

Chemisorption: a Review

Sunil Jayant Kulkarni

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

ABSTRACT

Chemisorption occurs due to chemical bonding and mostly this is irreversible. The adsorption is accompanied by liberation of heat, which is significant in chemisorption. Chemisorption phenomenon is very important for catalysis. In case of catalyzed reactions, the reactants adsorb on the catalyst active sites and forms complex. According to investigations by various researchers, the important phenomenon in chemisorption of metal ions is formation of chemical bonds between the surface of solids (adsorbent) and heavy metals.

Key words: Kinetic models, Rate limiting step, adsorption rate, thermal stability.

INTRODUCTION

Adsorption is one of the important unit operations in chemical engineering. Adsorption is classified as physical adsorption and chemical adsorption. Physical adsorption is reversible while chemisorptions are irreversible. Physical adsorption occurs due to Vander Waals forces of attraction. So the bonding is loose and reversible. Chemisorption occurs due to chemical bonding and mostly this is irreversible. The adsorption is accompanied by liberation of heat, which is significant in chemisorption. Chemisorption phenomenon is very important for catalysis. In case of catalyzed reactions, the reactants adsorb on the catalyst active sites and forms complex. Chemisorption and related mechanism studies are carried out by various investigators. Current review summarizes research and studies on chemisorption.

CHEMISORPTION: A REVIEW

Yu et.al. carried out studies on CO₂ capture by absorption and adsorption.^[1] In their review, they studied various mesoporous solid adsorbents impregnated with polyamines and grafted with aminosilanes. They also discussed factors

such as selection of adsorbent, cost, adsorption rate, CO₂ adsorption capacity, and thermal stability. They also proposed more effective and less energy-consuming regeneration techniques for CO₂-loaded adsorbents. Ho and McKay carried out an investigation on chemisorption kinetic models.^[2] In their work, they reviewed kinetic models describing the sorption of pollutants. They evaluated rate models including Elovich equation, the pseudo-first order equation and the pseudo-second order equation. Their study indicated that chemisorption processes could be rate limiting in the sorption step.

Peden et.al. used chemically modified Pd (10) for hydrogen absorption.^[3] According to their studies, submonolayer coverages of sulfur cause the kinetics to become surface dominated. The dissociative chemisorption of molecular hydrogen becomes the rate-limiting step. Al-Anber discussed chemisorptions.^[4] The adsorption approach was studied with respect to heavy metals. According to them the important phenomenon in chemisorption of metal ions is formation of chemical bonds between the surface of solids (adsorbent) and heavy metals (adsorbate). Sun and Weinberg

studied kinetics of dissociative chemisorption of methane and ethane on Pt(110).^[5] In their investigation, they measured initial probabilities of dissociative chemisorption of methane and ethane on the highly corrugated, reconstructed Pt surface. They kept gas temperature constant at 300 K and varied surface temperature.

Crowley et. al., in their work, studied heterogeneous reactions on solid substrates.^[6] In their work, they evaluated kinetic and photochemical data for atmospheric chemistry. Brinzari et.al. carried out investigation on chemisorptional approach to conductivity kinetics.^[7] They studied conductivity kinetics of thin film SnO₂: Pd gas sensors. They carried out experimental study and theoretical simulation of gas sensitive characteristics. They proposed the existence of neutral atomic form of chemisorbed oxygen. They determined rate of absorption/desorption reactions of molecular oxygen. Chin and Iglesia carried out investigation on catalytic CH₄-O₂ reactions on palladium.^[8] They examined elementary steps and their kinetic relevance in CH₄-O₂ reactions on Pd clusters by using kinetic and isotopic data and effects of cluster size. According to them, the root cause for reactivity differences is effects of cluster size and metal identity and their O* binding energy. Bao et.al. investigated a chemisorption refrigeration and power cogeneration system.^[9] Their investigation was one of its kind and they explored the possibility of a small-scale cogeneration unit by combining solid-gas chemisorption refrigeration cycle and a scroll expander. They identified proper operating conditions for cogeneration. They studied cogeneration performance for the viability of this concept by interrogating modeling of two components. Beurden carried out an investigation on catalytic aspects of steam-methane reforming.^[10] He discussed the chemistry of methane-steam reforming. He also dealt with properties of reforming catalysts. Stepova et.al. used modified bentonite for chemisorption of H₂S.^[11]

They studied mechanism and kinetics of this process. They analyzed the adsorbent by elemental and BET surface area analysis. Statistic t-criterion was used by them for studying models adequacy.

Centiand Perathoner studied reaction mechanism and control of selectivity in catalysis by oxides.^[12] Their emphasis was on the role of chemisorbed species on the surface reactivity. Zhan et.al. carried out an investigation on the principal reactions in coal oxidation at moderate temperature.^[13] They used thermo-gravimetric analysis coupled with differential thermal analysis (TGA/DTA) for mass change and heat evolution of a sample. Oxygen chemisorptions increase with increase in oxygen concentration. This, according to them, results in speeding up the oxidation process. Wei and Iglesia investigated kinetic and isotopic measurements for catalysts.^[14] Also they explored the conditions that rigorously excluded transport and thermodynamic artifacts. Chan et.al. carried out investigation on a kinetic characterization for the Diels-Alder reaction.^[15] They studied cyclopenta- diene with 2-mercaptobenzoquinone chemisorbed to a gold substrate. The reaction assumed pseudo first order kinetics and rate didn't increase linearly with the concentration of diene. Studies were carried out by Baltacioglu et.al. to study low temperature CO oxidation kinetics.^[16] They carried out reaction over activated carbon supported Pt-SnOx catalysts. The power function of rate expression inducted negative dependence on oxygen and positive dependence on carbon monoxide. According to Bond, as the size of supported gold particles falls below 3 nm, its activity to a number of oxidations and hydrogenations starts to increase dramatically.^[17] Also an increased propensity to chemisorption can be observed. According to them, kinetic activity is strength and extent of chemisorption of the reactants. Johansson et.al. carried out an investigation on adsorption of hydrogen on palladium and palladium hydride at 1 bar.^[18]

CONCLUSION

Adsorption is one of the important unit operations in chemical engineering. Adsorption is classified as physical adsorption and chemical adsorption. Physical adsorption is reversible while chemisorptions are irreversible. Physical adsorption occurs due to Vander Waals forces of attraction. So the bonding is loose and reversible. Chemisorption occurs due to chemical bonding and mostly this is irreversible. The adsorption is accompanied by liberation of heat, which is significant in chemisorption.

