CO<sub>2</sub> capture by solid sorbent and biomass fast pyrolysis.
- 6) Process design and techno-economic evaluation (TEE) for pre-and post-combustion CO<sub>2</sub> capture process and biomass fast hydrolysis for production of biofuel.

### List of Projects (Ongoing) as Project Manager from SINTEF

#### 1. H2BioOil-Integrated H2BioOil process for efficient biofuel production

Duration: 2015-2018

Budget: 1, 2 M USD

Project leader: Prof. De Chen, Dept. of Chemical Engineering, NTNU

Co-project leader: Dr Kumar Ranjan Rout, SINTEF

#### 2. MBCL-Moving Bed Carbonate Looping for Post Combustion CO<sub>2</sub> capture

Duration: 2017-2020

Budget: 4, 5 M USD

Project leader: Dr Asbjørn Strand, Fjell Technology Group AS, Norway

Co-project leader: Prof. De Chen, Dept. of Chem. Engg., NTNU, Dr Kumar Ranjan Rout, SINTEF

### 3. LTP3C Tech-Low Temperature Post Combustion CO<sub>2</sub> Capture Technology

Duration: 2017-2020

Budget: 1, 1 M USD

Project leader: Prof. De Chen, Dept. of Chemical Engineering, NTNU

Co-project leader: Dr Kumar Ranjan Rout, SINTEF

### 4. CLD-Chemical Looping Desulfurization of Producer Gas from Biomass Gasification

Duration: 2017-2020

Budget: 1, 2 M USD

Project leader: Prof. Edd Anders Blekkan, Dept. of Chemical Engineering, NTNU

Co-project leader: Dr Kumar Ranjan Rout, SINTEF

### 5. Oxychlorination of Ethylene-Center for industrial Catalysis Science and Innovation (iCSI)

Duration: 2016-2023

Budget for the oxychlorination work package: 3, 02 M USD

Work package leader to SINTEF: Dr Kumar Ranjan Rout, SINTEF

## Short Summary of Post-doctoral Research

### Part I: Multi-fluid circulating fluidized bed reactor model

*A multi-fluid Eulerian model has been derived from kinetic theory of granular flows, free path theory and an empirical friction theory. The numerical model implementation is based upon the Finite Volume Method with a staggered grid arrangement. The developed model is validated with data produced from the pilot plant producing 10 Nm<sup>3</sup>/h H<sub>2</sub> from upgraded biogas by sorption enhanced steam methane reforming (SE-SMR) process at the HyNor Lillestrøm, Oslo R&D hydrogen station.*

### Part II: Design, assemble and operation of macro Thermo Gravimetric Analyzer (TGA)

*A fixed/bubbling bed reactor is hanged on a balance system to study kinetics of non-catalytic gas-solid reaction system and well-controlled flow through the sample bed will ensure accurate measurement of the kinetics. The reactor can operate at high temperature and pressure with steam. The reactor system is highly desired for the various process, i.e., CO<sub>2</sub> capture by solid sorbent, Sulphur capture from bio-syngas using solid sorbent etc.*

### Part III: Design, assemble and operation of H<sub>2</sub>BioOil Pilot plant

*A pilot plant (H<sub>2</sub>BioOil) is designed and assembled consisting of entrained flow fast-hydrolysis reactor (FHP) and a fixed bed reactor for catalytic upgrading of pyrolysis vapours. The plant has the biomass feeding capacity of 1Kg/hr and can operated at 20-bar pressure. The plant can operate either in series (FHP and fixed bed reactor operates together) or in parallel (FHP and fixed bed reactor operates independently).*

## Short Summary of PhD Research

*Ca-based synthetic solid sorbent (CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>) was prepared using co-precipitation method and spray drying technique. N<sub>2</sub> adsorption, XRD and SEM are used to characterize the physical properties of the developed solid sorbent. Multi-cycle experiments were performed to study the kinetics of CO<sub>2</sub> capture by solid sorbent in a standard TGA. Gas-solid reaction kinetics depends on the effect of gas-solid contact. Therefore, a laboratory scale fixed bed reactor setup was built to study the kinetics of CO<sub>2</sub> capture by solid sorbent. Furthermore, a kinetic model was developed and fitted with the experimental data obtained from the fixed bed reactor setup. Multi-component mass diffusion models have been developed to calculate mass transfer limitations for a porous catalyst particle suitable to fixed bed- and bubbling bed reactors. Both the single and multiphase reactive flow models of the fixed bed reactors were developed solved and validated by the experimental data*

of laboratory scale fixed bed reactor for sorption-enhanced steam methane reforming (SE-SMR) process.

### PhD Candidates (ongoing), Co-supervisor

1. Shirley E. Liland: Development of Catalysts and Materials for Compact reformer.
2. Isaac Yeboah: Rational design of bi-metallic catalyst for Catalytic Aldol Condensation.
3. Jianyu Ma: Development of high temperature sorbent for S removal from bio-syngas.
4. Andreas Papageorgiou: Development of low temperature solid sorbent for CO<sub>2</sub> removal.

