

Advances in Catalysis in Recent Times

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Catalysis facilitates the methods of changing the conversions at which chemical bonds are formed or broken. Research and development in the field of catalysis is fast undergoing changes.

This article, discusses new developments in the field of catalysis and elaborates on different processes for enhanced efficiency.



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Introduction

Literature and questions?

Catalysis, as we all know, is a multi-disciplinary science. Research and development in this field are fast undergoing changes with respect to time with the advent of sophisticated techniques which can resolve the “active sites” at the molecular level.^[1] It is a known fact that the major source of energy is found in chemical bonds. Catalysis facilitates the methods of changing the conversions at which chemical bonds are formed or broken. One of the advantages of catalytic processes is the concept selectivity in which the desired product is produced over an undesired one.^[2] Today, the catalyst scientists and engineers are attempting to understand how to design materials so that energy conversion will become economically viable and environmental degradation could be reduced to a large extent.

Even with this rapid and sophisticated developments in this field, there are still many unresolved questions, even though they are currently text book knowledge. We shall cite a few examples.^[3]

- (a) The epoxidation of ethylene with silver as catalyst:

Different conflicting models have been proposed on how the composition of the silver surface influences the selectivity of this reaction. The nature of surface oxygen species which determines the selectivity of the catalyst is still not established.

- (b) The hydrogenation of ethylene on metal surface:

The exact structure of the surface and adsorbed species during the reaction are still not unambiguously resolved? The points to be resolved are: is it the naked metal surface, or the surface filled with organic intermediates are the active sites or active species?

- (c) Basic insight into the synthesis of Zeolites for use as catalysts:

What role does molecular template recognition play in building intermediates at a molecular level, when producing a zeolite? Or is the building of the structure a collective process, in which molecules are reorganized in a gel, without molecular recognition on a piecemeal basis?

- (d) The role of particle size effect in the famous Fischer

Tropsch synthesis:

Several groups have reported on particle size effects for cobalt catalysts in Fischer Tropsch synthesis. These effects have been denied by the statement “cobalt is cobalt is cobalt”. In these days, one may notice the postulation of a theory to understand the (non-)existence of the particle size effect.

- (e) Photo-catalyst or photo-electrochemical electrodes for the splitting of water: In spite of nearly 5 decades of intense research in this area with over nearly a few hundreds of semiconductors examined as possible materials, even then, there is not even a single material which will promote the photo/electro-decomposition of water to generate fuel hydrogen economically and in a commercially viable manner.^[4]

- (f) Material development for the reduction of carbon dioxide and dinitrogen: This area is pursued vigorously today. Even though number of studies have been already reported, still the extent of reduction products is at milli- or micro-mole levels.^[5] These are some of the typical issues for which exact answers are yet to evolve.

The main objective of nano-catalysis is to produce catalysts with 100% selectivity, high activity, low energy consumption, and long lifetime. This can be achieved only by controlling the size, shape, spatial distribution, the facet exposed, ratio of surface to bulk composition and electronic structure, and thermal and chemical stability of the individual nano-components.

2. The Status of Energy Conversion Process

Even though we have not yet succeeded in evolving a viable process for the generation of hydrogen for use as combustion fuel, there are other avenues in energy conversion processes where considerable progress has been made. Even in the photo-catalytic or photo-electrochemical decomposition of water, the introduction of new materials namely organic inorganic perovskites typical example being methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) has shown promise in converting photon energy into electricity (solar cells) or generating fuel hydrogen greater than 20% efficiency. The bottlenecks in exploiting such materials for utilizing solar energy conversion can be expected to be solved soon.^[6]

In the conventional fossil fuel scene, there are improvements in cracking heavy crude oil. Research in FCC (Fluid Cracking Catalyst) catalysts and processes is still alive even though this process is known for over 80 years. The changes in the available feedstocks, other renewables and light oils, and the demand for propylene, gasoline, and middle distillates require devel-

opments in both catalyst and process. Resolution in the modern analytical tools enables the nanometer-range particles being thoroughly analyzed which revealed the interaction between the matrix and the zeolite, and analysis of the pore system in both micro- and meso-pore range.

