

Catalysis for Energy and Environmentally Benign Technologies

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Abstract: Catalysis research for energy and environment has a tremendous opportunity to improve our environment. The environmental catalysis has made a step forward and it is a more challenging pathway for innovation in science relying on many disciplines. New catalytic process can produce clean up as well as cleaner technologies. The challenges for catalysis research in the 21st century are identified, based on the current knowledge of catalysis researchers, recent fundamental and applied developments and current long-term objectives of the global energy and environmental protection processes. Any process efficiency now assigns economic values to eliminate waste and avoiding the use of hazardous chemicals and there are many exciting new developments in the application of organic synthesis work.

Also catalysis is likely to become a key element in the conversion of liquid and or gaseous fuels into hydrogen for fuel cells application. Several catalyst systems are likely to emerge for different fuel cell types and on different fuel processors. The present catalyst technology need further progress in catalyst development and integration, cost reduction and successful field test program for fuel-to-fuel cell processor to eventually gain general customer acceptance.

This presentation briefly discusses the R & D work currently under exploration at IICT that illustrates the catalytic technologies for solving environmental issues to provide sustainable development. The lessons learned in the past and related achievements will be illustrated and discussed to emphasize the role of environmental catalysis as a driver for improving quality of life, health and environment.

Keywords: Heterogeneous Catalysis, Environment, Clean Technology, Zero Waste, Green Chemistry, Fuel cells

Introduction:

Catalysis process research has a tremendous opportunity to improve our environment. Catalysis is the backbone for the chemical industries as well as for energy production. New catalytic processes that generate less waste, the waste conversion to co-products, to protect ozone layer, to combat the greenhouse effect, to create environmentally safer transport and to solve environmental problems of energy production will bring development of environmentally safer products. This overview presentation describes energy and environmental catalyst technology R&D problems carried out in our laboratory that offer an insight into future manufacturing practices. The manufacture (using green chemistry) of chemicals with decreased waste and pollutants will continue to be actively pursued by many chemical

manufacturers with increasing successes. New and cleaner catalytic routes are changing the way in which bulk and fine chemicals are made. Green manufacturing will continue to be a high priority for chemical production well into the 21st century. The catalytic R & D work in our group is divided into catalysis for energy and environment and has experienced a long period of growth and it is impossible to cover or even to mention all the significant contributions made over several years of hard research work. In view of this an attempt is made here to briefly describe the recent representative contributions in energy and environmental areas to our judgement of the developed process work in green manufacturing and clean energy production.

The conversion of different forms of energy has been central importance in Science and Technology. The R & D developments in several aspects of

environmental catalysis are required for cleaner water, air and soil. Research for an integrated catalytic reforming for fuel cells and catalytic combustion promise power generation with ultra low emissions are under the investigation world wide. New and cleaner catalytic routes are changing the way in which bulk and fine chemicals are made. Shelton et al. [1] described the two useful measures of environmental impact of chemical process by E-factor defined as mass ratio of waste to the desired product, and the atom utilization calculated by dividing the molecular weight of all substances produced in stoichiometric equation. Processes employing acids and bases requiring neutralization or stoichiometric redox reagents represent the major source of waste production in the form of salts and heavy metals and have high E-factor and low atom utilization [1-3]. Reactions employed in fine chemicals industry particularly include Friedel-Crafts alkylations, acylations, protection of functional groups, mediated by Lewis acids such as AlCl_3 , FeCl_3 , BF_3 , reduction with metal hydrides or metals such as zinc or iron and stoichiometric oxidations with dichromate or permanganate, all of which generate prohibitive amount of industrial waste. The work up of products from nitrations, sulphonations and many other acid catalyzed reactions involves neutralizations and concomitant generation of salts such as NaCl , Na_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ generate industrial waste.