### Master Students, Co-supervisor

Ellinor Sofie Smith Wiker, Bilal Yousaf, Juejing Sheng, Erling Olav Sollund, Eline Nesdal Sundli, Ane Sofie Lilleng, Maria Olsvik, Siri Stavnes

### Invited/keynote Lectures

**Keynote lecture 1:** Rout K. R., Meyer J., Norheim A., and Jakobsen H. A. *Thermo Gravimetric Analyzer (TGA) Fixed-bed Reactor to study the kinetics of CO<sub>2</sub> capture with solid sorbent*, CHISA, 2014, Prauge, Czech Republic.

**Keynote lecture 2:** Rout K. R., Zhu J., Baidoo, M., Fenes E., Virgili G., Chen D. *New Approach of Kinetic Modeling of Redox Catalytic Cycles: Study of Ethylene Oxy-chlorination Process*, APCRE 2017, China

**Invited lecture 1:** Rout K. R. *CO<sub>2</sub> capture by Solid Sorbent: Application to Pre-combustion and Post-combustion Processes*. Johannes Kepler Universitat, Linz, Austria and Austrian Chemical Society, 2015

**Invited lecture 2:** Rout K. R., Zhu J., Baidoo, M., Fenes E., Virgili G., Chen D. Deactivation of Oxychlorination catalyst, Haldor Topsoe Catalysis Forum, 2015

### Patent

Chen D., Rout, K. R., Strand, A. Gas capture system, UK patent Filled, GB1703719.3

### Scientific Journal Papers

1. Rout, K. R., Fenes, E., Baidoo, M. F., Fuglerud, T., Chen, D. Understanding of K Promoter Effects on Oxychlorination of Ethylene by Operando Spatial-time Resolved UV-Vis-NIR Spectrophotometry, *J. Catalysis*, 2017, 352, 218-228

2. Baidoo, M. F., Fenes, E., Rout, K. R., Fuglerud, T., Chen, D. [On the effects of K and La co-promotion on CuCl<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts for the oxychlorination of ethylene](https://doi.org/10.1016/j.cattod.2017.06.040), *Catalysis Today*, <https://doi.org/10.1016/j.cattod.2017.06.040>

3. Wang, H., Blaylock, DW., Dam, AH., Liland, SE., Rout, K. R., Zhu, Green, WH., Holmen, A., Chen, D. [Steam methane reforming on a Ni-based bimetallic catalyst: density functional theory and experimental studies of the catalytic consequence of surface alloying of Ni with Ag](#), *Catalysis Science & Technology*, 2017 7 (8), 1713-1725

4. Rout, K. R., Baidoo, M. F., Fenes, E., Zhu, Z., Abdollahi, R., Fuglerud, T., Chen, D. Highly Active and Stable CeO<sub>2</sub> Promoted CuCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Oxychlorination Catalysts Developed by Rational Design Using Rate Diagram of Catalytic Cycle, *ACS Catalysis*, 2016, 6, 7030-7039

5. Rout K. R., Jakobsen H. A. A Numerical Study of Fixed Bed Reactor Modelling for Steam Methane Reforming Process. *Canadian Journal of Chemical Engineering*, 2015, Volume 93:7

6. Rout K. R., Jakobsen H. A. Simulation of pellet model with multicomponent mass diffusion closure using least squares spectral element solution method. *Canadian Journal of Chemical Engineering*, 2013, Volume 91 (9): 1547-1567

7. Rout K. R., Jakobsen H. A. A numerical study of pellets having both catalytic- and capture properties for SE-SMR process: Kinetic- and product layer diffusion controlled regimes. *Fuel Processing Technology*, 2013, Volume 106: 231-246

8. **Rout K. R.**, Hillestad M., and Jakobsen H. A. A numerical study of pellet model consistency with respect to molar and mass average velocities, pressure gradients and porosity models for methanol synthesis process: Effects of flux models on reactor performance. *Chemical engineering research & design*, 2013, Volume 91 (2): 296-317
9. **Rout K. R.**, Feroso, J., Chen, D., Jakobsen H. A. Kinetic rate of CO<sub>2</sub> uptake of a synthetic Ca-based sorbent: Experimental data and Numerical simulations. *Fuel*, 2013, Volume 120: 53-65
10. **Rout K. R.**, Jakobsen H. A. Reactor performance optimization by the use of a novel combined pellet reflecting both catalyst and adsorbent properties. *Fuel processing technology*, 2012, Volume 99: 13-34
11. **Rout K. R.**, Solsvik J., Nayak A. K., Jakobsen H. A. A numerical study of multicomponent mass diffusion and convection in porous pellets for the sorption-enhanced steam methane reforming and desorption processes. *Chemical Engineering Science*, 2011, Volume 66 (18): 4111-4126

