

# Heterogeneous Reactions: A Review on Studies and Research with Emphasis on Kinetic Aspects

Sunil J. Kulkarni

Datta Meghe College of Engineering, Airoli, Navi Mumbai, Maharashtra, India.

Received: 10/01/2016

Revised: 13/01/2016

Accepted: 13/01/2016

## ABSTRACT

Chemical reaction engineering is important and one of the most important part of chemical engineering. The reactions are divided as homogeneous and heterogeneous. Heterogeneous reactions can be catalytic and noncatalytic. The catalytic reactions involve gas solid and solid liquid reactions. Kinetic modeling is important aspect from controllability and optimality point of view. Catalyst preparation and simulation of complex kinetics are areas of keen interest for investigators. The current review summarizes research on heterogeneous reactions.

**Key words:** kinetics, parameters, decomposition, catalyst, characteristics.

## INTRODUCTION

Chemical engineering contains two important areas, mass transfer and reaction engineering. The unit processes and operations such as absorption, adsorption, drying, and crystallization are being used as major operations in industries. [1-5] Many of these operations have environmental significance. [6-9] Chemical engineering involves many chemical reactions, both heterogeneous and homogeneous. The chemical reaction depends on temperature and pressure, which are two important operating parameters. Heterogeneous reactions are catalytic or non catalytic. [10] Various non catalytic reactions involve gas liquid, solid liquid and gas solid reactions.

## RESEARCH AND STUDIES ON HETEROGENEOUS REACTIONS

Delaat and Gallard carried out an investigation on catalytic decomposition of hydrogen peroxide by Fe (III) in homogeneous aqueous solution. [11] They described a kinetic model for the

decomposition of hydrogen peroxide by ferric ion in homogeneous aqueous solution (pH <3). According to them; the use of the kinetic model allows a better understanding of the effects of operational parameters. Their model adequately simulated the complex kinetics of decomposition of H<sub>2</sub>O<sub>2</sub> by Fe (III) in homogeneous aqueous solution.

A research was carried out by Mihut et al on kinetic and spectroscopic characterization of cluster-derived supported Pt–Au catalysts. [12] They prepared silica supported bimetallic Pt–Au catalysts. They observed that catalysts prepared by incipient wetness impregnation from individual Pt and Au precursors exhibited characteristics very similar to those of monometallic Pt catalysts. Bagdanoff and Stoltz carried out an investigation on palladium-catalyzed oxidative kinetic resolution with ambient air as the stoichiometric oxidation gas. [13] They discovered the most mild and selective conditions for the oxidative kinetic resolution of secondary alcohols by

catalytic palladium to date. The most important practical implications of their investigation were room temperature reactivity in nonflammable solvents and a significant increase in the resolution selectivity. Marwood et.al carried out an investigation on the catalytic hydrogenation of carbon dioxide. [14] They applied transient mechanism for carbon dioxide methanation. They suggested that presence of formate species was indicative of formate adsorbed on the surface.

Qi and Xiuyang investigated kinetics of non-catalyzed decomposition of d-xylose in high temperature liquid water. [15] They studied the kinetics of non-catalyzed decompositions of xylose and its decomposition product furfural in high temperature liquid water (HTLW) for temperature from 180 to 220°C and under pressure of 10MPa. Velonia et. al carried out an investigation on single enzyme kinetics. [16] They reported the direct observations of the real-time catalysis and substrate kinetics of a single-enzyme-catalyzed reaction, using a simple method, a robust enzyme. They were able to monitor single enzyme turnovers for extended periods of time (hours). They used these measurements to unravel hidden characteristics in the catalytic behavior of individual enzymes. According to them, the real-time catalysis and substrate kinetics of a single-enzyme-catalyzed reaction, is possible for a commonly used, robust enzyme by using confocal fluorescence microscopy and a simple method.

Wang and Lu carried out an investigation on carbon dioxide reforming of methane to produce synthesis gas over metal-supported catalysts. [17] They presented a comprehensive review on the thermodynamics, catalyst selection and activity, reaction mechanism, and kinetics of this important reaction. According to their studies carbon deposition causing catalyst deactivation is the major problem inhibiting the industrial application of the CO<sub>2</sub>/CH<sub>4</sub> reaction. According to them, in

order to avoid coking, the operating temperature must be in an optimal range (for CH<sub>4</sub>/CO<sub>2</sub> ratio of 1, 870-1040 °C). Yang et.al carried out an investigation on activation effect in the hydrolytic kinetic resolution of epoxides on [Co(salen)] catalysts confined in nanocages. [18] They concluded that the cooperative activation effect can be enhanced in the nanocage of mesoporous materials. They developed an efficient solid chiral catalyst for the hydrolytic kinetic resolution of epoxides. They also observed that the solid catalyst can be easily recycled by filtration without any apparent loss of catalytic activity.

