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ROLE OF HETEROGENEOUS CATALYSTS IN CHEMICAL INDUSTRIES- A REVIEW

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Abstract*: A catalyst is a foreign matter that increases rate of chemical reaction, without taking part in the reaction. It may be homogeneous, heterogeneous or biocatalyst. For the last 50 years, catalyst has become heart of chemical industries for production of fuel, bulk chemicals, fine chemicals and pharmaceuticals. This review includes the role of heterogeneous solid catalyst in chemical industries. Various types of supported and unsupported catalyst are discussed. Which includes metal oxides, pure metal catalysts, zeolites, silica based molecular sieves. Important physical and chemical properties like surface area, pore size distribution, surface acidity, pore volume that characterizes catalyst are summarized. Important catalytic reactions in petroleum refinery those have satisfied requirement of desired fuels are discussed, applications those have contributed significantly in growth of chemical industries, society and environment are also mentioned.

Keywords: **Heterogeneous catalyst, Molecular sieve, Supported catalyst, Unsupported catalyst, Zeolite**

I. INTRODUCTION

Catalyst is a substance, when used in chemical reaction increases the rate of reaction. The first effect of catalysis was observed by Faraday near 1800s [10]. He examined ability of Platinum to accelerate oxidizing reaction. Catalyst provide alternative path to reactants to form product. It reduces activation energy of the reaction, and hence increases the rate of reaction. Catalyst may be homogeneous, heterogeneous or biocatalyst (enzymes) [15]. It may vary from an atom to a molecule of large structure of zeolites or enzymes [7]. On the basis of only stoichiometric non catalytic reactions, chemical industries of 21stcentury could not have developed to its present status. Rate of reaction can be increased by changing parameters such as temperature, pressure and concentration. But change in these parameter may be harsh for operation or more expensive. Thus in present scenario, performing non catalytic reactions are economical not viable. Here in this review, we have discussed role of particularly heterogeneous solid catalyst in chemical industries. Supported and unsupported catalysts are discussed in detail. Various physical and chemical properties, such as surface area, pore size distribution, surface acidity which characterizes catalysts are discussed. Finally the

application of various successful catalysts in refineries and petrochemical industries are listed.

II. MECHANISM OF CATALYSIS AND PROPERTIES OF CATALYST

A solid compound which is used as catalyst in either liquid or gas phase reaction is termed as heterogeneous catalyst. This solid catalyst is a porous in nature. Reactant molecules diffuses from bulk to catalyst surface, from surface to the inside the pores. Where it adsorbs, reacts to form product on catalytic sites. Formed products desorbs back to pore mouth and then in bulk.

Figure 1: catalytic reaction between A and B [7]

These solid catalysts are characterized by physical and chemical properties. Performance of catalytic reaction depends on physical structure, morphology of catalysts. Therefore various advanced analytical methods are used in catalysis research to characterize solid catalysts and to search for correlations between structure and performance of catalysts. Specific surface area measured in terms of m^2/gm of catalyst gives idea of available free surface of catalyst. Specific surface area of various catalyst ranges from 50 m^2/gm to 1500 m^2/gm [17]. Surface area is measured by adsorption and desorption of liquid nitrogen. This is known as BET analysis.

Pore size of catalyst is one of the most important property of catalyst. Depending on the size of pore, catalysts are classified into microporous (pore size < 2nm), mesoporous (2-50 nm) and macro porous (> 50 nm) catalyst [1]. Molecules enter in catalyst pore depending on size of molecules and size of pore. Molecules which have large diameter cannot enter smaller diameter pores. Thus Porosity of catalyst plays important role in petroleum industries because of higher molecular size hydrocarbons are present in crude oils. In case of supported catalyst, metal is loaded on support material. In this type of catalyst active catalytic part is only metal particle but not the support. It is important to know the actual catalytic area of catalyst. To know this, chemisorption of gas like H_2, CO, NO, N_2O are used. These gases permanently adsorb on metal particle and will not adsorb on support surface. Crystallite size and crystallite size distribution of catalyst is determined by X-ray diffraction method [1], While Morphology of crystallite is observed by electron microscopic techniques. Another important property of catalyst is its acidity in most hydrocarbon conversion. Acidity is measured by temperature programmed desorption of base, which is pre-adsorbed on catalyst.

