

The Ever Changing Faces of Catalysis

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1 Introduction

Catalysis is essentially a surface Phenomenon. Most of the industrial and natural processes are only taking place at the surface. In this sense, the basis understanding of these processes has to be different from the general science knowledge that one normally acquires in education by studying the bulk processes. Understanding the surface is essentially more difficult than studying the bulk material, since sustaining the surfaces in the same condition for long duration for examination is difficult. There are a variety of surface species that can be present which are usually termed as the “active centres”[1] and many of these centres have characteristics different from that of the similar species in the bulk like the coordination geometry (both number of surrounding species and also the geometrical distance to the neighbours), ad atoms, and vacancy. A simple representation of a possible defect surface is shown in Fig.1. Processes taking place on the surface have many features which are different from the processes taking place in the bulk. Catalysis in its various manifestations accounts for any country’s economy and also for the energy needs and to some extent environmental cleanliness. Even though thermal catalysis was predominating till recently, today there are other means of activating and among them both

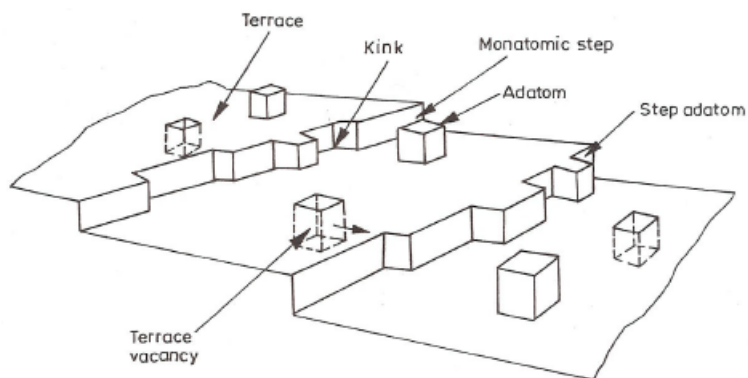


Figure 1: Representative model of a surface with the active species indicated

photocatalysis and electrocatalysis seem to be dominating the research efforts. This situation has arisen due to the fact that reactions like decomposition of water for fuel production, reduction of carbon dioxide for completing the energy cycle and synthesis of ammonia from reduction of dinitrogen are engaging the attention of catalyst scientists and the efforts have been intensified in the last three to four decades even since Fujishima and Honda [2] demonstrated the possible decomposition of water on TiO_2 surfaces. Historically, heterogeneous catalysis started in identifying the so called active sites, but the situation is complicated since the active sites are not only those that are a priori present on the surface but can also manifest at the call of the reactant molecules (surface reconstruction or surface segregation) as well normally inactive sites can become active by spill-over phenomenon. Catalyst scientists have spent decades of intense research in identifying these active sites and also to formulate governing principles for the generation of these active sites. Originally, in the absence of experimental tools to directly view these active sites, the identification of these active sites have been attempted in terms of so called structure activity correlation a technique popular in drug manufacture. These correlations can be based on the lattice parameters (geometric factor) or electrical properties (number of charge carriers, density of states and other related parameters) and these correlations have been used to identify the most active surfaces. These correlations mostly identified in the form of volcano shaped and notable contributions have come from the group of Noreksov et al.[3]. They have also proposed three dimensional correlations diagrams for identifying the optimized catalyst system. These attempts to identify and optimize the active sites led to the development of a host of techniques that could probe surface species at the molecular level. These techniques mostly operate in the mode of employing one of the four particle (electrons, ions, neutrals and photons) or four field (thermal, electrical, magnetic and sonic waves) which induce the emission of particle beams whose analysis in terms of number, chemical identity energy and angular distribution provide the necessary information on the structure, geometry and energy state of the adsorbed state. These techniques have been successfully employed for elucidating the structure and reactivity of adsorbed species which have provided a number of vital information for formulation of active catalyst system[4]. However, these developments have been successful in identifying the possible active sites in a functioning catalyst and the predictive possibility appears to be limited at present.

2 Designing of Catalysts

The designing and fabrication of catalysts with appropriate textural and other surface functions have been important and most challenging till now. The recently developed method, namely Liquid Crystal Templating mechanism has been extensively employed for generating solid surfaces with surface areas of 1000s $\text{m}^2 \text{g}^{-1}$. This methodology has opened up an avenue for generation of area, surface function modulated solids which can be exploited as active catalyst materials. In general, in this method a surfactant forms a micelle around which the inorganic precursor deposits and subsequently the surfactant is removed to generate architected solid material. In essence the possibilities so far exploited are given in Table 1.

