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Title: New Perspectives in Heterogeneous Catalysis: Bench-Scale Reactivity Studies, Physicochemical Characterization, and Future Research Directions

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ABSTRACT

As is often stated (and as the contents of a famous quote by Heinz Heinemann teach us), the field of catalysis as a whole and its sub-disciplines (homogeneous & heterogeneous catalysis, bio-catalysis, computational catalysis, and electro-catalysis) is very mature, but can be revitalized by new discoveries which can help spur new research in the field and also importantly spur creativity and innovation, which can prime further advancements in this area. However, an outside-the-box thinking and a focused effort in a large plurality of disciplines that constitute catalysis is necessary. In this vein, we have articulated a vision for the science of catalysis and its 3 areas – bench-scale reactivity studies, physicochemical characterization, and future research directions. In the first, we attempt to take a look at where we can depart from the traditional way of collecting and reporting experimental data from bench-scale reactivity studies, and where further enhancements in catalytic reactor design and peripheral systems such as catalyst baskets, impellers and stirrers, baffles and other flow modulation devices, inert coatings and liners for reactor internals, new designs for thermocouples, static and in-line mixers, on-line and chromatographic sampling loops and valves, new high-performance materials for gaskets and O-rings, et cetera, are possible. We have also devised new schemes for automated control systems for continuous operations, high-throughput screening, and heuristics-based algorithms for reactor design and scale-up. In physicochemical characterization, we have identified several novel new areas where we feel that an additional focus and research effort will fetch rich dividends. In this realm, advanced spatiotemporal characterization studies including single atom and single site studies, imaging of phenomena on the catalytic surface including adsorption, surface reaction and catalytic turnover, and desorption will have an important future. While this contribution will not consider the area of computational catalysis (and advances), it suffices here to note that the future lies in the development of hybrid methods (parallel and serial) which can model the typical multi-scale phenomena that is typically encountered in protein translocation and signal transduction, charge transport, enzymatic catalysis, surface chemistry, and self-assembly in complex fluids. Finally, the future research directions are very important, as they help pave the way for the present, and we have crystallized and articulated a few very important concepts/ideas which we believe will have an emergent presence for years to come - Some of the important ones include a new definition of structure sensitivity or facile reactions, surface reaction engineering or surface kinetics, thermodynamics and kinetics of nucleation and crystal growth, surface potential energy diagrams for these phenomena, concept of crystal planes and orientation, molecular traffic control, spectroscopic/microscopy-based analysis of nucleation/crystal growth, molecular and modular catalysts, molecular imprinting and receptors, et cetera.

A. INTRODUCTION

Ever since Lord Berzelius coined the term "catalysis" in about 1835 and spawned the formal development in this field, it is a shining star on the forefront of scientific and industrial development, and indeed for energy, environmental, and economic security of the United States. Catalysis is thus extremely significant in both scientific and industrial perspectives and the importance of catalysis and its allied disciplines such as homogeneous catalysis, heterogeneous catalysis, photo- and electro-catalysis, computational chemistry and catalysis, and the emerging field of molecular heterogeneous catalysis (at the interface between homogeneous and heterogeneous catalysis) cannot be overstated. Catalysis finds itself as a multidisciplinary field at the interface of physics, chemistry (inorganic, organic, physical), biosciences, materials science, and chemical physics and biology, and has very remarkable impacts on the energy and economic security and our sustainable future. Catalysis is a key pillar of the global industrial chemical and petrochemical sector, and 85% of all chemical products are produced with at least one catalytic step. Catalytic chemistry and catalytic processes contribute to about 20% of the US Gross Domestic Product (of over $16 trillion). The United States is a leading producer of both commodity (bulk) and fine chemicals in the world, and 15 of top 50 chemical producers in the world are United States companies. Importantly, catalysis is critical for a clean, sustainable, and secure energy future, regardless of the energy option considered (coal, natural gas, biomass, solar, nuclear, hydrothermal, etc.). As stated above, an understanding of the different areas including heterogeneous, homogeneous, biocatalysis, photocatalysis, and electrocatalysis is thus necessary for the development of atom-economical (and, thus green) and sustainable processes.

Today, Catalysis has become a powerful tool in the bulk chemicals and petroleum sectors, as well as in fine chemicals and pharmaceuticals. Although it is often mentioned that the field of catalysis is mature, one should remember a famous quote by H. Heinemann: "*It may appear that a field or even the whole of catalytic technology is relatively mature. This is, however, a misconception because history teaches us that fields which appear mature are suddenly revitalized by a major discovery.*" The interdisciplinary field of catalysis (and its sub-disciplines) is thus poised for major progress in the 21st century [1]. As stated above, this progress can come from synergistic collaborations and interactions by scientists and researchers from many disciplines such as chemistry, biosciences, chemical engineers, biochemists, and even mechanical engineering. The progress in catalysis is usually centered on two areas: rational design and discovery of novel catalysts and a development of an understanding of their action (including spatiotemporal characterization) and mechanistic chemistry, with high-throughput screening and combinatorial chemistry, and development of sustainable and atom-efficient catalytic processes [1]. It is thus the subject of this paper to report new perspectives and concepts (from our frame of reference) in heterogeneous catalysis, in each of the 3 important areas – Bench-scale reactivity studies and scale-up, physicochemical characterization, and future critical directions for research.

In the United States, the problem of sustainable energy and future energy and economic security is a very pressing challenge (the transportation sector and interstate commerce contribute to about 20% of the overall economy). The field of catalysis and its sub-disciplines lies at the heart of this challenge. The United States government, and in particular, the U.S. Department of Energy have long recognized this problem of sustainable energy. The solution is clearly not incremental advances in energy science, but transformative discovery in the fuels/energy area guided by science. Thus, to mitigate the dependence on the foreign oil and in its quest for the development of environmentally friendly, sustainable fuels and alternative energy sources, the U.S. Department of Energy has funded 32 Energy Frontier Research Centers (EFRC's) in 33 States and the District of Columbia. These integrated, multi-PI centers involve partnerships among universities, national labs, not-for-profit organizations, and for-profit firms (typically with a cost share, and/or matching contribution), and are enabled to conduct fundamental research focusing on one or more "grand challenges" and user-inspired basic research needs in energy/alternative fuels, identified in planning efforts by the scientific community. The outcome of these research centers (currently funded for the 2nd 5-year cycle, through 2019) will decisively enhance the United States energy and security, and will also help protect the global environment. It is clear, however, that new discoveries and development of new processes for chemicals/fuels or energy science, in general, cannot come at the expense of environmental protection, and whenever possible, a firm focus on environmentally conscious manufacturing is absolutely necessary.