Catalysts are used to convert environmentally hazardous materials into harmless compounds. The photochemical oxidation reactions are now members of so called Advanced Oxidation Processes. In this presentation it is also "focused" on the perspective of photocatalytic purification process for industrial wastewaters and their usage in organic synthesis too.

Catalysis for Fuel-to-Fuel cells

There is a growing interest in the use of H_2 as an alternative fuel mainly due to environmental aspects. For hydrogen generation to fuel cell systems reforming

technologies from various fuels is one of the main field of investigation. There are four basic methods for hydrogen production as present; water electrolysis, gasification reactions, partial oxidation reactions of heavy oils and steam reforming reactions. Catalysis is likely to become a key element in the conversion of liquid or gaseous fuels into hydrogen for fuel cells. This conversion, commonly referred to as fuel processing, most often involves, either hydrocarbons, like methane, propane/LPG, and higher liquid hydrocarbons or alcohols, e.g methanol, n-dodecane (diesel fuel) and ethanol although, in principal, any hydrogen contain compound may be applied, such as di-methyl ether and ammonia. Alcohols could constitute a good supply of hydrogen, as they are efficient hydrogen reservoirs and could avoid the difficulty of hydrogen distribution.

In this context many efforts have been applied in our group to the production of hydrogen from reforming of methanol by using several home made catalysts as well as methanol synthesis and LT shift catalysts (4a-d). A series of Cu-Zn-Al-O catalysts were prepared and characterized by TPR, surface area, metal area, XRD and SEM-EDAX analysis. All those systems were evaluated and correlation of activity and stability of methanol steam reforming catalysts with Cu/Zn ratio derived by SEM-EDAX analysis is observed. The stability of these catalysts is also supported by the method of preparation, low temperature reducibility and the presence of reversibly oxidizable Cu species observed by TPR of fresh and used catalyst as given in reference (4-c).

Laboratory and industrial results elucidate the general features of the deactivation of supported metal catalysts in various fuel-to-fuel cell reactions. Most catalyst types formulations contain stabilizers and promoters. They can be alumina, alkaline earth oxides and other oxides. These additional materials have several roles, including the inhibition of sintering and absorption of catalyst poisons. Many are susceptible to thermal sintering via surface

migration process. Operating temperatures must be restricted, usually, using below 300°C especially for copper based catalysts.

Alkylations and Acylations

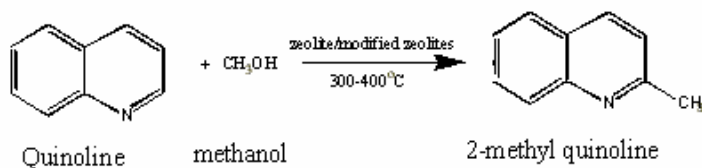
Alkylations are the most important reactions in organic chemistry while heterogeneously catalysed alkylations by Friedel-Crafts reactions are well known. Catalyst like AlCl₃, TiCl₄, BF₃, FeCl₃ used in the conventional Friedel-Crafts reactions are replaced because of corrosive nature, economic factors and other environmental

problems. The introduction of zeolites as alternative catalysts has proved to be a major break through in the acid catalysed reactions because of their reusability, shape selectivity, high thermal stability and they can be easily tailored to fit the desired reaction. Alkyl quinolines are widely used in metallurgy, corrosion inhibitors in polymers, and as analytical reagents in toxicology and in the synthesis of agrochemicals and they are prepared by alkylating quinoline with high selectivity using zeolites and modified zeolites.