Table 1: The possible modes of generating porous solids[5]

	Surfactant	Inorganic precursor	type	Example
Direct pathway (ionic interactions)	cationic Anionic	anionic cationic	S^+I^- S^-I^+	MCM MCM type materials
Mediated pathways (ionic Interactions)	cationic Anionic	cationic anionic	$S^+X^-I^+$ $S^-M^+I^-$	Acid Prepared Materials (APM)
Neutral Pathways (Hydrogen bonding)	Neutral Neutral	neutral neutral	S^0I^0 N^0I^0	Hexagonal Mesoporous silica Mesoporous Structural Units
ligand assisted pathways (covalent)	neutral ,	neutral ,	S-L ,	Tech Molecular Sieves (TMS) ,

3 Photo-catalysis

According to the glossary of terms used in photo-chemistry [IUPAC 2006 page 384] photo-catalysis is defined “as the change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible or infra red radiation in the presence of a substance the photo-catalyst that absorbs light and is involved in the chemical transformation of the reaction partners.” When a semiconductor (or an insulator) is irradiated with light of suitable wavelength corresponding to the energy of the band gap, electrons occupying the usually or mostly filled energy levels in the valence band will be transferred to an allowed energy state in the normally empty conduction band thus creating a hole in the valence band. This electron-hole pair is known as exciton. These photo-generated electron-hole pairs promote the so called redox reaction through the adsorbed species on the semiconductor or insulator surface. However, the band gap of the insulators will be usually high and as such generating of such high energy photons will not be comparatively easy and hence insulators are not considered as possible candidates for Photo-catalysis. Generally, metals cannot be employed as photo-catalysts since their occupied and unoccupied energy states are overlapping with respect to energy and hence the recombination of electron-hole pair will be the most preferred process and hence the conversion of photon energy to chemical energy using metals will not be advantageous. However in recent times due to the possibility of making materials in nano state, a new phenomenon is reported which is called plasmonic catalysis caused by the plasmon excitation on metal particles. This aspect will be briefly discussed in a subsequent section.

It is generally considered that the energy position of the top of the valence band of a semiconductor is a measure of its oxidizing power and the bottom of the conduction band is a measure if its reducing capacity. It is therefore necessary one has to know with certain level of certainty the energy positions of the top of the valence band and bottom of the conduction band so that the reactions that these excitons can promote can be understood. Photo-catalytic destruction of organic pollutants in water is based on photo-chemical process involving semiconductors. When a semiconductor is irradiated with UV (usually but it can be any other radiation as well) light of wavelength appropriate for excitation from valence band to the conduction band of the chosen semiconductor an exciton is created. The photo-chemical oxidation of the organic substrate normally proceeds by the adsorption of the substrate on the surface of the semiconductor

Table 2: comparison of electro-catalytic activities of various electrodes for methanol oxidation

catalyst	EAS ($\text{m}^2.\text{g}^{-1}$)	Onset potential(V)	I_f/I_b	mass activity ($\text{mA}.\text{g}^{-1}$ Pt)	specific activity $\text{mA cm}^{-2}\text{Pt}$
Pt/C	23.3	0.41	0.80	191	0.81
Pt/STA-C	33.0	0.31	1.11	37	1.12
Pt-Ru/C	17.2	0.30	0.91	204	1.18
Pt-Ru/STA-C	25.6	0.24	1.05	53	1.96
Pt-Ru(JM)	22.5	0.25	0.95	271	1.20

EAS = ElectrochemicalActive area; STA = silicotungstic Acid; I_b and I_f are current in backward and forward sweep of voltage.

with transfer of electrons with the hole generated. However other possible oxidation processes can also take place with radicals generated (OH radical if the solvent is water) at the surface of the semiconductor surface. Thus a variety of surface reactions are possible and photocatalysis can thus be in future employed for the generation or production of chemicals as well.

4 Electrocatalysis

Electro-catalysis and bio-catalysis have some common features. Of late electro-catalysis has assumed importance especially for the reduction of carbon dioxide.[6]. Keggin type poly oxometallates have been already employed for promoting chemical reactions either in homogeneous or pseudo-liquid phase conditions. Their electro-chemical activity is evaluated for Oxygen Reduction Reaction (relevant for the development of fuel cells and other electrochemical energy conversion devices).