III. CLASSIFICATION OF CATALYSTS

Catalysts are important in many chemical reactions, such as processing of fuels, bulk and fine chemicals. Some catalysts are simple in form of pure metal particles while some are combination of complex compounds.

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A) Metal oxides

Metal oxides catalysts are made up of combination of metal and oxygen atoms. Depending on the metal, these catalysts have different electronic properties. Various metal oxides include Al_2O_3,SiO_2, TiO_2, NiO, ZnO, TiO, NbO, MCM-41, ZrO_2, and MgO [11]. Out of all these oxides, Al_2O_3 and SiO_2 are the most common. These are used as either pure active material or used as support for other active materials.

B) Molecular sieves

Alumino-silicates are most common and complex multicomponent oxide used as catalyst. These molecular sieves are made up of specific framework. Al atom is attached to four Oxygen atom. Si atom is also attached to four oxygen atoms. Successive attachment of these primary units forms framework. All types of Zeolites come into this category of molecular sieves. These zeolites are crystalline microporous materials having pore diameter of 0.3-0.7 nm [8]. This specific pore size enables it as shape selective catalyst [14]. Thus it allows reactant molecules having diameter <0.7 nm. Zeolites Y (faujasite), mordenite, beta, ZSM-5 are successful catalysts among the all zeolites. Besides these zeolites other molecular sieves like AlPO (alumino phosphate) and SAPO (silicoaluminophosphate) are emerging as new generation catalysts [8].

C) Metals

Pure metal catalyst have played important role in industrial catalytic process [12]. Raney nickel, Pt gauze, Ru, Co, Pd has been prepared with surface area of 30-100 m^2/g [3]. Advantage of these types of pure metal catalyst is that they possess high activity. In some case these metals are loaded on support material like alumina and silica to enhance efficiency of the metal catalysts.

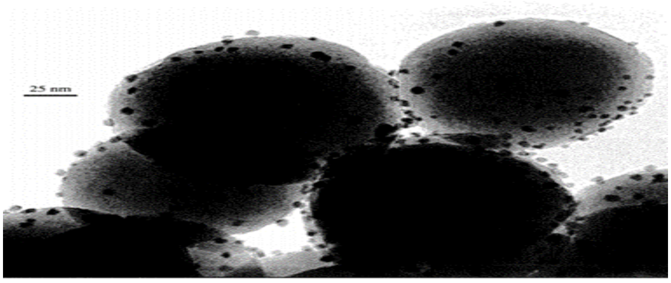

Figure 2: Rhodium metals supported on silica support [9]

D) Carbides

Carbides of some transition metals are unique. They have melting point more than 3000 K, hardness more than 2000 kg/mm^2 strength > 3000 MPa [13]. Two important carbides are of tungsten and molybdenum. They can be synthesized with surface area of 100-300 m^2/gm. These carbides have potential to replace rare earth catalyst [16].

E) Metal – Organic Frameworks

Metal organic frameworks (MOFs) are crystalline, highly porous solids. Metal ion is attached with long chain organic molecule, which forms three dimensional porous channel same as in case of molecular sieves. First MOF was synthesized in 1999 of Zn metal [6]. It was named MOF-5 and It's specific area was found to be 2900 m^2/g. MOF-177 has an even larger specific surface area of 4500 m^2/g [5].These MOFs have low thermal stability, thus not used at high temperatures. Palladium MOFs have successfully catalysed alcohol oxidation and olefin hydrogenation reactions [4]. Researchers have high expectation from these MOFs in field of catalysis.

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TABLE 1: INDUSTRIALLY IMPORTANT CATALYST AND THEIR ROLE [1, 7, 15, 17]