Selective synthesis of 2-methyl quinoline over Zeolites

Selective vapour phase synthesis of 2-methyl quinoline by alkylation of quinoline with methanol was carried out over HY, HZSM-5(30), CrHY, CeHY, LaHY, LaKHY and CeHZSM-5(30) zeolites in a fixed bed reactor at atmospheric pressure. The yield of 2-methyl quinoline over modified zeolites especially of doubly promoted LaKHY was found to be higher

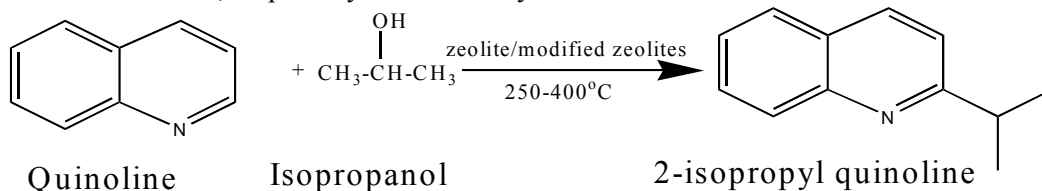
than those of unmodified zeolites. The maximum yield of 2-methyl quinoline obtained was 60.6 wt% at 91.5 wt% selectivity over LaKHY zeolites (Table 2). The active sites responsible for the methylation were found to be more Lewis acidic sites that are available over zeolite systems [5].



Vapour Phase isopropylation of quinoline over hy Zeolites

The vapour phase isopropylation of quinoline is carried out over HY and modified HY. The yield of 2-isopropylquinoline was higher over modified zeolites; especially over doubly

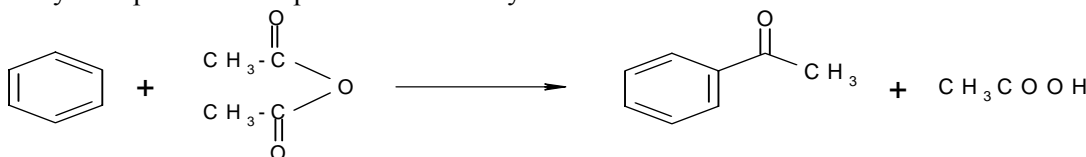
promoted LaKHY zeolites the maximum yield of 2-isopropyl quinoline obtained was 48.8% with 82.9% selectivity. The reaction favours on moderate Lewis acidic sites [6].



Benzene Acylation to Acetophenone over cehzsm-5

Benzene acylation was carried out with acetic anhydride as an acylating agent in vapour phase over HZSM-5 (Si/Al=30 & 280), HY, V modified HZSM-5(30) zeolite catalysts at atmospheric pressure. The yield of acylated product acetophenone selectivity

was found to be 95% at 86.4% conversion of acetic anhydride over Ce-modified HZSM-5(30) where Bronsted acid sites are active for this reaction [7].



Vapour Phase Acylation of Furan and Pyrrole over Zeolites

Vapour phase acylation of furan and pyrrole was carried out over HZSM-5 (19.7), HZSM-5(30), HZSM-5(280), CeHZSM-5(30), LaHZSM-5(30), HY and CeHY zeolites. The catalytic activity of zeolite catalysts was dependent on reaction temperature and the

type of cation promoter used in the modification of the zeolite surface. The activity of catalysts varied with the acidity of the zeolite systems tested and the yields of 2-acetyl furan and 2-acetyl pyrrole are 67.5% and 75.5% respectively [8].