In heterogeneous catalysis, the reactants and the products are often in the gas phase, and the reaction takes place over a solid catalyst, in a fixed-bed configuration. Some examples of large-scale industrial processes are the synthesis of ammonia (Haber-Bosch process), oxidation of ethylene to ethylene oxide over a silver catalyst, synthesis of methanol from carbon monoxide and hydrogen (over copper-zinc catalysts supported on γ-alumina), oxidative dehydrogenation of methanol for production of formaldehyde (over silver gauze catalysts), and steam reforming of methane for production of hydrogen. Most catalytic reactions in the chemical and petrochemical sectors including as above are gas-solid reactions. One key example is the catalytic cracking of heavy hydrocarbons feedstocks in millisecond (ms)-scale contact time reactor configurations. Nanotechnology and nanomaterials are often the key foundation of organic reactions and heterogeneous catalysis. Most catalytic materials are precious, and thus expensive, and so are usually dispersed as nanometer-sized particles (with low effective loading and a high degree of mono-dispersity) on high-surface area inorganic carriers [2, 3]. An example of the inorganic carrier matrix like silica and the precious group metal nanoparticle like platinum dispersed on the inorganic carrier is schematically given in Figure 1 [4]. Instead of the more common gas-solid (fixed-bed) reaction configuration, with examples as given above, it is also common to have a three-phase reactor configuration. In a three-phase process, the catalyst particles are usually

slurried in the inert liquid phase, and the gas phase reactants are bubbled through the liquid medium. The role of the liquid medium is usually to absorb the exothermic heat of the reactions. The liquid phase can also only be a solvent, which provides a soluble medium for the reactants as well as the products. A variant of the slurry reactor (or, bubble column) configuration is the trickle bed reactor, where liquid reactants flow downward (under gravity flow or pressure flow) over a fixed catalyst bed. A few other reactor designs are also present in industrial practice (but less common) – fluidized-bed reactors, transport reactors, riser reactors, moving-bed reactors, catalytic membrane reactors (of different types), etc. One popular example of a transport bed application is the DuPont ABB Lummus ALMA maleic anhydride process, initially introduced by DuPont as an alternative to the conventional fixed-bed reactor configuration, popularized by Monsanto and then Huntsman Petrochemical Corporation (after Monsanto's MAn business divestiture to Huntsman). Riser reactors find a myriad of applications in the petroleum refining industry, and are typically featured with a regenerator with a split-stream purge and recycle of catalyst solids.

As stated earlier, the role of a catalyst is to enable industrially important chemical reactions to be carried out efficiently (i.e., under high reactant conversions and product selectivities/yields) under practical (and mild, not too harsh) reaction conditions. It is clear that the chemical industry of the present 21st century could not evolve and sustain on the basis of stoichiometric, non-catalytic routes alone, as these are resource-intensive routes that are not eco-friendly. Chemistry and the chemical industry have thus done right (partly necessitous) in moving away from the stoichiometric and non-catalytic routes of the pre-catalytic era starting about 1960s [5]. The earlier processes based on stoichiometry of organic reactions and traditional catalysis were considered to be the "Force and Hammer" approach, and were replaced by the newer, more chemo-selective processes based on new catalysis and bio-catalysis, called as the "Knife and Scalpel" approach (Table 1). Catalysis is thus important in accelerating the chemical reactions by orders of magnitude, thereby bringing them under the optimal thermodynamic regime. Catalysis also allows the chemical reactions to be carried out at lower temperatures and pressures, which results in lower operating and fixed costs (capital costs). Unfortunately, even though chemistry, and in particular, catalytic chemistry, have a high impact on our everyday life, in terms of the products chemical, biological, and life sciences industries bring to us, the chemical industry still has a very poor public image. While this may be in part due to misconception, some of the clear environmental catastrophes like the Bhopal disaster in India of 1984, the Exxon Valdez grounding in Alaska in 1989, and the BP oil spill off the United States coastlines, have contributed to what is a very real perception. Clearly, there is thus a need to do more, to develop environmentally benign (friendly) processes, which are also sustainable. Thus, another tenet or principle of green chemistry and manufacturing, originally introduced in the 1990s, is "Resource Management" and "Sustainability". A sustainable chemical process is one

that allocates and uses resources appropriately to meet the needs of current generation, but at the same time, without sacrificing the ability to meet the needs of the future generations. The strategic goal of sustainable development thus relies on the practical approaches of green chemistry, green manufacturing and engineering, and renewable energy, and relies on operational and enforcing tools like catalysis and catalytic chemistry, process intensification, and waste management.

From fundamental considerations, catalysis is an interdisciplinary science that encompasses many length and time scales over which the surface phenomena take place [6]. The adsorption of a single molecule on the surface active site, the surface reaction, turnover, and product back diffusion are all microscopic phenomena, which occur on the nanometer (length) and pico- to femtosecond (time) scale. Understanding the elementary reactions on the surfaces (on preferential crystal planes) of the catalyst that involve the steps of molecular or dissociative adsorption and the breaking of bonds in the substrates on the catalyst surface and to form newer product bonds requires most advanced experimental techniques and theoretical descriptions. These advanced techniques include analytical microscopy, spectroscopy, and computational chemistry. The surface phenomena occur at on the nanoscopic time and length scales and on small active particles, with typical dimensions of between 1 and 10 nm, and inside the pores of support particles (μm range on mesoscopic (i.e. observable scale)). The characteristic time scales on which catalytic events occur vary more or less in parallel with the different length scales discussed above. The activation and breaking of a chemical bond inside a molecule with or without adsorption occurs in the picosecond to femtosecond regime, completion of an entire reaction cycle from complexation or surface adsorption between catalyst and reactants through separation from the product may take anywhere between microseconds for the fastest reactions to even minutes for complicated reactions on surfaces. On the mesoscopic level, diffusion in and outside pores, and through shaped catalyst particles may take between seconds and minutes, and the residence times of molecules inside entire reactors may be from seconds to minutes, or even effectively, infinity, if the reactants end up in unwanted byproducts such as coke, which stay on the catalyst [6].

It is clear that understanding catalysis and mechanisms of catalytic reactions at the atomic scale is a difficult task. This is the domain of surface science. Surface science affords studies of model catalysts and single-crystal surfaces under ultra-high vacuum (UHV) conditions, of the order of 10^{-10} Torr [7-10]. Single crystals do not possess a grain boundary, as opposed to polycrystalline materials, which are comprised of many crystals (or, with grains), and thus have many boundaries. Clearly, both single crystals and polycrystalline (or, bulk) materials or metals are low surface area materials and are to be distinguished from metal aggregates or nanoparticles which have a high surface area to volume ratio. In metal aggregates or nanoparticles, the grain

size and grain width are comparable.   The metal aggregates (including size-selective clusters) are the primary materials used in catalysis, while single crystals form the basis of all surface science studies. Thus, most surface sensitive techniques require UHV conditions and are suited for well-characterized, low-surface area systems such as model catalysts or single crystals. A further important advantage of single crystals is that any preferential crystal plane can be selectively cut and exposed (which is not the case with another class of materials, thin films, which are high-surface materials, with many crystal facets, although it should be noted that epitaxially grown thin films can be akin to single crystals). However, due to the practical complexities and inherent nature of catalysis, most practical catalytic operations are catalyzed by metal aggregates or nanoparticles dispersed on an inert inorganic carrier matrix (typically high-surface area, up to 400 m^2/g), at pressures of 1 atm or greater. Because of these differences between the surface science domain and the catalysis domain, there exist three "gaps" in these two fields [7, 10]:

- The materials gap
- The pressure gap
- The complexity gap

The pressure gap is perhaps the most serious and is thus caused by the $\sim$ 13 orders of magnitude difference in pressure from a standard surface science experiment ($\sim 10^{-10} - 10^{-6}$ mbar) to an operating catalyst ($\sim$ 1$-$100 bar). UHV conditions are, however, a prerequisite for surface science as they allow one to prepare atomically clean surfaces for studies, to maintain these surfaces in a contamination-free state for the duration, and permit low energy electron and ion-based techniques, such as LEED, XPS, and UPS, to be used without the undue interference from the gas phase. Thus, one of the key underpinning issues that bring the surface science studies in question is that the structure-function relationships and kinetics developed for studies of model catalysts (or single crystal surfaces) under UHV conditions may not be applicable for these relationships and kinetics under the catalytic control in the catalysis domain. For highly non-idealized cases as reactions with chemically-modified surfaces with promoters and poisons and for advanced cases of bimetallic catalysts, the connections between surface science and catalysis are even more tenuous. It is thus clear that good correlations are needed between the surface science studies with model systems and catalysis studies, in order to be able to glean useful information from model studies to gain understanding of "real" or working catalyst systems. Such information can be invaluable for improvement or enhancement of existing catalysts or in development of newer systems.

