

Catalysis Research

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Preamble:

The Chemistry Group's research and development work on heterogeneous catalysis are succinctly summarised in this overview. The Chemistry Group has a long history of working on catalysis-related projects, from fundamental studies to departmental applications and for the preparation of new materials. The basic studies were focused on monitoring the transient surface species, elucidating the reaction mechanism, investigating the dynamics of adsorbate molecules inside porous materials, and establishing the structure-activity relationship in catalytic processes. Extensive research has been conducted on the development of catalytic materials for mitigating hydrogen emissions in nuclear reactors, reducing environmental pollution, gas reconstitution for sealed-off CO₂ lasers, photocatalytic water splitting, decomposing sulfuric acid, decomposing hydriodic acid, generating uranous nitrate, and removing dioxins and furans. A brief historical account of the catalyst developments in some of these areas is attempted to be provided, with a focus on how research priorities changed to address more recent challenges in keeping with departmental needs. It is noteworthy to add that the nation's latest PHWR (KAPP-3) is now employing the hydrogen mitigation catalyst developed in the group. At last, the future direction of research and development in heterogeneous catalysis is also discussed.

The beginning of an era:

The solid-state studies section (SSSS) in Chemistry Division of the then Atomic Energy Establishment, Trombay (AEET), which was renamed as the Bhabha Atomic Research Centre (BARC) in 1967, was led by Dr. M. D. Karkhanawala from 1960 to 1972. The Chemistry Division was then headed by Dr. Jagdish Shankar. Around this time, a comprehensive solid-state chemistry research programme was initiated, first in the premises at Cadell Road, Prabhadevi and later in its permanent location at Trombay. Research on a variety of topics was taken up, including X-ray crystallography, solid-state reactions, phase transformation involving uranium and thorium oxides, diffusion of fission products in materials like stainless steel, radiation damage in solids, and thermodynamic and thermo-analytical investigations of reactor materials.

Another important activity in the section pertaining to “studies on radiation induced damage in solids” was taken up with an emphasis on identify in gradation-generated

electron/hole trapping states and emission centres in solids, especially in wide band gap inorganic materials, such as alumina, and magnesia. An in-house thermoluminescence (TL) emission recording apparatus, complete with a temperature programming facility, a photomultiplier tube, and an amplifier was put together for this project. Important insights into the nature of the crystallographic defect states produced in the lattice of wide gap solid materials upon exposure to certain electromagnetic and particle irradiations were obtained by combining the TL measurements with investigations employing alternative methodologies like Electron Spin Resonance (ESR) and Photoluminescence (PL) spectroscopy. These investigations made use of irradiation facilities like the Van de Graff accelerator's α -particle beam, the CIRUS neutron beam source, and the Chemistry Division's Co^{60} γ -irradiation cell. This knowledge came in handy when, in the 1970s, the Chemistry Division was required to begin an R&D programme on catalysis in order to meet certain DAE requirements. Aluminosilicate molecular sieves with diverse pore properties and chemical compositions started to surface as novel materials for gas adsorption and catalysis applications around this time. The initial specialised study topic looked into how ionizing radiation might increase the catalytic activity of a zeolite supported noble metal catalyst (Ru, Pt) for carbon monoxide (CO) and carbon dioxide (CO_2) hydrogenation reactions at low temperature. The goal was to remove all traces of the contaminants CO and CO_2 from the H_2 stream, which was to be used in DAE's heavy water production facilities. The expectation was that the energy stored in the wide gap aluminosilicates as result of γ -irradiation would eventually transfer to the nanoscale noble metal particles scattered across the zeolite surface, thus providing the necessary activation energy for a catalytic reaction and hence facilitating the reaction at a low temperature so as to prevent the overheating of H_2 stream meant for heavy water production.

Radiation effects in catalytic reactions:

A laboratory was set up for radiation-catalysis research in the MDRS (Multi-Disciplinary Research Scheme) premises located in the basement of Modular Laboratories. An in-house gas chromatograph facility, equipped with two injection ports for the pulse injection of a reactant gas, on-line gas-sampling valves, and TCD/FID gas detectors was fabricated in order to conduct *in-situ* radiation catalysis research utilizing a Co^{60} γ - radiation source available in Chemistry Division. The ongoing work in an adjacent laboratory on the indigenous development of gas chromatographs to meet the requirements of Nuclear Power Stations in our country made possible the setting up of a dedicated facility for this work. A mini temperature-controlled catalytic reactor (accommodated within the shaft of γ -cell) with its outlet connected to TCD/FID gas detectors was also developed (Fig. 1). The flexible stainless tubing (~1.5 mm diameter) connected to the inlet and outlet of the catalytic reactor facilitated the upward and downward movement of the reactor within the γ -cell shaft.