Chen et. al carried out an investigation on kinetic isotopic effects in oxidative dehydrogenation of propane on vanadium oxide catalysts. [19] They measured kinetic isotopic effects (KIEs) for oxidative dehydrogenation of propane on 10 wt% V<sub>2</sub>O<sub>5</sub>/ZrO<sub>2</sub>. They observed that the methylene C–H bond is activated in the rate-determining steps for propane dehydrogenation and combustion reactions. They also found that the measured propane oxidative dehydrogenation KIEs were in agreement with theoretical estimates using a sequence of elementary steps.

Wei and Iglesia carried out an investigation on isotopic and kinetic assessment of the mechanism of reactions of CH<sub>4</sub> with CO<sub>2</sub> or H<sub>2</sub>O to form synthesis gas and carbon. [20] They used nickel catalyst in the experiments. They observed that turnover rates for forward reactions of CH<sub>4</sub>/CO<sub>2</sub> and CH<sub>4</sub>/H<sub>2</sub>O mixtures were proportional to CH<sub>4</sub> pressure (5-450 kPa) and independent of the partial pressure of the CO<sub>2</sub> or H<sub>2</sub>O coreactants (5-450 kPa). Li and Breaker investigated kinetics of RNA degradation. [21] They provided the kinetic parameters which provide theoretical limits for the stability of RNA polymers and for the proficiency of RNA-cleaving enzymes. Lee et.al explained a new methodology for the synthesis of homochiral compounds. [22] They

described an enzyme/metal combo reaction, EMCR for the dynamic kinetic resolution (DKR) of allylic alcohols.

Sanz et.al carried out an investigation on autocatalyzed and ion-exchange-resin-catalyzed esterification kinetics of lactic acid with methanol. [23] They presented the esterification kinetics of lactic acid with methanol without addition of catalyst and catalyzed by ion-exchange resins. They evaluated the effect of catalyst type, stirrer speed, catalyst size, catalyst loading, initial reactant ratio, and temperature on reaction kinetics. They observed that the reaction in the catalyst surface was the rate-controlling step. It was also observed that the reaction rate increased with temperature and catalyst loading. Steijns et.al investigated the mechanism of the catalytic oxidation of hydrogen sulfide. [24] They derived an oxidation-reduction mechanism from the kinetics of catalytic oxidation. According to these studies, the chemisorption of oxygen and the reaction between dissociatively chemisorbed H<sub>2</sub>S and chemisorbed oxygen were the rate controlling steps.

## CONCLUSION

The use of the kinetic model allows a better understanding of the effects of operational parameters. Catalysts prepared by incipient wetness impregnation from individual Pt and Au precursors exhibited characteristics very similar to those of monometallic Pt catalysts.

Carbon deposition causing catalyst deactivation is the major problem inhibiting the industrial application of the CO<sub>2</sub>/CH<sub>4</sub> reaction. The chemisorption of oxygen and the reaction between dissociatively chemisorbed H<sub>2</sub>S and chemisorbed oxygen are rate controlling steps in catalytic oxidation of hydrogen sulfide.

## REFERENCES

1. Sunil Jayant Kulkarni, Ajaygiri Kamalgiri Goswami, Nilesh Shinde,

- Treatment and Recovery for Flue Gases: a Review, International Journal of Research, 2015, 2(6), 515-519.
2. Sunil J. Kulkarni, Removal of phenol from Effluent in Fixed Bed: A Review, International Journal of Engineering Research and General Science, 2014, 2(4), 35-39.
3. Sunil J. Kulkarni, Ajaygiri K. Goswami, Adsorption Studies for Organic Matter Removal from Wastewater by Using Bagasse Flyash in Batch and Column Operations, International Journal of Science and Research, 2013, 2(1), 180-183.
4. Sunil J. Kulkarni, A Review on Studies and Research on Crystallization, International Journal of Research & Review, 2015, 2(10), 615-618.
5. Sunil Jayant Kulkarni, Ajaygiri Kamalgiri Goswami, Adsorption for Waste Gas Treatment: A Short Review, International Journal for Research in Applied Science & Engineering Technology, 2014, 2(12), 513-514.
6. S.J. Kulkarni, Dr. J. P. Kaware, Isotherm and Kinetics of Phenol Removal by Adsorption-A Review, International Journal of Research, 2014, 1(8), 287-293.
7. Sunil J. Kulkarni and Dr. Jayant P. Kaware, Removal of Cadmium from Wastewater by Groundnut Shell Adsorbent-Batch and Column Studies, International Journal of Chemical Engineering Research, 2014, 6(1), 27-37.
8. Veena Ramachandran, Tanmay Uttam Gound, Sunil Kulkarni, Biofiltration For Waste Gas Treatment- A Review, International Journal Of Ethics In Engineering & Management Education, 2014, 1(4), 8-13.
9. Sunil J. Kulkarni, Nilesh L. Shinde, A Review On Hydrogen Sulphide Removal From Waste Gases, International Journal Of Advanced Research In Science, Engineering And Technology, 2014, 1(4), 187-189.
10. Sunil J. Kulkarni, A Review on Studies and Research on Catalysts with Emphasis on Catalyst Deactivation, International Journal of