### Oral Presentation

1. **Yeboah, I. Rout, K. R.**, Xuezhi, D. A tandem aldol and hydrodeoxygenation reactions of Bio-Oil oxygenates fraction to hydrocarbon, [North American Catalysis Society Meeting 2017](#), Denver
2. **Fenes, E.**, Baidoo, M. F., **Rout, K. R.**, Fuglerud, T., Chen, D Rational Design of CuCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> based Oxychlorination Catalysts, [North American Catalysis Society Meeting 2017](#), Denver
3. **Liland, SE**, Wang, Y, Qi, Y, **Rout, K. R.** Chen, D. Unprecedented Active and Stable Ni-Co Bimetallic Catalyst for Steam Methane Reforming: Combined DFT, Microkinetic Analysis and Kinetic Study, [North American Catalysis Society Meeting 2017](#), Denver
4. **Liland, SE**, Yousaf, B., **Rout, K. R.**, Wang, Y., Chen, D. Unprecedented Active and Stable Ni-Co Bimetallic Catalyst for Steam Methane Reforming. 16th International Congress on Catalysis, Beijing, China
5. **Fenes, E.**, Baidoo, M. F., **Rout, K. R.**, Fuglerud, T., Chen, D Quantitatively defining promotor influence on catalytic activity and stability in ethylene oxychlorination, Natural Gas conversion Symposium 2017, **Tromsø**, Norway
6. **Wang, Y.**, Xiao, L, Qi, Y., Liland, SE., **Rout, K. R.**, Zhu, Y., Yang, J., Chen, D., and Holmen, A. Microkinetic analysis of steam methane reforming over transition metal surfaces: Combined DFT calculations and UBI-QEP method, EuropaCat 2017, Florence, Italy
7. Fenes, E., Baidoo, M. F., **Rout, K. R.**, Fuglerud, T., Chen, D First Ionization energy as Descriptor of Alkali Metal Promoted Cu-based Oxychlorination Catalysts, EuropaCat 2017, Florence, Italy
8. **Rout, K. R.**, Fenes, E., Baidoo, M. F., Fuglerud, T., Chen, D. Kinetic Study of Oxychlorination Process by Combined in-situ Mass- and Spatial-time Resolved UV-Visible Spectrophotometry. EuropaCat, Kazan, Russia.
9. **Rout K. R.**, Fuglerud T., Chen D., Jakobsen H. A. Modeling and Simulation of Oxy-chlorination Reactor, ISCRE, 2014, Bangkok
10. **Rout K. R.**, Jakobsen H. A. CO<sub>2</sub> Capture by a Synthetic, CaO-based Sorbent in a Fixed-bed Reactor, Energy and Material Research Conference, 2012, Torremolinos, Malaga, Spain
11. **Rout K. R.**, Jakobsen H. A. Simulation of multi component mass diffusion pellet model using least square spectral element method for steam methane reforming process. CHISA 2012, Prauge, Czech Republic
12. **Rout K. R.**, Jakobsen H. A. Steady-state modelling of heterogeneous model of methanol synthesis. 2<sup>nd</sup> Trondheim Gas Technology conference, 2011, Trondheim, Norway
13. **Rout K. R.**, Jakobsen H. A. A Comparative Study Of Mass- And Mole Based Multi-component Diffusion In Porous Pellets For Steam Methane Reforming Process. 8<sup>th</sup> International Conference on COMPUTATIONAL FLUID DYNAMICS (CFD) in the Oil & Gas, Metallurgical and Process Industries, 2011, Trondheim, Norway

14. **Rout K. R.**, Solsvik J., Nayak A. K., Jakobsen H. A. A Numerical Study of Multi-component Mass diffusion and Convection in Porous Pellets for the Methanol Production. AIChE Annual Meeting 2010, Salt lake city, Utah, USA

### Poster Presentation

1. **Baidoo, M. F.**, Zhu, J., Virgili, G. A. Fenes, E., **Rout, K. R.**, Fuglerud, T., Chen, D Transient and Steady State kinetic study of the catalytic cycle of the oxychlorination of ethylene, Natural Gas conversion Symposium 2017, **Tromsø**, Norway
2. **Baidoo, M. F.**, **Rout, K. R.**, Fenes, E., Fuglerud, T., Chen, D. Rational Design of Cu-based Catalyst for Oxychlorination Process by Combined Mass Spectrometry and Spatial-Time Resolved *in situ* UV-Visible Spectroscopy. EuropaCat, 2015, Kazan, Russia.
3. **Rout K. R.**, Jakobsen H. A. Two-zone bubble bed reactor model for sorption enhanced steam methane reforming process. International Symposium on Chemical Reaction Engineering (ISCRE) 2012, Maastricht, The Netherlands.
4. **Rout K. R.**, Solsvik J., Jakobsen H. A. A Numerical Study of Multi-component Mass diffusion and Convection in Porous Pellets for the SE-SMR Process. Gas-to-Liquid 2010, Braga, Portugal.