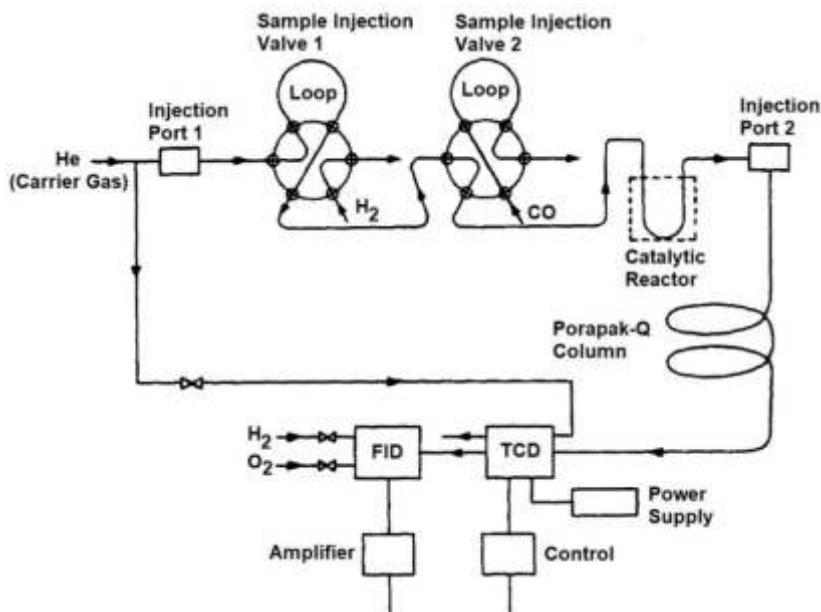


Fig.1: Schematic of the experimental setup used to study the effect of γ -radiation on catalytic activities of the noble metals deposited over zeolites as a support. During irradiation, the U-shaped catalytic reactor was lowered along with the γ -cell shaft.

With the utilisation of this apparatus, in-depth investigations were carried out regarding the impact of γ -radiation on the catalytic activity of Ru and Pt metals, supported over large surface area materials such as zeolites or alumina to provide highly dispersed nano-size metal particles. The nature and reactivity of the transient species formed during the catalytic reaction were monitored systematically. The reactions of CO and CO₂ methanation were performed at various temperatures as well as for various ratios of CO:H₂ and CO₂:H₂ gases in reactant streams. These investigations showed a considerable boost in catalytic activity on γ -irradiation, caused by radiation-induced storage of energy in zeolite support (in trap centres) and its subsequent transfer to the metal sites. The mechanistic routes responsible for this phenomenon were elucidated in detail.

The Catalysis Group has maintained the tradition of indigenously developing instruments and systems for catalysis related studies by the researchers themselves. This has led to the setting up of a number of experimental facilities, including a temperature-programmed desorption/reduction system, a setup for the laboratory evaluation of hydrogen mitigation catalyst, a setup for testing catalysts for CO oxidation, catalytic reactors for the decomposition of sulfuric acid and hydriodic acid, photocatalytic water splitting for hydrogen generation, photocatalytic CO₂ reduction, and the removal of volatile organic compounds (VOCs). Other experimental facilities include a sealed-off cw-CO₂ laser and cells dedicated for *in-situ* FTIR, EXAFS and quasi-elastic neutron scattering studies, etc. These have all contributed to the advancement of catalysis research work in the group, as addressed in the section that follows.

Evolution of catalysis research (1984-till date):

In accordance with departmental directives, the catalysis studies were expanded, focusing on basic research concerning heterogeneous catalysis in relation to environmental pollution control and energy conversion processes. In order to address the challenges requiring catalytic solutions for the DAE activities, emphasis was also placed on applied research. Appropriate support and collaboration from other DAE departments were also received. A brief overview of some of the major assignments accomplished by Chemistry Group's catalysis section is given as follows:

Catalyst for H/D exchange:

Catalysis group pursued a research program on the development of a water-repellent catalyst for HD/H₂O isotopic exchange reaction. Hydrophobicity of a catalyst was a prerequisite because the catalysts needed to be operational under the stream of liquid water and the condensation of water in the pores renders a normal Pt/activated charcoal catalyst inactive during activity evaluation. Attempts were made to coat activated charcoal powder with a thin film of Teflon (Polytetrafluoroethene, PTFE). For this purpose, a batch of activated charcoal powder was exposed to tetrafluoroethene (TFE) vapour at an optimised condition of pressure and temperature, and the mix was then subjected to gamma irradiation (⁶⁰Co source) for the polymerization of the TFE vapour to form a thin (~0.1 μm) polymeric film of Teflon (PTFE).