REFERENCES

1. Cheng-Hsiu Yu, Chih-Hung Huang, Chung-Sung Tan, "A Review of CO₂ Capture by Absorption and Adsorption", *Aerosol and Air Quality Research*, 2012, 12,745–769.
2. Y. S. Ho and G. McKay, "A Comparison of Chemisorption Kinetic Models Applied to Pollutant Removal on Various Sorbents", *Institution Of Chemical Engineers Trans Icheme*, November 1998, 76, Part B, 332-340.
3. Charles H.F. Peden, Bruce D. Kay and D. Wayne Goodman, "Kinetics of Hydrogen Absorption by Chemically Modified Pd(110)", *Surface Science*, 1986, 175, 215-225.
4. Mohammed A. Al-Anber, "Thermodynamics Approach in the Adsorption of Heavy Metals", Chapter from the book *Thermodynamics - Interaction Studies - Solids, Liquids and Gases*, Dr. Juan Carlos Moreno Piraján (Ed.), In *Tech Open*, 2011,1, 737-766.
5. Y.-K. Sunal, W. H. Weinberg, "Kinetics of dissociative chemisorption of methane and ethane on Pt(110)-(1 × 2)", *J. Vac. Sci. Technol*, May -Jun 1990, A 8 (3), 2445-2448.
6. J. N. Crowley, M. Ammann, R. A. Cox, R. G. Hynes, M. E. Jenkin, A. Mellouki, M. J. Rossi, J. Troe, and T. J. Wallington, "Evaluated kinetic and photochemical data for atmospheric chemistry: Volume V – heterogeneous reactions on solid substrates, *Atmos.*", *Chem. Phys.*, 2010,10, 9059–9223.
7. V. Brinzari, G. Korotcenkov, J. Schwanka, Y. Boris, "Chemisorptional Approach To Kinetic Analysis Of SnO₂/Pd-Based Thin Film Gas Sensors", *Journal of Optoelectronics and Advanced Materials*, March 2002, 4(1), 147-150.
8. Ya-Huei (Cathy) Chin and Enrique Iglesia, "Elementary Steps, the Role of Chemisorbed Oxygen, and the Effects of Cluster Size in Catalytic CH₄-O₂ Reactions on Palladium", *J. Phys. Chem.*, 2011, 115, 17845–17855.
9. Huashan Bao, Yaodong Wang, Anthony Paul Roskilly, "Modelling of a Chemisorption Refrigeration and Power Cogeneration system", *Applied Energy*, 2014, 119,351–362.
10. P. van Beurden, "On the Catalytic Aspects of Steam-Methane Reforming", *ECN-I--04-003*, Dec.2004, 1-27.
11. Kateryna Stepova, Yaroslav Gumnitsky and Duncan Maquarrie, "Mechanism And Mathematical Model of H₂S Chemisorption on Modified Bentonite", *Chemistry and Chemical Technology*, 2009, 3(3),169-173.
12. Gabriele Centi and Siglinda Perathoner, "Reaction Mechanism and Control of Selectivity in Catalysis by Oxides: Some Challenges and Open Questions", *Int. J. Mol. Sci.*, 2001, 2, 183-196
13. Jing Zhan, Haihui Wang, Feng Zhu, Shengnan Song, "Analysis on the Governing Reactions in Coal Oxidation at Temperatures up to 400°C", *International Journal of Clean Coal and Energy*, 2014, 3, 19-28.
14. Junmei Wei and Enrique Iglesia, "Isotopic and Kinetic Assessment of the Mechanism of Reactions of CH₄ with CO₂ or H₂O to Form Synthesis Gas and Carbon on Nickel Catalysts", *Journal of Catalysis*, 2004, 224,370–383.
15. Eugene W. L. Chan, Muhammad N. Yousaf, and Milan Mrksich, "Understanding the Role of Adsorption in the Reaction of Cyclopentadiene with an Immobilized Dienophile", *J. Phys. Chem.*, A 2000, 104, 9315-9320.
16. Fatma Soyal Baltacioglu, Berrin Gulyuz, Ahmet Erhan Aksoylu, Zeynep Ilsen Onsan, "Low Temperature CO Oxidation Kinetics over Activated

- Carbon Supported Pt-SnO_x Catalysts”, Turk J Chem., 2007, 31, 455 – 464.
17. Geoffrey C. Bond, “Chemisorption and Reactions of Small Molecules on Small Gold Particles”, *Molecules*, 2012,17, 1716-1743;doi:10.3390/molecules17021716.
18. M. Johansson, E. Skulason, G. Nielsen, S. Murphy, R.M. Nielsen, I. Chorkendorff, “Hydrogen Adsorption on Palladium and Palladium Hydride at 1 bar”, *Surface Science*, 2010, 604,718–729.

How to cite this article: Kulkarni SJ. Chemisorption: a review. *International Journal of Research and Review*. 2017; 4(4):15-18.