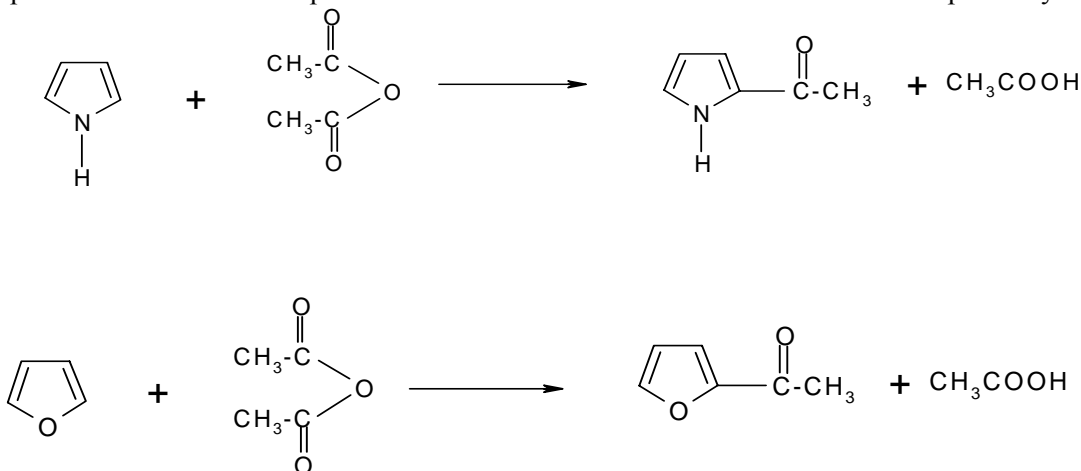


Table 1: Salient features of studies on Friedel Crafts alkylation and acylation reactions of the compounds tested are presented below

Catalyst	Substrate	Alkylating/ Acylation agent	T _R ° C	Feed molar ratio	Product	Yield Wt%
LaKHY	quinoline	Methanol	350	1:3	2-methyl quinoline	60.6
LaKHY	quinoline	Iso-propanol	350	1:3	2-propyl quinoline	48.8
LaKHY	toluene	n-propanol	300	1:1	p-cymene	68.5
HZSM-5(30)	furan	Acetic anhydride	150	1:1	2-acetyl furan	67.5
HZSM-5(280)	pyrrole	Acetic anhydride	250	1:1	2-acetyl pyrrole	75.5
CeHZSM-5(30)	benzene	Acetic anhydride	250	1:2	Aceto phenone	82.1

Weight hour space velocity = 0.5h⁻¹ Reaction temperature = T_R

Feed molar ratio = Substrate: Alkylating / acylation agent

Vapour phase Synthesis of anthraquinone from phthalicanhydride and benzene over chromia based catalysts: an Eco-friendly Process

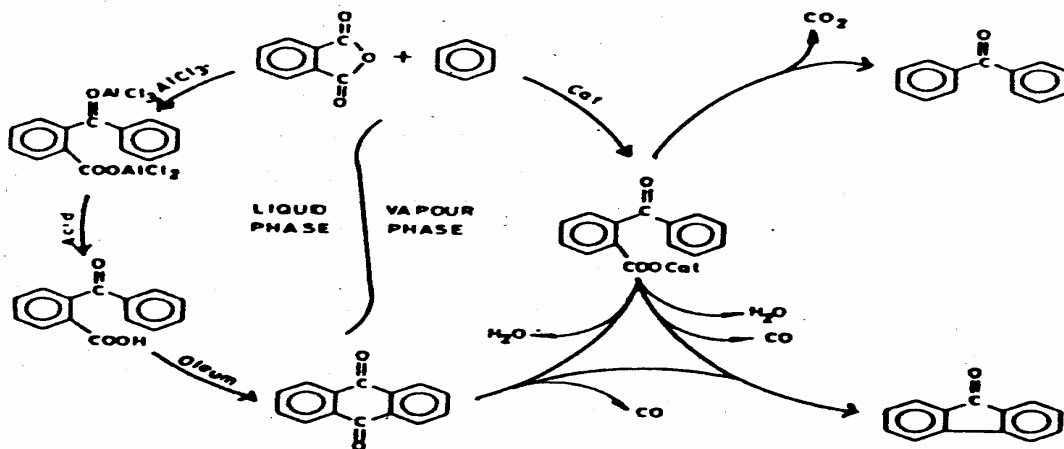
The conventional route for the synthesis of anthraquinone is a two step process. Use of Lewis acid like AlCl_3 as a catalyst to condense phthalic anhydride and benzene is the first step and dehydrocyclisation of the

intermediate o-benzoylbenzoic acid to anthraquinone in oleum is the second step. A convenient acylation of benzene with phthalic anhydride was carried out in a down flow reactor at atmospheric pressure in the temperature range of 300 to 430 °C using Cr_2O_3 / magnesol and the results are given in Table 2 (Fig:1) [9].