However, modern sophisticated analytical tools examine a limited number of catalyst particles while industrial practice involves particles many orders of magnitude higher. The interpretations based on the observations on a few particles should be carefully and with caution extended to situations in industrial practice especially when one wants to fine tune the catalyst performance. The challenges in this endeavour and the ways to overcome them are summarized in Table 1.

Since the improvements in conventional FCC catalysts will have far reaching consequences in terms of coke burning and green-house gas emission, examination of these catalyst systems under operando conditions has become the necessity today.

3. Alternate Activation of Molecules – Photo-catalysis

In addition to the conventional thermal catalysis, other forms of activation will be increasingly employed in the future. One of the already taking the centre stage is photocatalysis. Even though activation by photons is not a new concept, the available powerful light sources like Lasers have hastened this type of activation of molecules. Ever since water photoelectrochemical decomposition was demonstrated by Fujishima and Honda^[8], this mode of activation has come into prominence. Photocatalysis has been pursued effectively in the last two or three decades due to various reasons including the use of solar radiation. One way of harnessing solar radiation is the so called solar or photovoltaic cells, wherein the light energy is directly converted into electricity. The anxiety to introduce new materials for photocatalysis has paved the way for a new generation of solar cell materials, namely, the hybrid organic inorganic perovskites. There are many reports on the studies on the use of these materials as photocatalysts and it will occupy the attention of scientists for next few years.^[9]

Photo-catalysis has attained a prominent position in these years. The basic principle of photo-catalysis generation of electrons in the conduction band (reducing power) and hole in the valence band (oxidizing power) and their use in subsequent redox reaction. The values of the redox potentials are usually associated

Challenges in the development of modern FCC	How to face them
1. Cracking of the bottom of the barrel (resid or heavier feedstocks)	Matrix must be more accessible Pore structure in the catalyst must be tuned. The catalyst must be tolerant to poisons
2. Improve selectivity to propylene	Specific catalysts and process parameters Alternate zeolites may be used
3. Selectivity to middle distillates	Matrix must be made more active Control over hydrocracking by zeolites
4. Biomass conversion	Tolerance to poisons (especially to alkaline metals) Tolerance to the high acidity of bio-oils

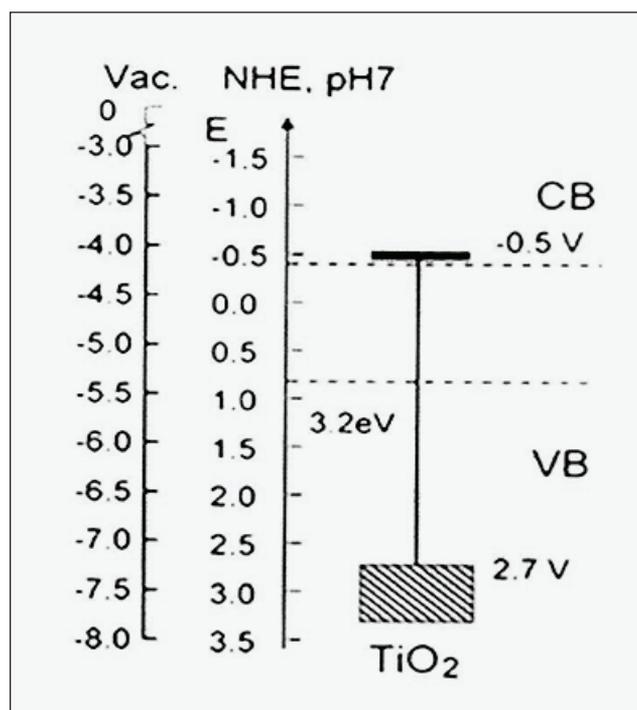


Fig.1. The positions of bottom of the conduction band and top of the valence band for TiO₂ semiconductor. The potential values are given both in electrochemical scale and absolute scale on the left. On the right the water decomposition potentials to evolve hydrogen and oxygen are given at a pH value of 7.

with the position of the top of valence band (oxidation potential) and bottom of the conduction band (reduc-

tion potential) in electrochemical scale (refer to Fig.1.).