Fortunately, extensive studies have been undertaken in the last 2 decades that attempt to bridge these gaps between surface science studies and catalysis studies [7, 10]. Using model systems with increasing degree of complexity or even model catalysts is a way to bridge the materials gap. It has now been shown that single crystal and model catalysts can be effectively used to model a variety of surface-catalyzed reactions. In fact, for structure-sensitive reactions, good to excellent correlations have been obtained for kinetics observed with single-crystal models and more realistic supported metal nanoparticles, which suggests that the surface chemistry and perhaps the mechanism for these two systems (models and supported nanoparticles) is identical. For the pressure gap, one can use surface sensitive techniques that work in the presence of a gas phase, such as temperature desorption spectroscopy (TDS), infrared reflection absorption spectroscopy (IRAS), electron spin resonance and electron pulse resonance (ESR and EPR), sum-frequency generation (SFG), scanning tunneling microscopy and environmental scanning microscopy (STM and ESTM), and small-angle X-ray scattering and X-ray absorption spectroscopy (SAXS and XAS). These studies with newer instrumentation systems have shed light on several key areas in surface science and catalysis [11-14]. The key areas and discoveries include kinetics of several important reactions, such as the methanation reaction of H_2 and CO, CO oxidation, and hydrogenation and hydrogenolysis, assessment of structure sensitivity, i.e., if a reaction is structure sensitive or not, reactions over chemically modified surfaces such as those with poisons or promoters, and bimetallic catalysts. Investigations have also been conducted on the structure-function relationships in supported metals with respect to particle size and support effects, as well as on detailed morphological modeling and analysis of model oxides and metal aggregates supported on these model oxides, using scanning tunneling (STM) and atomic force microscopies (AFM). A summary of the conventional and new (cutting-edge) tools for physicochemical characterization of solid catalysts (including surface science techniques) is given in Table 2.

It is clear that the development of newer instrumentation systems for molecular-scale studies of gas-solid interfaces and the development of newer model systems including metal nanoparticles have led to the advances in surface science studies [10, 13, 14]. In part, these have been able to bridge the gaps between surface science and catalysis. It is necessary that we are able to use the techniques, SFG and STM, to monitor nanoparticles, as they undergo reactions, i.e., in-situ, in the gas/solid or gas/liquid phase. A final grand challenge is the combined molecular studies of homogeneous, heterogeneous, and bio-catalysis, which is a enabling tool in unraveling the molecular aspects of catalytic nanosystems and to discern the driving forces for catalytic turnover and chemical selectivity.

After the foregoing orientation on catalysis and its sub-disciplines (homogeneous, heterogeneous, bio-catalysis and computational catalysis) including its importance as a key pillar of the industrial sector and economy, sustainability and green chemistry, examples of groundbreaking innovations in chemical and petrochemical manufacturing, and the more scientific considerations in pressure, materials, and complexity gaps, design of new catalytic materials, and catalytic reactors, it is clear that exciting challenges beckon us ahead such as in physicochemical characterization and future critical directions in research and development. We will consider these challenges and opportunities in this report. Thus, we will outline new ideas/concepts for further research in physicochemical characterization of catalysts and new paradigm shifts/future critical directions for research and also focus on the area of reactivity studies and design of catalytic reactors. In this area, we will strive to introduce some new tangible ideas in collection and analysis of rate data from catalytic reactors. We believe that this is the one area that needs to be viewed critically from a new lens, to identify the lacunae in the current experimental procedures – and we believe there are many - as reported in the prior journal literature - as well as highlight new experimental tools to be used in catalytic reactors and bench-scale experimental systems that enable us to overcome the problems that lead to experimental errors in data collection and analysis.

B. NEW PERSPECTIVES IN HETEROGENEOUS CATALYSIS

B.1 Reactivity Studies and Laboratory Reactor Design

The development of an industrial catalytic process starts very often at the laboratory, with experiments designed to screen several potential catalysts and the selection/design of an appropriate laboratory reactor for kinetic studies. It is thus very important to collect accurate and meaningful kinetic data on the laboratory scale (free from experimental artifacts (measurement errors) and disguises such as heat and mass transport limitations) because the success of the industrial-scale reactor depends on the scale-up factors and parameters developed from the laboratory data [2, 15-18]. The elements that govern a proper choice and design of a laboratory catalytic reactor for experimental studies and a brief description of the different catalytic reactors that are available for catalytic studies has been given earlier in recent works [16-18].

In a typical study, the reactants in the gas phase are contacted with a fixed catalyst charge (say, in a differential fixed-bed reactor system (for intrinsic kinetic studies), or other reactor types), at specified conditions of temperature, pressure, and space velocity (defined as volumes of gas at normal temperature and pressure conditions (25 ^{o}C and 1 atm) per unit volume or unit mass of the catalyst charge per unit time), and the catalyst performance features including conversion (of

a basis reactant), selectivity (to principal product), yield, specific reaction rates (per unit mass of catalyst), areal reaction rates (per m^2 of active metal surface), and turnover frequencies (mol/mol metal. time, but more correctly defined as molecules of products per mol of active metal per sec) are assessed. The moles of active metal are determined from dispersion (H_2 or CO chemisorption measurements) studies, which estimate the fraction to total atoms of metal that are on the surface (and are thus available as active sites for the surface reaction). It is interesting to note that the phenomenon of interstitial diffusion, i.e., diffusion of a reactant molecule in the interstices of the metal crystallites, is never considered in any analysis. Thus, it is conceivable here that one can define a new term called "active (or, true) metal loading (molar basis)", based on such dispersion studies, say, as a product of overall metal loading and fractional dispersion. It is also perhaps more proper to report specific reaction rates (per mass or mole of catalyst) with this "active metal loading" as the basis, as it is intuitive that the specific reaction rates as reported otherwise will underestimate the true reaction rates (higher loading when compared to true metal loading, as above).

- Conversion, Selectivity, and Yield: The conversion, selectivity, and yield are defined as follows, for a simple chemical reaction:

$$A + B \rightarrow C + D \tag{1}$$

Let A be the limiting reactant and let N_{A0} be the number of moles of (limiting) reactant A fed to the reactor inlet (N_{B0} is the number of moles of reactant B). C is the desired product, and N_C is the number of moles of product C. The total moles of product are then $N_C + N_D = N_P$.

$$\text{Conversion} = \frac{N_{A0} - N_A}{N_{A0}} \text{ x } 100 \text{ \%} \tag{2}$$

$$\text{Selectivity of product C} = \frac{N_C}{N_C + N_D} \text{ x } 100 \text{ \%} \tag{3}$$

$$\text{Yield of product C} = \frac{N_C}{N_{A0}} \text{ x } 100\% \tag{4}$$

- Specific Reaction Rate and Turnover Frequency: The specific reaction rate can be defined on the basis of catalyst particle volume or mass (or, bed volume or mass), and the areal rate is frequently defined on the basis of overall surface area or the metal surface area. The turnover frequency (TOF), a very important performance feature, as it enables to compare data obtained on similar reactions and catalysts in different experimental tests and laboratories, is defined as molecules of reactant or product per surface metal atom per sec, and has the units of sec^{-1}. Thus TOFs (or areal rates, rates based on active metal

surface areas) are gathered and reported in any proper catalytic study, as it can help benchmark the performance of an experimental catalyst in laboratory which can also be a reference or starting point for catalytic studies in other laboratories. In Section B.1, we attempt to refine the definitions of turnover frequency further, to include microscopic quantities such as time scales of elementary steps that lead to one catalytic turnover.