Table 2: vapour phase condensation of benzene and phthalic anhydride over chromia and magnesol

Catalyst	Composition	Reaction temp °C	Carrier gas	% PTHAN conversion	BEPN	% Selectivity 9- FNONE	Anthro-quinone
AQCAT-1	9% Cr_2O_3 / MgO + SiO_2	430	CO_2	4	25	8	30
			CO_2	17	27	19	28
AQCAT-2	9% Cr_2O_3 / Magnesol	430	CO_2	28	17	11	26
AQCAT-3	12% Cr_2O_3 / Magnesol	350 430	CO_2	9	45	7	27
			CO_2	35	40	10	18
AQCAT-4	18% Cr_2O_3 / Magnesol	400	CO_2	62	38	26	25
AQCAT-5	18% Cr_2O_3 / Magnesol	400 430	CO_2	24	30	19	31
			CO_2	57	44	33	6
AQCAT-6	9% Cr_2O_3 / Magnesol	430	N_2	52	20	12	21

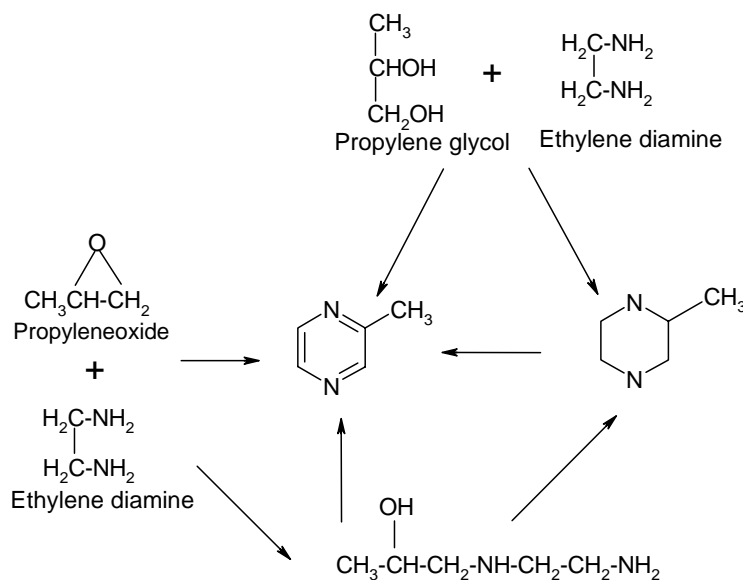
PTHAN= phthalic anhydride, BEPN = Benzopnenone, 9-Fluronone



Synthesis of 2-methyl pyrazine

2-methyl pyrazine (2-MP) is the pivotal intermediate for obtaining 2-cyanopyrazine

and on hydrolysis gives pyrazinamide, a well known anti-tubercular drug. 2-MP can be synthesized by various methods [10] as is shown in the scheme.



β - Hydroxypropylethelenediamine

Vapour Phase Esterification of Carboxylic acids with Primary and Secondary Alcohols over $\text{H}\beta$, HZSM-5 , HY , DHY , and $\gamma\text{-Al}_2\text{O}_3$: an Ecofriendly Route

Industrial methods for the synthesis of esters involve the use of mineral acids such as H_2SO_4 , H_3PO_4 and ion exchange resins. Application of solid acids like metal oxides and zeolites in the place of mineral acids is highly desirable as such processes are environmentally safe. Esterification of acetic acid with $\text{C}_2\text{-C}_4$ alcohols is studied over $\text{H}\beta$, HZSM-5 , HY , DHY , and $\gamma\text{-Al}_2\text{O}_3$ in the Table-3 Esterification of Acetic Acid with $\text{C}_2\text{-C}_4$ alcohols