These values are assumed to be the same as determined from measurements at semiconductor/air interface (for example from diffuse reflectance measurements) or computed by semi-empirical methods. The values of the redox potentials may be decided based on semiconductor/solution interface. The redox potential values may be considered as floating parameters when considered at the interface under catalytic reaction conditions. This may be one way to mimic natural photosynthesis.

4. Carbon dioxide Based Processes

Carbon dioxide, so far considered as a waste material, has been considered as a valuable C1 starting material source for the generation of a variety of chemicals and fuels.^[10] In Table 2 typical potential values are given for CO₂ reduction to various products. In addition, CO₂ can also be converted to useful chemicals by other means and typical ones are shown in Table 3. A more comprehensive listing is available elsewhere for example ref.10.

Another catalytic reaction that will receive attention in the coming years is the Nitrogen Reduction Reaction (NRR). Electrocatalysts based on conducting polymers and metal-phthalocyanine complexes showed low ammonia yield under ambient conditions.^[12] In essence, great efforts are necessary to improve either electrocatalysts or noble metal-based catalyst development (for example some early transition metals and metal chalcogenides) for ammonia synthesis under ambient conditions. Some other exotic systems like FeN₄ and other metal nitrides have been shown to be active for NRR reaction theoretically but they have to be proved experimentally.

5. Biomass Conversion Processes

There is a change in the starting feedstock from fossil fuels to biomass. Biomass conversion

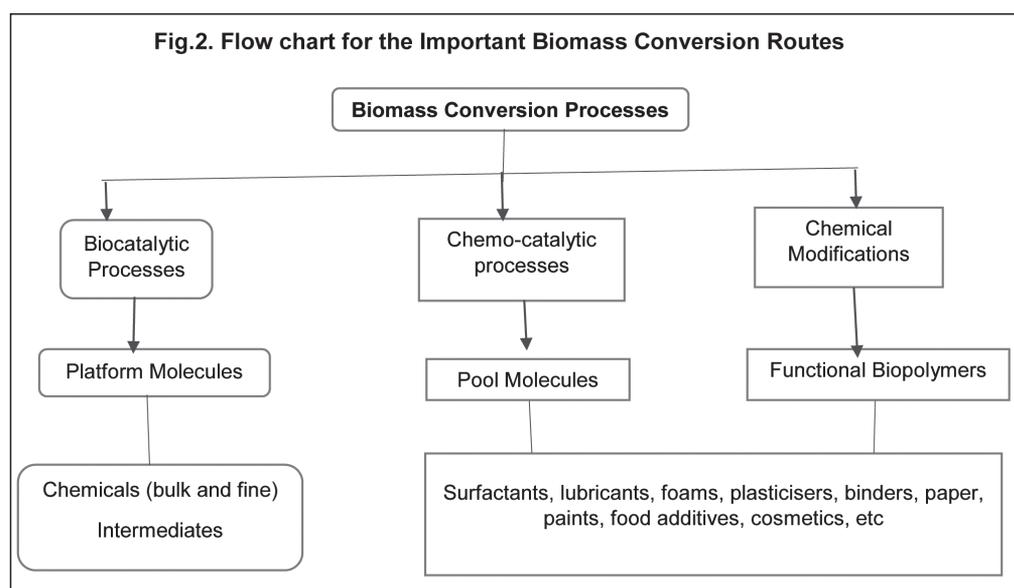
Table 2. Standard reduction potentials for CO₂ reduction reactions and hydrogen evolution reaction at pH 7. [Reproduced and expanded from ref.11]