The powder samples were pelletized and over them required amount of nano-size platinum metal particles were dispersed. Pt particles provided requisite active sites for isotopic exchange reaction. By this methodology, it became possible to increase the active surface area of the catalysts and thus to achieve an enhanced activity compared to a conventional charcoal-based H/D exchange catalyst. The thin layer of Teflon film helped in making the catalyst water repellent and hence in keeping the catalytic activity unaffected from water condensation. This catalyst was tolerant to other contaminants too such as ppm levels of CO and CO₂ in H₂ gas.

Augmentation of experimental facilities for catalysis research:

Around 1987-88 two important instruments, a micro-calorimeter and a FTIR spectrophotometer equipped with an external sample compartment were procured to augment the catalysis research in the Group. These equipments were hyphenated in-house with requisite injection ports, gas flow assembly, and thermal conductivity detector etc. and enabled the catalysis research group to conduct detailed *in situ* studies on the transient species formed over a catalyst surface during the progress of a reaction. Also, an indigenous ⁵⁷Fe and ¹¹⁹Sn Mossbauer Spectroscopy system and instrumentation for the temperature-programmed desorption (TPD) and the temperature programmed reduction (TPR) measurements (built by utilizing indigenous components) augmented the catalysis research in those days. Another important accomplishment was the fabrication of a water-cooled and stainless steel made reaction cell for the high-temperature high-pressure *in situ* infra-red (IR) spectroscopic investigations during the course of adsorption or reaction over a catalyst surface under

variable temperature and pressure conditions. This IR setup was improved further with the support from the erstwhile Central Workshop presently known as Centre for Design & Manufacture (CDM) and played a major role in elucidation of mechanistic aspects of various catalytic processes. Incidentally, a complete IR cell setup along with requisite fittings and a vacuum system was supplied to the R& D Centre of Indian Oil Corporation, Faridabad. Subsequently, this cell was modified with provisions for *in situ* irradiation using UV and visible irradiation sources (Fig. 2). On similar lines, another SS-cell equipped with Be-windows was developed for *in situ* EXAFS study of catalytic materials at INDUS-2, RRCAT, Indore (Fig.3).

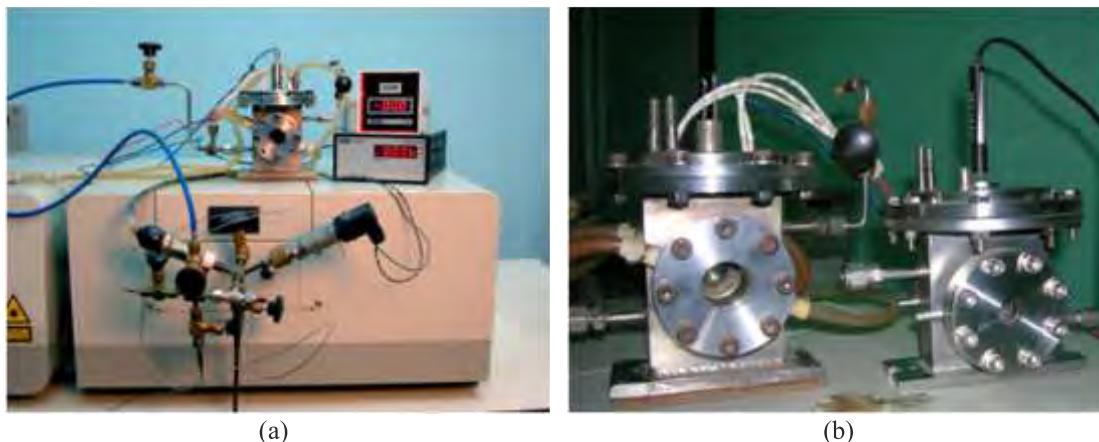


Fig. 2: IR cells without (a), and with photo irradiation facility (b), developed indigenously to monitor surface transient species *in situ* over catalysts/photocatalysts