- Research & Review, 2015, 2(10), 410-414.
11. Joseph Delaat And Hervea Gallard, Catalytic Decomposition of Hydrogen Peroxide by Fe (III) in Homogeneous Aqueous Solution: Mechanism and Kinetic Modeling Environ. Sci. Technol., 1999, 33, 2726-2732.
  12. Corina Mihut, Claude Descorme, Daniel Duprez, and Michael D. Amiridis, Kinetic and Spectroscopic Characterization of Cluster-Derived Supported Pt–Au Catalysts, Journal of Catalysis, 2002, 212, 125–135.
  13. Jeffrey T. Bagdanoff and Brian M. Stoltz, Palladium-Catalyzed Oxidative Kinetic Resolution with Ambient Air as the Stoichiometric Oxidation Gas, Angew. Chem. Int. Ed. 2004, 43, 353–357
  14. Machel Marwood, Ralf Doepper, Albert Renken, In Siru Surface and Gas Analysis for Kinetic Studies under Transient Conditions: The Catalytic Hydrogenation of CO<sub>2</sub>, Environ. Sci. Technol., 1999, 33, 2726-2732.
  15. Jing Qi and Lu Xiuyang, Kinetics of Non-catalyzed Decomposition of D-xylose in High Temperature Liquid Water, Chin. J. Chem. Eng, 2007, 15(5), 666-669.
  16. Kelly Velonia, Ophir Flomenbom, Davey Loos, Sadahiro Masuo, Mircea Cotlet, Yves Engelborghs, Johan Hofkens, Alan E. Rowan, Joseph Klafter, Roeland J. M. Nolte, and Frans C. de Schryver, Single-Enzyme Kinetics of CALB-Catalyzed Hydrolysis, Angew. Chem. Int. Ed., 2004, 43, 2–6.
  17. Shaobin Wang and G. Q. (Max) Lu, Carbon Dioxide Reforming of Methane To Produce Synthesis Gas over Metal-Supported Catalysts: State of the Art, Energy & Fuels, 1996, 10, 896-904.
  18. Hengquan Yang, Lei Zhang, Lin Zhong, Qihua Yang, and Can Li, Enhanced Cooperative Activation Effect in the Hydrolytic Kinetic Resolution of Epoxides on [Co(salen)] Catalysts Confined in Nanocages, Angew. Chem. Int. Ed., 2007, 46, 6861–6865.
  19. Kaidong Chen, Enrique Iglesia and Alexis T. Bell, Kinetic Isotopic Effects in Oxidative Dehydrogenation of Propane on Vanadium Oxide Catalysts, Journal of Catalysis, 2000, 192, 197–203.
  20. Junmei Wei and Enrique Iglesia, Isotopic And Kinetic Assessment Of The Mechanism Of Reactions Of CH<sub>4</sub> With CO<sub>2</sub> Or H<sub>2</sub>O To Form Synthesis Gas And Carbon On Nickel Catalysts, Journal of Catalysis, 2004, 224, 370–383.
  21. Yingfu Li and Ronald R. Breaker, Kinetics of RNA Degradation by Specific Base Catalysis of Transesterification Involving the 2'-OH Group, J. Am. Chem. Soc., 1999, 121, 5364-5372.
  22. Donghyun Lee, Eun A. Huh, Mahn-Joo Kim, Hyun Min Jung, Jeong Hwan Koh, and Jaiwook Park, Dynamic Kinetic Resolution of Allylic Alcohols Mediated by Ruthenium- and Lipase-Based Catalysts, Organic Letters, 2000, 2(15), 1-4.
  23. M. T. Sanz, R. Murga, S. Beltrán, and J. L. Cabezas, Autocatalyzed and Ion-Exchange-Resin-Catalyzed Esterification Kinetics of Lactic Acid with Methanol, Ind. Eng. Chem. Res., 2002, 41, 512-517.
  24. M. Steijns, F. Derks, A. Verloop, and P. Mars, The Mechanism of the Catalytic Oxidation of Hydrogen Sulfide- Kinetics and Mechanism of Hydrogen Sulfide Oxidation Catalyzed by Sulfur, Journal Of Catalysis, 1976, 42, 87-95.

How to cite this article: Kulkarni SJ. Heterogeneous reactions: a review on studies and research with emphasis on kinetic aspects. Int J Res Rev. 2016; 3(1):73-76.

\*\*\*\*\*