Reaction	E ⁰ [V vs SHE]
2H ⁺ (aq)+2e ⁻ → H ₂ (g)	- 0.414 V
CO ₂ (g)+e ⁻ → CO ₂ ⁻ (aq)	- 1.85 V
CO ₂ (g)+H ⁺ (aq)+2e ⁻ → HCOO ⁻ (aq)	- 0.67 V
CO ₂ + 2H ⁺ + 2e ⁻ → HCOOH	- 0.61 V
CO ₂ + 2H ⁺ + 2e ⁻ → CO + H ₂ O	- 0.53 V
CO ₂ (g)+H ⁺ (aq)+2e ⁻ → CO(g)+OH ⁻ (aq)	- 0.52 V
CO ₂ (g)+3H ⁺ (aq)+4e ⁻ →H ₂ CO(l)+ ⁻ (aq)	- 0.49 V
CO ₂ + 4H ⁺ +4e ⁻ → C = 2H ₂ O	- 0.20 V
CO ₂ (g)+5H ⁺ (aq) +6e ⁻ → CH ₃ OH(l)+OH ⁻ (aq)	- 0.40 V
CO ₂ + 6H ⁺ +6e ⁻ → CH ₃ OH + H ₂ O	- 0.38 V
CO ₂ (g)+6H ⁺ (aq)+8e ⁻ →CH ₄ (g)+2OH ⁻ (aq)	- 0.25 V
CO ₂ + 8H ⁺ + 8e ⁻ →CH ₄ + 2H ₂ O	-0.24 V
2CO ₂ + 14H ⁺ + 14 e ⁻ → C ₂ H ₆ +4H ₂ O	- 0.27 V
3CO ₂ + 18H ⁺ + 18e ⁻ → C ₃ H ₇ OH + H ₂ O	- 0.31 V

Table 3. Typical modes of activation of carbon dioxide and the typical products formed in each method [adopted from ref.11].

	Category	Typical product
CO ₂ transformation	Chemical (non-hydrogenative)	Carbonates, carbomates, etc
	Chemical (hydrogenative)	Hydrocarbons, MeOH, EtOH etc
	Photochemical	Co, HCOOH, CH ₄
	Electrochemical	CO, HCOOH, CH ₃ OH
	Biological	EtOH, Sugar, CH ₃ COOH
	Reforming	CO + H ₂
	Inorganic	Carbonates, M ₂ CO ₃

to platform chemicals and fuels will be the major endeavour that will be pursued in the coming years since it will be one of the sustainable pathways.^[13] A huge number of chemical products can be manufactured from biomass as starting material. Though alternate



pyrolysis or gasification routes are already known, processes through depolymerization and fermentation of biopolymers are now extensively examined for building intermediates, specialties and fine chemicals. Even in this attempt these processes need to be cost competitive with respect to the alternate synthesis routes from fossil resources since these chemicals already have a market. These conversions based on alternate raw material source can be considered to follow green chemistry principles. A flow chart for the possibility is shown in Fig.2.

6. Nanomaterials as Efficient Catalysts

Nano-catalysis is a fast-growing field that use nano-materials as catalysts for a variety of homogeneous and heterogeneous catalysis. Heterogeneous catalysis represents one of the oldest commercial practices of nanoscience; nano-state of metals, semiconductors, oxides, and other compounds have been already widely used for important chemical reactions.

Although studies employing surface analytical tools have contributed to our understanding of catalysis, most commercial catalysts, are still produced by mixing, shaking and baking and after treatment of mixtures of multi-components; their nanoscale structures are not well controlled and the synthesis-structure-performance relationships are poorly understood. Due to their complex physico-chemical properties at the nanometer scale, even characterization of the various active sites of most commercial catalysts proves to be still elusive.