Acid:Alcohol (1:1 molar ratio) ml/hr	% conv. 100	% conv. 125	% conv. 150
Ethanol			
1	79.5	88.6	95.2
2	65.2	78.2	88.6
4	59.3	64.3	78.4
6	51.5	58.1	67.2
n-propanol			
1	80.9	87.2	93.2
2	63.3	75.1	82.1
4	56.2	60.0	65.1
6	30.0	48.3	54.2
Isopropanol			
1	46.8	52.3	55.1
2	27.2	35.2	43.2

temperature range of 100-150°C using different feed rates of 1:1 (mole ratio) acetic acid:alcohol mixture. High conversion and selectivity obtained on $\text{H}\beta$ zeolite shows that $\text{H}\beta$ zeolite has suitable acidity/acid site strength to carry out esterification reaction [11]. Vapour phase esterification of acetic acid was studied in the temperature range of 100-150 °C using ethanol, n-propanol, isopropanol, n-butanol, isobutanol and sec-butanol $\text{H}\beta$ zeolite and the results are shown in table-3.

4	19.4	24.9	35.2
6	13.5	17.1	25.0
n-butanol			
1	74.2	78.4	83.6
2	60.0	65.3	78.2
4	53.1	60.1	69.1
isobutanol			
1	59.5	84.1	92.0
2	42.2	55.3	60.8
4	30.2	41.2	55.2
6	25.0	32.3	50.1
sec-butanol			
1	60.1	78.2	83.2
2	41.2	48.1	64.3
4	23.1	33.4	46.7
6	9.8	20.0	28.1

Synthesis of N-containing Heterocyclics

N-containing heterocyclic compounds like phenylpyridine and substituted phenyl pyridines are useful intermediates in the synthesis of drugs, agrochemicals, herbicides, insecticides, desiccants, surfactant agents and anti-inflammatory agents. Indole and its derivatives are extensively used as intermediates in the synthesis of anti-inflammatory agents, antibiotics and dyes. In this regard our laboratory has developed eco-friendly synthesis of 2-phenylpyridine[12], 2-methyl-6- phenyl pyridine[13], 5-methyl-2- phenyl pyridine[14] 1,4-diazobicyclo (2,2,2) octane, 2-methylquinoxaline[15], 2-methyl quinoxaline[16], 3-methyl indole [17] and 3-isopropylindole[18] process at lab-scale. By utilizing the green chemistry all the N-containing heterocyclic compounds have been synthesized over bare and metal ion-modified zeolites [19,].

Photocatalysis for Organic Degradation/Synthesis

The importance of photocatalysis in recent years has become enormous and the work carried out in our laboratory for organic degradation/synthesis and also the work carried out in collaboration with our French partner on wastewater treatment of recalcitrant is highlighted briefly[20-38]. Photocatalysis is often proposed for the elimination of biorecalcitrant organic pollutants from wastewaters. In recent years the photocatalytic purification of water is carried out by illumination of large band gap semiconductor such as TiO_2 in the contaminated aqueous system. Zeolite-based photocatalysis is new and the recent work reported by Durga Kumari *et al.*[21] on an easy and efficient use of TiO_2 supported and TiO_2 + HZSM-5 zeolite combinate in the photodegradation of aqueous phenol and p-chlorophenol is unique. This approach of sense and shoot of the pollutant (see Fig:2)