Fig. 3: A SS-cell equipped with Be-windows for *in-situ* EXAFS study of catalytic materials at EXAFS beam line in INDUS-2 at RRCAT, Indore (developed in collaboration with Applied Spectroscopy Division & CDM)

Gradually, several new experimental facilities for characterization of catalytic materials such as temperature programmed desorption, reduction and oxidation system, BET surface area analyser, ESCA and Auger electron spectroscopy system, DR-UV-vis spectrophotometer, FTIR spectrophotometer with provisions of diffuse reflectance and high temperature-high pressure cells for *in-situ* catalytic studies, thermogravimetry-mass spectrometry (TG-MS), high temperature furnace, gas chromatography-mass spectrometry, spray pyrolysis and a potentiostat were procured by utilizing financial provisions made available under the Five-year Plans, Vision Schemes and DST projects. These facilities have enabled and equipped the catalysis group to take up detailed investigations.

Studies on surface transient species and mechanistic aspects of catalytic processes:

Utilizing the facilities available, detailed thermochemical studies were conducted on adsorption and hydrogenation of CO over noble metals supported on reducible oxide (Ru/TiO₂, Ru/Al₂O₃ etc.) catalysts and substituted Fe-Ti intermetallics (Fe_{1-x}Mn_xTi, Fe_{1-x}Ni_xTi, FeTi_{1-x}Sn_x). The role of the lattice oxygen, metal valence state, secondary phase and that of the metal-support interaction in these reactions were investigated in detail. TPD and ⁵⁷Fe and ¹¹⁹Sn Mössbauer spectroscopy studies revealed the presence of Fe clusters and surface restructuring in substituted Fe-Ti intermetallics during CO methanation and helped in establishing a correlation between hydrogen adsorption characteristics and catalytic hydrogenation properties of intermetallics. The surface-active species formed over the titania supported noble metals during the adsorption and hydrogenation of CO and CO₂ were investigated using FTIR and newly developed thermal desorption spectroscopy methods. The mechanistic routes and the transient species responsible for the deactivation of the catalysts in presence of S-containing gaseous contaminants were delineated in detail. Diversified studies on the oxidation of simple molecules e.g., CO using noble metals supported on reducible metal oxide catalysts viz., Pt/SnO₂, Pd/SnO₂, Pd/(α-Fe₂O₃ + SnO₂), Pd/(MnO₂ + SnO₂), Au/Fe₂O₃ etc were also undertaken. It was established that the energy released in the chemisorption of CO or CO₂ gives rise to a localized temperature surge at metal support interfaces and the additional energy thus available leads to the enhanced CO oxidation activity of the reducible oxide supported noble metals via accelerated lattice oxygen extraction.

Gas reconstitution catalyst for sealed-off cw-CO₂ laser:

In late 1980's, Laser Division, BARC and the Centre for Advanced Technology, Indore were pursuing fabrication of the indigenous sealed-off CO₂ lasers operating with CO₂, N₂ and He as lasing gas mixture. These lasers faced problems of loss in output power and arcing due to electron-induced dissociation of CO₂ to CO and O₂. To enhance the lifetime of these lasers, a suitable catalyst for gas-reconstitution was required to be developed and the problem was referred in 1987 to Chemistry Group. The prospective catalyst was required to possess high activity and also good stability for *in-situ* oxidation of CO to CO₂ under the ambient conditions of laser irradiation. The work also involved design and fabrication of a discharge tube, a laser and ultimately a sealed-off cw-CO₂ laser, which was accomplished with the support received from Laser Division. Instrumentation to evaluate the CO oxidation activity

of different catalysts was set up, taking due precautions in consideration of the toxic hazards of CO gas. After a series of experiments using different noble metal catalysts and for varying CO:O₂ ratio in reactant gas stream, a catalyst comprising highly dispersed Au particles over α -Fe₂O₃ as support material was chosen. A methodology was then developed to coat the inside surface of a laser tube with a thin layer of this catalyst and ultimately resulted in fabrication of a compact sealed-off cw-CO₂ laser (Fig. 4). This laser remained fully operational for about a year with a single gas fill and with almost constant power output. The role of the presence of impurities on laser operation was investigated.