The main objective of nano-catalysis is to produce catalysts with 100% selectivity, high activity, low energy consumption, and long lifetime. This can be achieved only by controlling the size, shape, spatial distribution, the facet exposed, ratio of surface to bulk composition and electronic structure, and thermal and chemical stability of the individual nano-components. The use of nano state of catalysts can give rise to various benefits in chemical industry which include energy efficiency, reduced environmental effects, waste water treatment, optimum use of feedstock, non-harmful chemicals as catalysts, minimum chemical waste and above all improved economy.

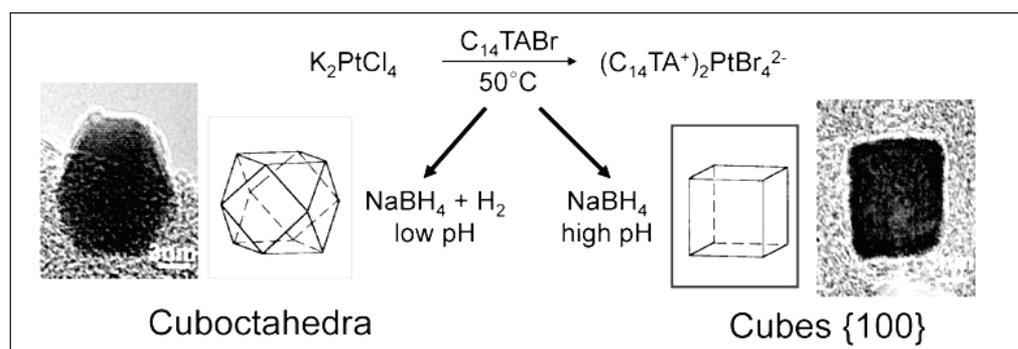


Fig.3. Preparation strategy for two differently shaped Pt nano-particles [reproduced from Ref 15]

One of the major achievements of the use of nano-state of catalysts is the profound effect of dimensionality (exposure of (111) face of iron produced nearly 600 times more ammonia as compared to other planes like (110) or (100) planes of iron catalyst) on the observed catalytic behavior. This can have serious consequences in our future generation of energy conversion (fuel cells, batteries and super capacitors) devices.

7. Perspective

The field of catalysis is at the cross road of success and sophistication or complexities. The identification of the so-called 'active site' and their control under catalytic ambient conditions (temperature, pressure, field) appeared to be uphill processes till now, but the advent of modern surface analytical tools have facilitated these processes.

New and efficient synthesis procedures have been developed for precise control of size, shape and chemical identity of the active sites thus ensuring selectivity and high turn-over numbers (TON).

Today the science and technology of catalysis are undergoing tremendous transformations. As an example, the preparation of different size and shaped nano scale Pt particles is illustrated in Fig.3.

The known best example of nano-catalysis is the gold nano-particles (around 5 nm) loaded on titania support which can promote the CO oxidation and epoxidation of hydrocarbons at room temperature^[16]. Similarly, in energy conversion (especially in carbon management) and transport, nano-materials with their characteristic quantum size effects can be advantageously employed.^[17]

Even in conventional thermal catalysis, hydro-talcites even when they are transformed into binary or ternary mixed oxides promote a variety of organic

transformations effectively.^[18]

With the application of a variety of surface analytical tools like various Electron Microscopies, (TEM, SEM, STM, AFM and so on) X-Ray Photoelectron Spectroscopy and its variations (like XPS, EXAFS, NEXAFS, XES and so on), one can look forward to a time scale where rational design of catalysts will become a reality.

The theory and practice of catalysis could now be resolved at molecular or atomic level and thus aim at 100% selective conversion in the desired direction. This situation will not only improve our understanding of the process of catalytic action but also contribute in a positive manner to the economy of the country.

Acknowledgement: *The author wishes to record his grateful thanks to Department of Science and Technology, Government of India for the establishment and support of the National Centre for Catalysis Research at Indian Institute of Technology, Madras.*

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