A balance between transport rates of reactants (to and from the catalyst surface, or the active site) and chemical reaction rates is the proper way to operate a commercial reactor. This is frequently called as the Weisz window for commercial operation, and is quantified to be 1 μmol/cm^3.s. This reaction rate translates into a TOF of 1 s^{-1}, for many catalysts. However, for laboratory reactors, the TOF values are frequently 1-2 orders magnitude lower than the value for commercial operation, as diffusion and transport do not play a role in surface reaction kinetics. A simple definition of TOF can be given as follows:

$$\text{TOF (s}^{-1}) = \frac{\text{rate of reaction (mol/g cat. s)}}{\text{catalyst loading (g metal/g cat)}} \text{ x } \frac{\text{atomic weight of metal (g metal/mol)}}{\text{fraction of total metal atoms that are surface metal atoms}}$$

$$(5)$$

In the above formula, the catalyst loading (g metal/g catalyst) is the experimental loading, determined using a tool such as inductively coupled plasma – optical emission spectroscopy (ICP-OES) or inductively coupled plasma – mass spectrometry (ICP-MS).

Some basic guidelines for proper collection and analysis of reaction rates in terms of TOFs are as follows [17-21]:

- The TOF data should be collected under surface-reaction control, i.e., in absence of extraparticle and intraparticle heat and mass transport limitations.
- The TOF and kinetic data should be collected in the absence of deactivation effects due to poisoning, coking, or sintering.
- The TOF data should be collected over wide ranges of temperature and partial pressures (of reactants), to enable easy comparison with data from other laboratories.
- For structure-sensitive reactions, i.e., for those reactions where the TOF is a function of the surface structure and the crystallite size, these effects of metal dispersion and crystallite size should be taken into account.

- Apparent Reaction Orders and Activation Energy: A key consideration in the experimental catalytic science is the determination of reaction orders with respect to reactants and the apparent activation energies of the reaction. Frequently, in gas-solid

reactions, the TOF is modeled as a function of the partial pressures (or, concentrations) of the reactants. Consider the synthesis of ethanol (and light alcohols) from syngas (with a H_2:CO of 1) over 2%Rh-2.5%Fe/TiO_2 catalyst, in a fixed-bed micro-reactor system, at nominal conditions of 543 K and 20 atm [22, 23]. The overall reaction can be written as:

$$2\ CO + 4\ H_2\ =\ C_2H_5OH + H_2O,\ \ \Delta H^o{}_R\ (298\ K) = -253.6\ KJ/mol \qquad (6)$$
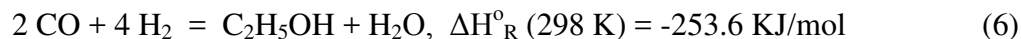
The reaction is thus highly exothermic. One approach to determine the activation energies and reaction orders with respect to H_2 and CO is from the plots of ln (TOF) vs. 1/T and from plots of ln (TOF) vs. ln (p_{CO}) or ln (p_{H2}). Frequently, in such cases, an inert such as He or Ar is used to dilute the feed, and the partial pressure of one of the reactants is varied while the other is held constant. For example, one strategy to determine the apparent reaction order with respect to H_2 is to hold the partial pressure of CO constant at, say, 2 atm, and change the partial pressure of H_2. Of course, the partial pressure of the inert will change as well, to make up the total pressure to a nominal 20 atm.

- Dispersion and Metal Particle Size: The final term, dispersion, is the fraction of the total metal atoms that are on the surface, which are considered to be active sites. As stated above, dispersion is frequently determined using surface titration of metal atoms using probe molecules such as H_2, CO, or O_2, and is called chemisorption. For most metals, a simple empirical relationship exists between metal particle size and dispersion, as:

$$d_p = 1.1/D \qquad (7)$$

where:

d_p = particle diameter (assuming spherical particles), and,
D = dispersion, fraction of total metal atoms that are surface metal atoms.

A detailed discussion of the several methods for the collection and analysis of laboratory data is available in many recent works [24-28].

After this brief prelude on the basic elements of reactivity studies and reactor design, it is now appropriate to put forth new ideas/concepts and new perspectives in this field. This (reactivity studies and reactor design) is considered to be a fairly mature area (important yet archaic in terms of new innovations) in heterogeneous catalysis. Be that as it may, we believe that our out-

of-the-box thinking and some original ideas/thoughts have allowed us to spawn and crystallize new ideas both in reactor design and systems design and in the experimental data collection and gathering that will undoubtedly benefit the current way ("old way") to collect and analyze data. We believe that there is the better way which should be embraced by those in the catalysis fraternity at the soonest. These ideas are listed in the following sections.

B.1.1 Design of catalyst baskets and design of precision tools for insertion of baskets

The first such new design is in the area of catalyst charging for fixed-bed reactors, design of a new insertion tool for catalyst boats and baskets at precise locations within bed to match the insertion of thermocouple devices, and the design of the said baskets. This is especially important as over 70% of all reported studies are carried out in fixed-bed configurations. This is geared toward a proper reporting of temperature (as in contact with the catalyst solids) in the experimental measurements. Temperature plays a very pronounced role in governing the rate of chemical reactions, which makes the measurement of temperature the single most important measurement in bench-scale studies of catalytic reactions.

A well-known rule of thumb states that the chemical reaction rate/and other derived metrics from it, increases by a factor of 2, with a temperature increment of 10 degrees. Therefore, well-placed and accurate probes (thermocouples) are necessary to provide the necessary control and measurement in catalytic reactions. Even an error of 1 degree can introduce large experimental errors in measurements of reaction rates and activation energies (and turnover frequencies). An important element of bench-scale studies is that the data be compared to prior art (benchmarking studies) or be compared with data from other laboratories in the same studies. Experimental artifacts (measurement errors) thus should be avoided at all costs, to assure the integrity of reported data. A proper calibration of the temperature probe is thus a vital necessity. In some cases where a single measurement may not be accurate or precise, perhaps a second unit such as an infra-red sensor can be used to provide a secondary and a more reliable estimate. It is also possible that the thermocouple junction or lead (active element within the sheath) can be placed in some type of magnetic disc/holder with an electronic chip which can sense and provide data output to a data acquisition/control system.

Frequently, the thermocouple is placed within the catalyst bed/basket to assure intimate contact of the catalyst solids and the probe, for a proper measurement. Clearly, the thermal capacities of the gaseous environment and the catalyst solids are different, and thus any probe that is not in contact with the catalyst particles can result in a serious underreporting and thus introduce large errors in measurement. It is therefore necessary to provide a high degree of precision in the placement of temperature probes such as thermocouples. In most tubular reactor configuration (such as, say, the Autoclave Bench-Top Reactor System (BTRS Jr.), or Parr designs), the thermocouple is introduced from the top and is placed at the center of the catalyst charge in contact with solids within the tube.