Reaction	Catalyst	Detail
Hydroprocessing	CoMo or $NiMo/Al_2O_3$	Removal of sulfur, nitrogen compounds from HC stream.
Reforming	Pt, Pt–Re	Reforming of naphtha to gasoline
Cracking	Zeolite Y, ZSM-5	Catalytic cracking of crude oil
Alkylation	Mordenite	Aromatic alkylation
	Zeolite beta	Aliphatic alkylation
MTG	ZSM-5, silicate-I	Methanol to gasoline
	Fe	Ammonia synthesis from N_2 and H_2
Oxidation	Silver metal	Oxidation of ethylene to ethylene oxide
	platinum – Rhodium grids	Ammonia oxidation in the nitric acid process
Polymerization	Cr, $TiCl_4/MgCl_2$	Polymerization of ethylene, propylene
Fischer Tropsch synthesis	Fe/Co on alumina	Direct production of hydrocarbon chains from synthesis gas.
	ZnO/Al_2O_3	Methanol synthesis from syn gas
Reforming	Ni on Al_2O_3	Steam reforming of methane to CO + H_2
Hydrogenation	Ni metal	Hydrogenation of vegetable oils
	Cu (as chloride)	Vinyl chloride (ethylene + Cl_2)
oxidation	V_2O_5	Sulfuric acid production
Automobile exhaust	Pt/Rh or Pd/Rh gauze	Pt/Rh or Pd/Rh converts NO_x, CO and HC to N_2, CO_2, and H_2O
NO_x reduction	V_2O_5 on TiO_2	control of NO_x emissions from nitric acid plants and power stations
VOC removal	Pt/Pd on Al_2O_3	Volatile organic compound oxidation at lower temperature of 200-400 ^oC

IV. CONCLUSION

- Catalysts have found tremendous applications in process industries. Without using catalysts it is almost impossible to manufacture chemicals in economical way.
- These catalysts have some specific life time. So deep search is required to increase life of catalysts.
- Modifications are required to increase strength, cryrstalinity and surface properties of catalysts to increase their effectiveness.
- Such catalysts should be synthesized those can replace conventional rare earth catalyst.

REFERENCES

[01] A.W. Chester and E.G. Derouane, Zeolite Characterization and Catalysis, Springer Science, 2009.

[02] E. Wagner, T. Fetzer in G. Ertl, and H. Kneozinger, Handbook of Heterogeneous Catalysis, Vol. 4, Wiley-VCH, Weinheim p. 1748, 1997.

[03] E. Wagner, T. Fetzer, H. Kneozinger, J. Weitkamp ,Handbook of Heterogeneous Catalysis, Vol. 1, Wiley-VCH, Weinheim, p.130, 1997.

[04] F. X. L. I. Xamena, A. Abad, A. Corma, H. Garcia, J. Catal. 250 , 2007.

[05] H. K. Chae, D. Y. Siberio-Perez, J. Kim, Y. Go, M. Eddaoudi, A. J. Matzger, M. O'Keefe, O. M. Yaghi, Nature 427, 2004.

[06] H. Li, M. Eddaoudi, M. O'Keefe and O. M. Yaghi, Nature 402, 1999.

[07] I. Chorkendorff and J. W. Niemantsverdriet, Concepts of Modern Catalysis and Kinetics, 2nd Ed. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2007.

[08] J. M. Thomas, R. G. Bell, and C. R. A. Catlow, Handbook of Heterogeneous Catalysis, Vol. 1, Wiley VCH, Weinheim, p. 286 1997.

[09] K. Datye , Topics in Catalysis, vol. 13, Kluwer Academic 2000

[10] O. Deutschmann, H. Knozingere, K. Kochloefl and T. Turek Heterogeneous Catalysis and Solid Catalysts Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2009.

[11] R. K. Grasselli and J. F. Brazdil: Solid State Chemistry in Catalysis, ACS Symposium Series 279, Amer. Chem. Soc., Washington, 1985.

[12] R. Schleogling, H. Kneozinger and J. Weitkamp , Handbook of Heterogeneous Catalysis, Vol. 1, Wiley-VCH, Weinheim, p. 54, 1997.

[13] S. J. Tauster, Acc. Chem. Res. 20, 1987.

[14] S. M. Csicsery. Shape-selective catalysis in zeolites, ZEOLITES, Vol 4, 1984.

[15] S. M. Roberts and G. Poignant, Catalysts for Fine Chemical Synthesis: Hydrolysis, Oxidation and Reduction. Volume 1, John Wiley & Sons, Ltd, 2002.

[16] S. T. Oyama, G. Ertl, H. Kneozinger and J. Weitkamp, Handbook of Heterogeneous Catalysis, Vol. 1, Wiley-VCH, Weinheim, p. 132, 1997.

[17] Santi Kulprathipanja, Zeolites in Industrial Separation and Catalysis. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2010.