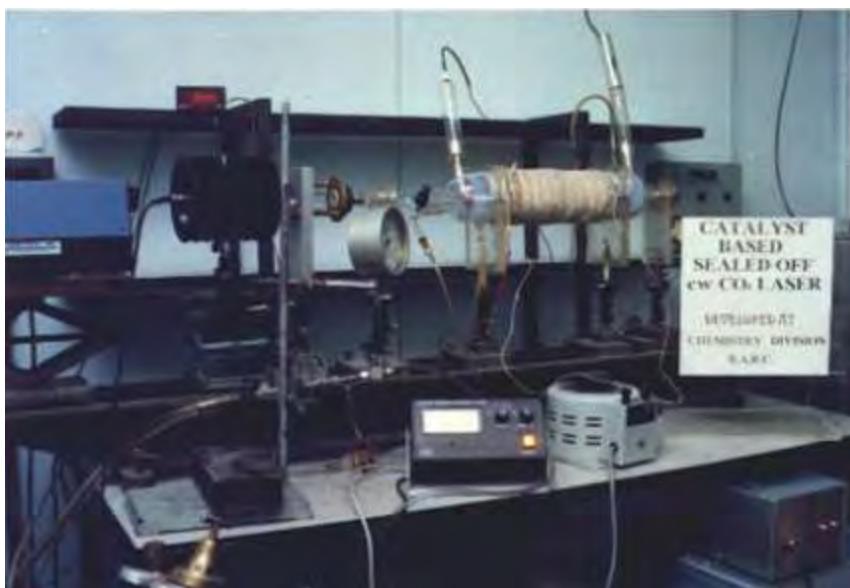


Fig. 4: Catalyst based sealed-off cw CO₂ laser (photograph taken in 1994)

To be able to conduct in-depth studies on CO oxidation over Au/Fe₂O₃ catalysts as a function of gold particle size and the oxidation state of the iron oxide support, this development effort was eventually expanded to a fundamental research programme. Using *in-situ* infrared spectroscopy and thermo chemical methods, a relationship between the size of the metal particles, the kind of surface transient species, and the catalytic efficiency of supported Au/Fe₂O₃ was established.

Host-Guest chemistry of zeolites:

Quasi-elastic Neutron Scattering (QENS) measurements conducted at Dhruva reactor (in collaboration with Solid State Physics Division) complemented the *in situ* FTIR spectroscopy studies (support received from Spectroscopy Division) and facilitated understanding of the entrapment and dynamics of molecular motion inside the channels of microporous and mesoporous zeolites as a function of their chemical composition and pore characteristics. The QENS method measures movement over the nanoscale, and therefore permitted a quantitative probe of intra-crystalline diffusion and migration of the small molecules within the micro- and meso-pores of zeolitic channels. The combined *in situ* FTIR, QENS and thermal-

desorption spectroscopy (TDS) studies for the first time revealed the existence of the weakly held clusters of small molecules, such as CO, CO₂, C₆H₆, C₂H₄, CH₃OH and cyclohexane etc, when occluded in zeolitic cages. These studies were further extended to the dispersion of the nano-size clusters of TiO₂ in the cavities of mesoporous MCM type zeolites. Investigations on the photoactivity of these supported TiO₂ clusters for the vapor-phase photo-oxidation reactions using visible-light for irradiation and as a function of their cluster size were carried out. The study also included *in situ* monitoring of intermediates using FTIR spectroscopy to better understand the mechanistic aspects and also to establish a structure-activity correlation.

Photocatalytic properties of uranyl species encapsulated in the mesoporous aluminosilicates:

Another applied-cum-basic research relating to DAE was carried out to assess the capacity of several wide-pore zeolites for the absorption/separation of uranyl species from nuclear waste and to investigate the photocatalytic activity of U-containing samples (collaboration: IIT, Bombay). In this program, extensive research was carried out to bind and encapsulate the uranyl groups and highly dispersed-U₃O₈ nanoparticles within the mesopores of MCM-41 and MCM-48 aluminosilicates. It was discovered that the structural characteristics of UO₂²⁺ species allowed them to interact with alcohols and a variety of other substrates by abstracting hydrogen atoms. As a result, these materials exhibited notable photo-oxidation activity for several organic molecules, such as benzyl alcohol, methane, methanol, and toluene. These studies demonstrated that when exposed to sunlight, nanostructured uranium oxides occluded in mesoporous zeolites may promote the mineralization of volatile organic compounds (VOCs). Based on these investigations, a relationship was established between the size of uranium oxide crystallites, the kind of surface transient species generated, and the reaction products formed during the photooxidation of organic molecules.