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For standard reactor tubes such as 3/8", ½", and 5/8" sizes, we propose a newer catalyst basket design in the form of "basket" or a "disc", with an open-top configuration. It can be fabricated out of a wire mesh (say, stainless steel 304 or 316) of different sizes, based on the choice of size of catalyst particles (and, intended loading). The catalyst will be lightly packed into the bed, and the basket will be inserted into the reactor tube, with a caliper-based insertion tool. The caliper-based insertion will insert the bed to such height within the tube that the thermocouple probe from the top will be at approximately ½ the depth of the bed, and thus integrally within the bed, in close contact with particles, for an accurate measurement. For shallow beds (typically encountered in differential fixed-bed designs), the insertion depth of the thermocouple can be such that the thermocouple can touch the base of the bed – the catalyst particles and the basket material have similar thermal conductivities, and this will not introduce any errors.

B.1.2 New high-performance polymeric materials for O-rings and gaskets

For conventional bolted closure pressure vessels in use as catalytic reactors (manufactured by original equipment manufacturers' such as Autoclave Engineers'/Parker, Parr Instruments, etc.), the confined metal seal design (Gasche^{TM} by Parker) is the most reliable method of sealing, even at high temperatures. It is shaped to effect a tight metal-to-metal seal on reactor body and cover, and is reusable over many openings and closings of the reactor vessel. These pressure vessels are available in different closure styles (ease of operation and maximum available working pressure), sizes (volumes), materials of construction (for temperature and chemical compatibility), and seal designs. These reactor systems find a myriad of applications in bench-scale catalysis research and studies of catalytic reactions, in batch or continuous modes.

In elastomeric (polymeric) materials, the traditional and most popular gasket (typically for Parr Instruments) is a flat gasket made of a PTFE fluoropolymer. Here, in these designs, the gasket is held in a recess in the reactor body, and a matching pilot on the reactor cover closes the recess with the gasket. The gasket is thus completely confined with the cover-body assembly, with only a small edge exposed to the reactor contents. The complete containment coupled with a high resistance to heat (extended applications at high temperatures (> 350 ^{o}C)) and excellent resistance to chemicals/solvents provides a reliable seal, at high pressures. In addition, the ability of PTFE to "flow" or "creep" under pressure (deform slightly to "expand" into recess) also helps to achieve a tight seal, which improves with every application. It is also a forgiving seal and does not require a "uniform" load for closure or effective operation, which is needed for metal seals.

In self-sealing designs, two gasket materials (called O-rings, as opposed to "flat" gaskets) are most common – the FKM fluoropolymer (available under trade name, Viton®) that shows good chemical resistance and temperature resistance to 225 ^{o}C and the FFKM perfluoropolymer

(Kalrez®) which exhibits broad chemical resistance and can be used to 300 $^{\circ}$C. Both Viton® and Kalrez® are elastomer products marketed by DuPont Performance Elastomers (based in Wilmington, DE). The latter material, Kalrez®, should be considered as an "exotic" material, as it costs about 100-times more than a Viton® O-ring. Two other elastomers are also commonly available as O-ring materials (but are more suitable for low temperature applications, <250 $^{\circ}$C) – Buna-S® and Buna-N®. The former is based on Styrene Butadiene formulation while the latter on Nitrile Butadiene (NBR) and Carboxylated Nitrile Butadiene (XNBR) formulations. Buna-S® is available in several commercial forms: Carom® (Chemische Combinat), Cariflex® (Shell Global Solutions), and Pliolite® & Plioflex® – Goodyear Tire and Rubber Company. Buna-N® is a tradename of Chemische Werke Huls. For high temperature applications (exceeding 350 $^{\circ}$C), a high performance material, Grafoil®, has been introduced (UCAR Carbon, Inc.). It consists of layers of flexible graphite bonded together to produce a gasket that is as easy to use as, say, flat PTFE, but with unlimited heat resistance (applications even to 650 $^{\circ}$C) and chemical compatibility.

A new-generation high-performance elastomer (a perfluoroelastomer, under tradename, Perlast®, by Precision Polymer Engineering Ltd.) has been recently introduced and touted as being superior to both PTFE (high chemical resistance with temperature limits of to 350 $^{\circ}$C) and FKM elastomers – it combines the chemical and thermal resistance of polytetrafluoroethylene (PTFE) and the elastomeric properties of fluorocarbons (FKM). Some of the superior characteristics of this perfluoroelastomer include high temperature stability (up to 330 $^{\circ}$C), exceptional chemical resistance, high reliability of seal quality at high pressures, excellent long-term high temperature compression set resistance, low permeability, and longevity.

A family of rubbers called as silicone rubbers are important engineering materials and find many applications in chemical industries. Silicone rubbers are based on a Si-O-Si backbone and have the general formula: $SiH_3(OSiH_2)OSiH_3$. Depending on the number of siloxane functional groups, silicones are termed as disiloxane, trisiloxane, etc. The materials having mainly organic functional groups attached to silicon atoms in the Si-O-Si backbone are called as polyorganosiloxanes of silicones. Uncrosslinked silicone rubbers need to be vulcanized and crosslinked to convert into elastomers or performance materials, with the following types of crosslinking methods: Pt-catalyzed addition curing, Peroxide curing, and Condensation curing. There are five main classifications of silicone rubbers: MQ – Silicone rubbers having only methyl groups on the polymer chain, PMQ – Phenyl and methyl groups, VMQ – vinyl and methyl groups, PVMQ – phenyl, vinyl, methyl groups, and FVMQ = fluoro, vinyl, and methyl groups. MQ, PMQ, and PVMQ classes are intended for extremely low temperature applications and are not commonly used, while VMQ and FVMQ categories are used for general purpose and applications involving fuel, oil, and solvent resistance. The key advantages of silicone rubbers are good thermal stability, constancy of properties over a wide temperature range (-100 to 250

^{o}C), ability to repel water (hydrophobicity) and form water-tight seals, and low chemical reactivity. Silicone rubber products are available from Wacker Chemie AG and Saint Gobain Performance Plastics under various trade names. For example, Wacker AG markets silicone rubbers under the brand names, Elastosil®, Powersil®, Semicosil®, Lumisil®, and Cenusil®.

B.1.3 New designs of reactor internals including protective coatings and liners

Protective internal liners and coatings for reactor vessels and other general purpose vessels are often used to provide protection and cross-contamination from corrosive solutions such as acids or alkali. These internal liners are available as polytetrafluoroethylene or glass inserts and slide into the cylinder body and require no additional fittings. It is intuitive that the addition of a polymer or glass insert (both with an order-of-magnitude lower thermal conductivity than, say, stainless steel) will slow down the rate of heat transfer into and out of the reactor vessel and it may be necessary to provide a more precise temperature control method, to prevent thermal inertia (or, accumulation of heat). Some original equipment manufacturers (Berghof Products + Instruments, Germany) offer protective internal *coatings* (not inserts) which are hermetically sealed and also based on PTFE materials. The PTFE coating offers excellent protection versus all chemicals (including strong acids and alkalis) which obviates the need for expensive special materials of construction, say, Hastelloy C-276. Bench-scale catalytic reactions are often carried out under very high temperatures (up to 450 ^{o}C) and pressures (100 atma) and in presence of a catalyst (typically a transition metal supported on an inorganic carrier), there is a possibility of metallic components of the catalyst leaching out and adhering /depositing onto the steel wall and/or trace impurities or components of steel material eluting out into the solution (akin to the suspension or sol-gel methods in catalyst preparation for deposition of metals onto substrates/carriers). In the analysis of the chemical reactions, these leaching and elution phenomena can cause confounding effects. The PTFE coating provides excellent protection versus these possibilities and thus is an ideal way to control these risks and the data confounding.