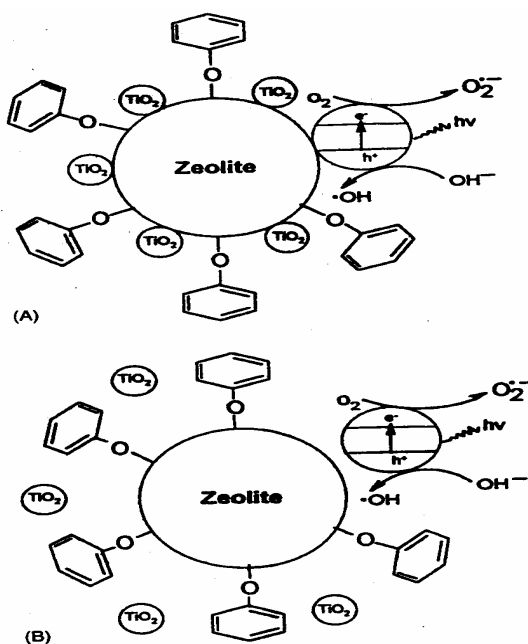


Fig. 2. Model depicting the photoinduced phenol degradation on (A) TiO_2 / HZSM-5 (SSD) catalyst and (B) TiO_2 / HZSM-5 (MECMIX) combinate.

sulfonated recalcitrant compounds especially toxic and non biodegradable compounds like 4-chloro-2-methylphenoxyacetic acid

(MCPA) a herbicide, 3-nitrobenzenesulfonic acid (3-NBSA), 2,5-anilinedisulfonic acid (2,5 ADSA), H-acid (4-amino- 5-hydroxy

-2,7-naphthalene disulphonic acid monosodium salt), Orange-G (azo dye), Acid Orange-7, meta and *p*-Phenylene diamine sulphonic acid are degraded with photocatalysis using TiO₂ suspensions and supported systems[21-28] The strong oxidation capacities, non-toxicity, chemical inertness of TiO₂ and its low price are the attractive properties making them to use as an effective photocatalyst. The process employing solar illumination with a slurry type photocatalytic reactors operation has shown to be a feasible technology for the treatment of small to medium volumes of wastewaters. The thin film fixed bed reactors are an efficient and attractive design for the treatment of larger scale wastewater systems and their construction offers economic advantages. Furthermore, the current energy crisis has led to the development of high priority of solar energy related research. Conversion of solar energy into chemical fuel has attained great importance. In this connection photocatalytic generation of hydrogen from hydrogen sulphide is an energy bargain. There are more useful alternative to the existing thermal catalytic process, that is Claus process used in H₂S processing [29-33].

Also several N-heterocyclic compounds like dihydropyrazine(DHP), trans-1,4,6,9-tetraazabicyclo[4.4.0] decane (TAD), 2-methylquinoxaline (2-MQ), quinoxaline(Q), 2-methylpiperazine(2-MP) and piperazine(P) have been synthesized [34-37] in artificial UV light and solar light using TiO₂/zeolite as photocatalyst. Photo reduction of carbon dioxide was performed using a batch reaction system. The reaction mechanism for the formation of C1-C3 is discussed with respect to the type of supported used for the photocatalyst [38]. The technologies for the wastewater applications or for organic synthesis or for fuel production either using artificial or solar light, will advantageously compete in the market, in particular, if more efficient photo catalysts are developed. Much work is needed to develop more precise methods for modeling the treatment of wastewaters according to the type of pollutants.

Concluding Remarks

Although new catalysts are greatly needed in various areas, it is not easy to realize those catalysts due to severe requirements for the catalytic performance. The design of active sites, reaction engineering, new catalyst materials, membrane catalysis, photo catalytic oxidations and combinatorial chemistry in catalyst design are some of the potential areas for the development of heterogeneous catalyst with high activity, selectivity and long life containing systems. As in other countries, cleaner or more environmentally friendly production materials and chemical energies are becoming more and more important. Examples are the changes to solid acid from liquid acid catalysts, less number of reaction steps, recycling of waste treatment and application of catalysis in a wide range of fuel-to-fuel cell applications have been a strong point of green catalysis or chemistry. Catalysis helps to minimization of number of process steps and use of milder processing conditions. Heterogeneous catalysis extends an advantage of simple separation and recovery for both gas and liquid phase operation. This paper describes some of the existing environmentally friendly process that are being studied and some developed in our laboratory.

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