Development of hydrogen mitigation catalyst:

In 1986, a challenging DAE requirement came up when Dr. Anil Kakodkar, then Head of the Reactor Engineering Division (RED), convened a meeting to discuss a vital research and development programme aimed at strengthening the safety of nuclear reactors in the event of a Chernobyl-type catastrophe (April 26, 1986). Senior scientists from various Divisions of BARC, were called for this urgent meeting. Each participating Division was given the task of developing a suitable device that could assist in keeping hydrogen concentrations in nuclear power plant containment atmospheres below the flammability limit of roughly ~4% in the event of a hypothetical core meltdown emergency arising from an unintentional loss of coolant situation.

Work in the Chemistry Group started after a comprehensive review of the relevant literature. It came to the realisation that, of the several stipulated methods for mitigating H₂ gas emissions in nuclear reactors, such as intentional ignition, argon inerting of containment areas, venting to the atmosphere, spraying water or foam, etc., catalytic recombination of H₂ and O₂ should be the best option in the event of a postulated loss of coolant accident because it is: i) a passive device that carries no risks; ii) quick response

method; iii) functional in presence of water vapour, iv) functional under the ambient temperature and pressure conditions, and v) possibility of remote deployment in the affected areas. In response to these demands, the chemistry division's catalysis group undertook the design and fabrication of a passive catalytic recombiner device. Pd metal was the obvious choice because of its well-known high catalytic activity for the $H_2 + O_2$ reaction, which depends on particle dispersion. For comparison analysis, other noble metals like Pt and metal combinations like Pt + Pd were used. In order to deposit metal particles, two distinct substrate materials were employed: i) thick, rough-textured polyester sheets that were specifically woven, and ii) wire mesh or a thin strip of corrosion-resistant stainless steel. A pre-treatment was applied to these support materials in order to increase their surface area and enhance the adherence of scattered noble metal crystallites.

A large number of samples with different metal content and particle size were then prepared. These samples displayed very high catalytic activity during the many repeated trials, the time required for the decrease of H_2 concentration in the reactor to half its initial value ($t_{1/2}$) varying from 0.5 to 20 min, depending upon the H_2/O_2 ratio and the metal content of a catalyst strip. The tolerance of the catalysts to the presence of water vapor or some anticipated contaminants such as CO and CO_2 was also tested. In the event of a high H_2 concentration, the possibility of catalytic panel overheating was given due consideration.

Eventually, somewhere in the late 1990s, Reactor Engineering and Reactor Safety Divisions (RED, RSD) built a 22,000-liter pilot plant scale laboratory for evaluating the efficiency of the catalyst panels under the conditions simulating a reactor containment. A large number of catalytic panels composed of stainless-steel mesh and coated with Pd were then fabricated and were proven to function extremely well for the H_2/O_2 recombination reaction when tested in our division as well as by using the RED pilot-plant facility. Members from RED and RSD played a crucial role in evaluation of catalyst performance at pilot plant scale.

A Task Force for "The development of Passive Hydrogen Recombiner Device (PHRD)" was constituted by the Director, BARC in October 1998 due to the significance of this endeavour. A final project completion report, that included the results of a large number of our experiments including the poisoning resistance studies, was submitted to RED in the year 2001 with a request to forward it to Nuclear Power Corporation (NPCIL) for their consideration. A prototype passive recombiner chamber was also designed and fabricated in Catalysis Group to demonstrate its utility for final application. The chamber could accommodate a large number of folded catalyst-bearing panels and had a provision of storing the panels in an inert gas environment for their protection from environmental pollutants.

At this stage, the programme remained dormant for almost ten years. However, on March 11, 2011, a catastrophic accident at Japan's Fukushima Daiichi Nuclear Reactor drew the attention of the DAE authorities and the world community once more. From then on, the activity continued with thorough assessments of the catalyst bearing panels prepared by the Chemistry, Material Processing, and Technical Physics Divisions of BARC at the Hydrogen Recombiner Test Facility (HRTF), which was set up at the Tarapur Nuclear Power Station's R&D Centre. A chimney type SS housing for placing the catalyst bearing panels, designed by NPCIL was used for these tests. Based on the test results, catalyst developed by Chemistry Division was deemed to be the best overall, and as a result, it was selected for large-scale

production at Electronic Corporation of India (ECIL), Hyderabad. For this purpose, BARC and ECIL signed an agreement (MoU) in March 2015. The passive catalytic recombiner devices (PCRDs) produced under this MoU were evaluated again at HRTF and met the acceptance criteria. Till date, more than 1000 PCRDs have been produced by ECIL and supplied to NPCIL for deployment in Indian PHWRs including the recently (July 22, 2020) commissioned 700 MWe Kakrapar Atomic Power Project (KAPP-3) where 80 such PCRDs are installed.