B.1.4 New designs on optional accessories and peripherals for laboratory reactors

Most of the literature on current designs of bench-scale chemical reactor systems and peripheral parts is available on the websites of vendors of these reactor systems, which includes Autoclave Engineers' Inc. (a subsidiary of Parker Hannifin Corporation), Parr Instruments, etc. It is important to make an informed choice on the bench-scale reactor system and peripherals to be used for experimentation into bench-scale catalysis and process studies. It is also important to understand that the basic responsibility for safety lies with the end user of the reactor systems.

It is thus essential to select a reactor assembly that has the desired features/capability, temperature/pressure rating, corrosion resistance in presence of acids/alkalis (right materials of

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construction), and other features that make it suitable for intended use. Very often, original equipment manufacturers of pressure vessels and chemical reactors, such as AE and Parr Instruments, offer their products in a variety of styles, designed to operate within certain temperature and pressure limits, gasket and closure/cover designs, and other elements for a safe operation. It is important, however, to preserve the sanctity of the original designs, and not make any substitutions or alter designs to original make/built of these systems.

Custom reactor systems are normally fabricated out of stainless steel alloy (T SS316), but other materials and alloys which offer higher temperature and pressure limits, corrosion resistance, and other safety features are also popular, for specific applications. For example, Parr Instruments offers some of the newer alloy materials including Alloy Cb-3, C1018 carbon steel, Alloy 400, Alloy 600, Titanium, Zirconium (Grades 702 and 705), Alloy B-2, Alloy C-276, and Alloy C-2000. Some of these alloys are parts of active patents (some have expired) and have commonly known trade names such as Monel, Inconel, Incoloy (all trademarks of Inco Alloys Int'l), Carpenter Alloy (Carpenter Technology Corporation), and Hastelloy (Haynes Int'l, Inc.). Another high performance and high strength metal, Tantalum, offers outstanding resistance to corrosive media like hydrochloric, sulfuric, nitric, and phosphoric acids, but is not available in billets (or, blocks) which can be formed into reactor bodies.

Some noteworthy new developments in the design of reactor accessories and peripheral parts (custom design) and the rationale for each are given below.

A principal component of any reactor system is the electrical heater/heating jacket mounted on the reactor body; different types are used for individual reactors to best meet the operational needs, heating load, and maximum operating temperature. Some standard heating assemblies include clamp-on band heaters (for small reactors, where maximum heat transfer is required due to limited surface area of the vessel), rigid heating mantles (quartz fabric mantles mounted in aluminum shells, limited to 350 $^{\circ}$C, and ceramic heaters (special purpose heaters with electric element embedded in ceramic body held in insulated metal casing). The ceramic heaters are designed to be used for temperatures up to 600 $^{\circ}$C. Aluminum block heaters are available as an option for most reactor vessels, made from solid blocks of aluminum with heater elements/wells machined into walls of these blocks. Aluminum block heaters are an important advance in the area of electric heaters and offer convenience of direct heat control and rapid cooling (on account of its higher thermal conductivity, and especially with optional cooling channels). The heating elements/wells, cooling channels, and electrical wiring are embedded within the aluminum casing, which allows for an even heat distribution, isolation of electrical wiring/connections, and rapid cooling. It is interesting to note that aluminum has a higher thermal conductivity (205 W/m. K) compared to stainless steel (12-45 W/m. K) and most alloys (Inconel at 15 and Hastelloy B/C at 10 W/m. K) and thus has better heat transfer characteristics, compared to, say,

SS316 used for casing. It is also perhaps prudent to consider copper as a casing material as it has an even higher thermal conductivity, 385 W/m. K. Copper is also a more malleable and ductile material, and can be easily formed into blocks for heaters.

Impellers and baffles form an important accessory of a reactor system. It is customary to find most bench scale chemical reactor systems equipped with turbine type impellers, which produce excellent mixing action over range of stirring speeds (usually up to 2000 rpm). The turbine type stirrers are usually available in 4-blade or 6-blade styles, and it is intuitively obvious that the smaller 4-blade types are used with the smaller micro- and mini-reactors (volumes up to 600 mL). For reactor volumes greater than 300 mL, two separate impellers mounted on the shaft (gas entrainment design) are common; one is mounted at the base of the reactor vessel to keep the solids/catalyst particles in slurry or suspension, the other impeller is mounted near the reactor vortex (at its bottom) to induce gas into the reactor slurry for reaction, through the gas entrainment shaft (hollow). These impellers provide excellent mixing action for liquids with effective viscosities of up to 50,000 cP (or, 50 N-sec/m^2). For more viscous liquids including polymer solutions, two different types of stirrers are available: Anchor stirrers, in three types, a U-shaped, flat bar anchor, two- or three-arm flat blade anchor with PTFE wiper blades, and a flat-blade paddle type anchor. These stirrers work best in vessels having a length to diameter ratio of 1.5 or less ("flat" vessels, with low aspect ratio), and at low speeds. Spiral stirrers, in stamped blade type and machined blade type, are also well suited for high viscosity materials, and require a heavy duty drive (such as direct drive motors with a gear box, with different gear ratios). Different HP ratings are available, from ¼ to ¾ hp, and a suitable gear box ratio such as 3:1 or higher 10:1 can reduce the speed from 1700 rpm to a lower value (say, 300 rpm), and a high torque value (80 in-lb$_f$ to 180 in-lb$_f$).

For baffles for use with bench scale chemical reactor systems, a removable baffle set is standard. It is important to understand that it is the relative motion of the impeller and the liquids at the tip of the impeller that controls the mass transfer (gas entrained into the slurry to the liquid medium) and baffles mounted on the reactor periphery/wall effectively limit the velocity of the liquid a the tip. While some baffling is provided by the internal components such as thermowell, dip tube and cooling coils, removable baffles are recommended for use with the gas entrainment impellers. In addition, standard baffling provides an increased power input (impeller power number and pumping number), suppresses vortex formation at the top of vessel, offers good mechanical stability (due to symmetric placement of the baffles nearly flush with the wall, around the axis), and results in near-optimal performance. These performance characteristics are backed up by extensive design and scale-up data.

A frequent question that arises in experimental bench scale research in catalytic reactor systems is how to add liquids, solids (mostly catalyst powders, in activated form), and other suspensions/slurries to a reactor system, while at high pressures and temperatures (i.e., during experimental runs in progress). It is an oft raised question as it is a non-standard design accessory. The reader is pointed to contents of some recent catalogs of OEM's of these high pressure reactor systems (Parr Instruments and Autoclave Engineers' Inc.) for more information. Some of these include metering pumps (HPLC pumps, for example), pressure pipettes as secondary vessels for addition of liquids, solids ports which use a ball valve to admit solids, and external and internal catalyst solids addition vessels.

While this is a matter of safe principles of lab reactor assembly and operation (given in Section B.1.5 that follows), it is customary to provide a circular sieve (small disc) on the product gas outlet connection (NPT or Swagelok) on the reactor cover that opens to the reactor body. Especially for those situations with high vortex, it helps to keep the slurry/suspension out the product outlet connection, which minimizes the risk of plugging the line, and consequent pressure buildup and/or overpressure.