The comparison of electro-catalytic activities of various electrode materials towards methanol oxidation(relevant for Direct Methanol Fuel Cells, DMFC)is given in Table 2.

5 Challenges Still in Catalysis

There are still some challenging aspects to be unravelled in catalysis. Some of them have been already initiated and some of them have to be explored. Let us list some of them at least.

- (1) Methanol production from methane;
- (2) syngas production by the oxidation of methane (natural gas);
- (3) ethylene production from methane;
- (4) methane to higher hydrocarbons;
- (5) ethanol from dimethyl ether;
- (6) Hydrogen peroxide production from molecular hydrogen and oxygen;
- (7) Nitric acid synthesis from nitrogen water and molecular oxygen.

Some of the reactions that have been already attempted but satisfactory activity levels have not yet been reached. These include (1) asymmetric synthesis; (2) water splitting for fuel production,(3) Carbon dioxide reduction to fuels or to generate useful chemicals and (4) photochemical reforming and (5)photo-

catalytic removal of pollutants. It must be remarked that the listing is only indicative and one should not consider the listing to be comprehensive. Efforts are on in each of these to develop appropriate catalyst for making the process economically viable but still there is no final word that had been said on any of these processes.

6 ROLE OF CATALYSIS IN SUSTAINABLE DEVELOPMENT

Sustainable development is generally defined as “Development, which meets the needs of the present without compromising the ability of future generations to meet their own needs”. The implication is that human development should be such as to “enable all people to meet their basic needs and improve their quality of life, while ensuring that the natural systems, resources and diversity upon which they depend are maintained and enhanced both for their benefit and for that of future”. A major impediment in achieving sustainable development is the environmental damage being caused by rapid population growth and industrialization. . It is now believed that catalysis can play a major role in environment protection (if not in reversing the damage already done) and enable sustainable development by a number of ways. Basically, catalysis can help in (i) primary pollution control through non-polluting processes that are atom efficient and produce negligible waste, (ii) secondary pollution control through end-of-pipe solutions, (iii) use of economically attractive alternate feedstocks, (iv) use of renewable feedstocks, (v) producing bio-degradable products, (vi) development of energy efficient processes and (vii) routes to alternate energy. The world catalyst business today is about US dollars 11 billion, of which nearly 30 % is in the area of environment catalysts (auto-exhaust, de-NOx etc). The rest of the business is shared nearly equally between refining, chemical and polymer industries. As stated earlier, one of the challenges lies in the conversion of natural gas to syngas and producing fuel from syngas through a variety of ways as shown in Fig.2. The most preferred source of alternate fuels is biomass,

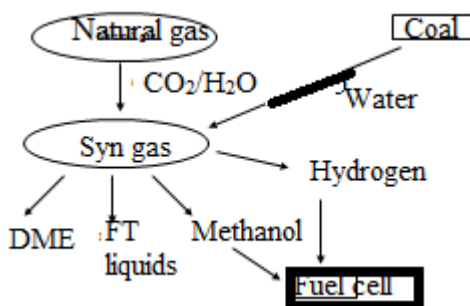


Figure 2: natural gas to syngas and subsequent transformation to fuels and chemicals

such as cellulosic materials like bagasse, wood chips, straw, and vegetable oils. Effective use of these materials and discontinuing the use of fossil fuels should

decrease the overall CO₂ load in the atmosphere as the production of these raw materials will help in depleting atmospheric CO₂. These raw materials can be converted into fuels and chemicals as shown in Fig. 3.

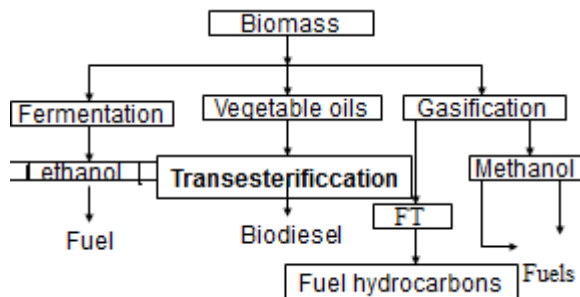


Figure 3: conversion of biodiesel for fuels

7 Summary

Catalysis plays a major role either in the conversion to fuels or for the production of chemicals (bulk or fine). The route adopted in the catalytic route may be considered to be a green process as compared to other chemical routes. Hence catalysis can play a vital role in a sustainable society.

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