Eventually, this lab study was successfully converted into a deployable technology, produced several high value research articles, and won multiple departmental honours. Fig. 5 summarises this developmental work.

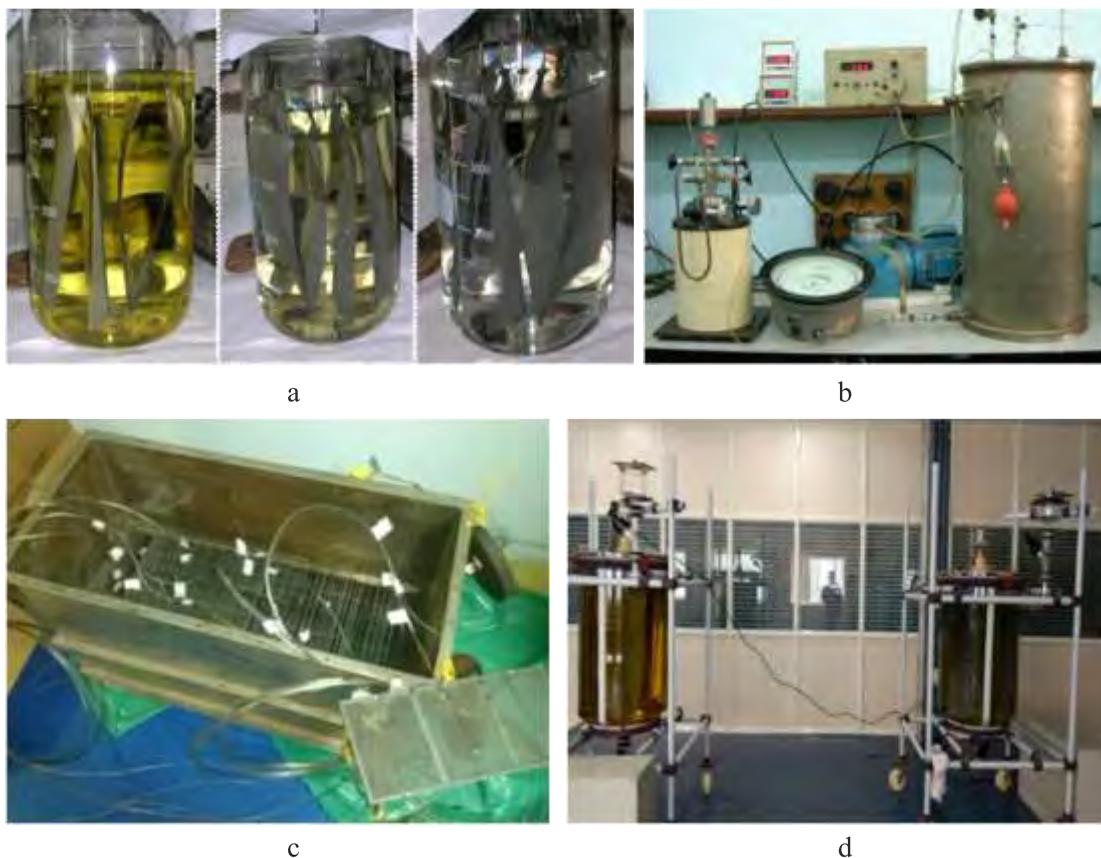


Fig. 5: Development of SS wire mesh supported noble metal catalyst for H_2 mitigation: (a) lab scale preparation, (b) experimental setup for activity evaluation, (c) passive catalytic recombiner device (PCRD) for evaluation at HRTF, Tarapur, and (d) large scale production of catalyst bearing panels for PCRDs at ECIL, Hyderabad

Catalyst for environment pollution control:

Additionally, efforts were made to produce highly active and chemically stable catalysts for use in pollution abatement and automobile exhaust management. In the 1990s, auto exhaust pollution and global warming emerged as the two most pressing challenges. A variety of mixed metal oxides, including $\text{YBa}_2\text{Cu}_3\text{O}_{6,9}$, $\text{La}_{1-x}\text{Mn}_x\text{VO}_4$, $\text{Th}(\text{VO}_3)_4$, ThV_2O_7 , $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$, $\text{La}_2\text{Ti}_{2(1-x)}\text{Fe}_{2x}\text{O}_{7-\delta}$ and $\text{CeO}_2\text{-Y}_2\text{O}_3$, were synthesised and characterised for their structural properties. The catalytic activity of these materials was then evaluated for the $\text{CO} + \text{NO}$, $\text{CO} + \text{N}_2\text{O}$, and hydrocarbon oxidation reactions, as well as the degradation of nitrogen oxides. In these oxides, the roles of lattice defects and lattice oxygen on catalytic performance were thoroughly examined.