B.1.5 New perspectives on reactor safety and incorporating safer principles for laboratory reactor assemblies and operation

Some recent lab safety incidents that unfortunately led to some catastrophic consequences and personal injuries at campus laboratories in the United States have prompted several agencies including the occupational safety and health administration (OSHA) and U.S. chemical safety board and their academic liaisons including environmental, health, and safety (EHS) departments at academic institutions take a fresh look and revisit the issue of safety procedures and practices in laboratory. Three such recent safety incidents at academic institutions (all in 2016) including ones at University of Hawaii, University of Calif. at Los Angeles, and Texas Tech University involving graduate students/postdocs working in laboratories have called the safety standards into question, and have led many including the U.S. Chemical Safety Board/OSHA to declare that the safety standards/training imparted to laboratory/academic personnel on many campuses are lax. Of course, this may partially factor in the inadequate and lackadaisical attitudes and individual accountability towards safety. Moreover, in some cases such as the one at University of Hawaii Natural Energy Institute, causes such as a static electricity discharge (a spark) from an unlikely source (forward pressure regulator on a flammable gas tank (55% H_2, 38% O_2, 7% CO_2) are difficult to foresee and avoid (It is, however, easy to see that the said gases in question, since a flammable mixture, should be metered in from different feed sources.) It is thus clear that safety is of paramount importance and we should take the rising number of safety incidents very seriously.

As in the University of Hawaii incident, where the said postdoc was simply adding a gas mixture containing H_2, O_2, and CO_2 at a low pressure/low flowrates (from a gas cylinder at moderate pressures, 8 atma) to a bacterial cell culture in a petri dish as a nutrient (for production of biofuels and bio-chemicals), it is clear that the safety incidents can occur anywhere and often without a warning (and as a surprise, unforeseen cause such as static discharge). However, it is intuitively obvious that safety issues/occurrences are perhaps more prevalent in the operation of high-temperature, high-pressure catalytic reactors and peripheral systems. From the personal experience of this author, who has extensive experience in the design, assembly, and operation of bench-scale reactor systems (including fixed-bed, fluidized-bed, and slurry reactor systems) and perhaps the only one who can vouch that he has never had a safety incident in over 20 years of operational and supervisory experience (!), some cautionary notes and comments about lab safety are definitely worth reader review and lab practice.

It is clear that incorporation of safety elements (with tangible units/modules) and safety factors should begin with reactor design and process flow/instrumentation diagrams for the reactor/peripheral system in question. Two of the important process systems that the author has been associated with during his doctoral and postdoctoral work are: Synthesis of methanol and dimethyl ether (DME) from CO-rich syngas in a slurry reactor and synthesis of light olefins ($C_2^=$ and $C_3^=$) from methanol/DME mixed feedstocks over molecular sieve zeolites. These high-temperature, high-pressure reactor systems involve extensive use of synthesis gas at high pressures (a mixture of H_2, CO, CO_2, and CH_4), both in compression stages (individual gases metered into a manifold and compressed to desired pressure and stored (typically >150 atm)) and metering feed syngas (net flow into and out of the reactor). Extensive safety features and units were incorporated into the design of these systems [It is interesting to note that these reactor systems still continue to be in good service (now at Ohio University (Athens, Ohio) and are used for bench-scale catalytic reactions in the laboratory) - originally designed in 1990s – perhaps as a result of the safety modules and preaching of safe operation by this author]: Provision of a rupture disc mounted on the reactor assembly, designed to "fail" at some value of reactor pressure (typically maximum allowable working pressure, MAWP), to vent the reactor contents in a safe manner, pressure relief valves (to reseal the reactor contents after excess pressure has been relieved), CO/H_2 combustible gas monitors/alarms designed to return audible beeps/warnings if the flammable gas concentrations exceeded a "safe" value (by leaks – H_2 is the lightest molecule known, and leaks can occur even after pressure tests, i.e., during operation, even after the reactor has passed the static pressure test under "cold" conditions), installation of non-return/check valves, and adequate pressure/leak tests before any operation. The reactor assembly tag (plate with engraved contents, as in original tag by Autoclave Engineers' Inc.) was also displayed at a very visible location on the cover, with key information useful to the

operating personnel such as maximum allowable working pressure, allowable temperature at this pressure, and material of construction, and relief/burst pressure (pressure at which a safety device such as a rupture disc will trigger for safety).

Several practical considerations from the standpoint of safety are apparent especially when the personal (hands-on operational and supervisory) experiences of this author over some 20 years are distilled and organized as follows. For the start-up operation of high-temperature, high-pressure reactor systems, it is of utmost importance to clean the reactor body (after emptying prior contents) and cover thoroughly, with the final touch-up with acetone. The area (recess or groove) where the gasket or O-ring is placed is very sensitive to even minor imperfections or smears (even a scratch or metal-to-metal "burr" on the groove can damage the seal). The seal should be placed properly on the groove (body) and the bolted closure vessel then closed up. It is necessary to follow proper tightening sequence for the bolts on the reactor cover, for 8 bolts on the reactor cover, a proper sequence will be 2 (first ortho-position), followed by 6, 3-7, 4-8, and finally 5-1, and it is customary to torque the bolted cover to about 40 ft-lb$_f$ higher torque than the recommended torque (usually 100 ft-lb$_f$, for a standard 1-L stirred autoclave with 8 hex-head bolts, from Autoclave Engineers'). The reactor assembly should then be tested under static "cold" conditions for pressure test.

It should be noted that the joints/connections are the "weakest" points in the reactor design/assembly and peripheral systems (tubings, valves, connections (unions, tees, elbows, other bends, reducers, adapters, etc). Proper use of sealing tapes (PTFE) and proper winding around threads (to avoid damage) and about ¾ to 1 complete turn (after finger-tight) by wrench is necessary. Swagelok threads do not require PTFE tapes. The swage threads (Swagelok/parker fittings) and NPT pipe threads are in opposite directions. It is necessary to check leaks around the gas regulator (no PTFE tapes are necessary around the compressed gas association (CGA) fittings) and the forward pressure regulators (Swagelok connections for gas egress lines). Utmost care is necessary when dealing with gas cylinders/regulators especially with flammable gases and all sources of ignition/sparks be kept away from compressed gases. It is important to keep all connections (such as those to tubing, regulators, and other instrumentation) tight and leak-free. It is thus necessary to periodically inspect the tubing or hoses (and the connections such as swage threads around Swagelok joints) to make sure that they are in good condition. Proper use of insulating tape like PTFE around all joints is necessary. This helps minimize the generation of static electricity around the regulators (an issue raised in the analysis of the University of Hawaii Natural Energy Institute incident) as sparks can lead to fires, especially with flammable gases. The gases should be added to the reactor in a controlled manner (through mass flow controllers at some set point (even lower than the actual set point, at higher flow rates), so that there are no surges and adiabatic heating/cooling around the gas regulator

assemblies (which can also lead to static discharges). The reactor depressurization sequence (after the reactions) should also be proper, and the gases should be let off in a very gradual manner. This is especially important for stirred autoclave (as in slurry reactor systems, with finely powdered catalyst) where there can be a risk of "flashing" of the reactor contents (slurry) which can lead to blockage of reactor exit lines (by slurry).