Catalyst for uranous nitrate production:

This developmental work was initiated in 2013 as a part of Chemistry Group-Nuclear Recycle Group collaboration program. Uranium-plutonium separation in the PUREX process is achieved by selective reduction of Pu(IV) to Pu(III) using uranous nitrate as reductant and hydrazine as stabilizer. Currently, the requirement of uranous nitrate in Indian reprocessing plants is met through by electrolytic reduction of uranyl nitrate. This electrolytic reduction process, however, suffers from a drawback of incomplete reduction with a maximum conversion of $\sim 60\%$. Catalytic reduction of U(VI) to U(IV) is being considered as one of the promising alternatives to the electro-reduction process due to fast kinetics and near total conversion. Various catalysts involving noble metals like platinum (Adams catalyst, $\text{Pt}/\text{Al}_2\text{O}_3$, Pt/SiO_2 etc.) have been reported for the reduction.

The issues that still needed to be resolved, nonetheless, were the lack of catalyst's stability and poorly sustained activity under severe reaction conditions. In this context, Chemistry Division and Process Development Division (PSDD) worked together to develop an active and stable zirconia-supported noble metal catalyst (Pt/ZrO_2). A significant quantity (10 kg) of this catalyst was produced through industrial partnership after it showed good performance for the reduction of uranyl nitrate to uranous nitrate at the lab scale. Using this catalyst, the uranous manufacturing plant at PSDD was able to achieve near quantitative ($\sim 97\%$) conversion of a 70-liter uranyl nitrate feed under ambient conditions by using hydrogen as a reductant.

Catalysts for the removal of dioxins and furans:

Polychlorinated p-dibenzo dioxins/furans (D&F) are the toxic/carcinogenic by-products, generated during combustion of solid municipal/bio-medical waste. These are also likely to be present in the off-gases during plasma incineration of radioactive solid waste containing rubber, plastic and cellulose at NRG. A number of oxide/mixed oxides catalysts such as $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ (VWT), WO_3/TiO_2 (WT) and $\text{V}_2\text{O}_5/\text{TiO}_2$ (VT) and nano- TiO_2 catalysts were explored for degradation of dioxin and furans. Catalytic degradation studies involving o-Dichloro Benzene (o-DCB), as a model chloro-compound were undertaken in air, at temperatures in range of 150-400 °C, employing an indigenously developed experimental setup. Among all, VWT catalyst was found to be most effective and yielded maximum

amount of CO₂ confirming mineralization of *o*-DCB. The trend in catalytic activity was found in order: VWT >> WT > VT >> TiO₂. Based on *in situ* FT-IR studies degradation mechanism of *o*-DCB over these catalysts was also proposed. A methodology for quantitative estimation of D&F in off-gases from plasma incinerator was also developed in collaboration with NRG.

Catalysts development for Net-Zero carbon emissions:

Chemistry Group has made significant contribution in the basic and applied research for the development of catalysts for sulfuric acid decomposition and hydriodic acid decomposition of iodine-sulfur process, electrocatalyst and membrane electrode assembly for CuCl/HCl electrolysis of Cu-Cl cycle, photocatalytic water splitting and CO₂ reduction. A brief summary of these works is presented in a separate chapter on Net Zero Emissions.

Way forward:

The Chemistry Group's catalysis research has consistently included both fundamental and practical aspects (primarily in relation to departmental goals), and this trend continues to exist even today. Currently, the catalysis group is working on developing (a) a new and improved hydrogen mitigation catalyst using the heat pipe concept; (b) a visible light active photocatalyst for solar hydrogen generation; (c) appropriate de-oxo catalysts and electrocatalysts to improve the product purity and the efficiency of the alkaline water electrolyser; and (d) low-temperature (~100 °C) active catalysts for the degradation of dioxins and furans (from the off-gases emanating from the plasma incinerator used in NRG). Specific attention is being paid to the mechanistic aspects of these catalytic processes.