Some general safety practices when dealing with compressed gases and gas cylinders are given below. Great care must be exercised when handling the different types of compressed gases, the cylinders, the CGA gas regulators used to control delivery pressure, tubing/connections/piping used for delivery lines, and the reactor vessels. Regular inventories of cylinders and checks of integrity (seals) are important. It is necessary to accurately label compressed gas cylinders (and flammability/NFPA codes) so they can be easily, quickly, and completely identified by laboratory personnel. Further, it is also necessary to label all gas lines properly, leading from a compressed gas supply (in-house supply or a gas cylinder) to identify the gas, the laboratory (if more than one, for in-house cases) and any relevant emergency phone numbers.

Finally, all laboratory personnel must be proactive to ensure that the laboratory is a safe working environment, especially with high-temperature, high-pressure catalytic reactor and peripheral systems. As a matter of safe principles and procedures, it should always be mandatory to wear appropriate apparel (aprons or safety coats) and proper eye (eye glasses/goggles), face (face shields/face masks), hand (gloves of appropriate type, common nitrile gloves for use with chemicals), and foot protection (closed-toe shoes at all times) when working in the laboratory. The institution is responsible for providing appropriate safety and emergency equipment for laboratory and emergency personnel. In addition, safety equipment, including spill control kits, safety shields, fire safety equipment (including fire extinguishers), respirators, safety showers, and eyewash stations should be available in well-marked highly visible locations in all laboratories.

B.1.6 New perspectives on laboratory data collection, reporting, and analysis

This is perhaps the most important part of this report. We believe that it is of utmost importance to revisit and refine the "old way" of collection and reporting/analysis of rate data for several reasons. A survey of the catalysis literature and review of recent experimental data in journals such as Journal of Catalysis, Applied Catalysis A/B, Catalysis Communications, J. of Molecular Catalysis A/B, etc. shows that there are several such areas where incremental and even transformational improvement is needed. While some of these drawbacks/lacunae can result from simple reporting errors and uninformed methods of data collection (which can lead to experimental (human) and/or instrumental errors) which call for incremental improvements, some transformational paradigms/thinking is necessary in some other areas. Of course, it is also

important to keep in mind several screening protocols for experimental tests to make sure that the kinetic rate data as gathered can serve the hypothesis framed at the start of experimental plan and that there are no confounding effects. For example, for intrinsic kinetic rate data, it is absolutely essential to carry out the experiments in a differential reactor (differential beds, with low reactant conversions, <10%) and make sure that the reactions are under surface reaction/kinetic control, and there are no confounding effects due to heat or mass transport limitations, both external and internal to catalyst particle.

It is also crucial in bench-scale research to be able to compare the experimental data to data from other laboratories on same/similar catalysts (for benchmarking with prior literature, for example). A commonly accepted metric for this comparison is turnover frequency (TOF) of a chemical reaction (typically measured/reported in the units of moles or molecules of product/mol surface metal. sec). While it is important to observe some common precautions for TOF data (kinetic or surface reaction control, no transport disguises, collection of data over a range of temperatures and pressures, no deactivation, etc.), we believe it is the intermediate experimental steps during operation of a bench-scale reactor system and collection of data (that lead to the precautions as reported above) are more important. For example, in the data collection steps, a key substrate which is not labeled or not reported properly can confound further analysis (it is clear that a same substrate or reagent from different catalogs (say, SAF, Strem Chemicals, Fischer Chemical Company, Alfa-Aesar, etc.) can have different properties/characteristics. Based on the author's personal experience of over 20 years, it is clear that the experimental data should be collected with proper care and precautions. For example, as reported in Section B.1.1 above, a proper reporting of temperature (thermocouple probe in integral (physical) contact with the catalyst solids) is absolutely critical in the experimental measurements. Temperature plays a very pronounced role in governing the rate of chemical reactions, which makes the measurement of temperature the single most important measurement in bench-scale studies of catalytic reactions. As given in Section B.1.1, we have provided newer designs of catalyst baskets and insertion tools (based on calipers) for proper placement of the thermocouple probes in physical proximity of the catalyst. This is especially important as over 70% of all reported catalysis studies are carried out in fixed-bed configurations. It is further important to extend these precautions to all other parametric measurements, such as pressure, mass/molar flow rates, and compositions (as with a gas chromatograph). In parametric measurements, both precision and accuracy are important and it is also important to make sure that all instrumentation is calibrated properly. This is especially important for gas chromatographs and columns (TCDs, FIDs, and other detectors). Column conditioning (or, preconditioning) is thus important and it is important to ensure that the column does not see any "foreign" molecules (other than intended for analysis) or the column loading is in excess of capacity. These factors can irreversibly change the response factors of the column/chromatograph and affect all further analysis. Of course, it is

important to check all mathematical calculations and analysis (say, as in Excel spreadsheet) to assure integrity and accuracy of reported data. In case of errors in the formulae as entered into the Excel spreadsheet, the calculations will be erroneous and will lead to erroneous conclusions, i.e., which are contrary to the experimental data (non sequitar).

Apart from the proper care/precautions in data collection and analysis which can lead to incremental but important changes in the "old way", we believe that any real progress in the field of experimental heterogeneous catalysis and data analysis will come only in the form of transformation thinking in the philosophy of data reporting and analysis. A clear break from "old way" and a departure from the prior methods are essential as we look ahead to the next 15-20 years. It is important to emphasize here the distinction between new perspectives in bench-scale reactivity studies (this Section, B.1) and new perspectives in future research directions/paradigm shifts in heterogeneous catalysis (Section B.3).

Basically, the new methods we highlight here in bench-scale reactivity studies call for newer, more correct definitions of several common measures/metrics in the collection and analysis of reaction rate data. As reported above, a commonly reported metric for kinetic data and comparison is turnover frequency (TOF) of a chemical reaction (typically measured/reported in the units of moles or molecules of product/mol surface metal. sec). We believe that this definition of turnover frequency is meaningless, as it involves a macroscopic observable quantity (based on integral time, sec) and a microscopic quantity that is based on measurements and calculations (mol of surface metal, based on activated chemisorption measurements). It is also important to note that the word, TOF, implicitly assumes that the measurement is for a catalytic turnover cycle, or, one catalytic turnover, on the surface. This, by definition then, should incorporate microscopic quantities, ONLY. This is further confounded for chemical reactions carried out in the liquid phase, where the catalyst is slurried in a liquid medium (slurry or bubble column slurry) or trickle bed. The presence of an additional medium and also the presence of gas bubbles in the liquid and also the catalyst pore network make the analysis of these calculations very complex for reactions in the liquid phase. We believe that it is simply not possible to properly "define" TOF for liquid phase reactions.

As for the question of how do we correctly define the TOF for gas-phase reactions (if it is even possible – please see discussion later), we can think that we can use the reactor residence time or space time (inverse space velocity) as the basis. However, this is also an erroneous way as it is simply a reassignment of the volumetric flow rate (of the principal reactant). It is also easy to see that the denominator, mol surface metal, is simply a quantity that is calculated from metal loading and dispersion (or, surface metal atoms per surface atoms of the probe). As stated above, this quantity is simply the "effective metal loading". We therefore believe that we should find a way to base the "macroscopic" quantity, mol of product per unit time (which is simply the

reactor product molar flow rate, moles per unit time), on a surface/microscopic quantity. In addition, the bases of time should ideally derive from time scales of the surface reactions, or, catalytic turnover, typically in picoseconds or even lower, femtoseconds. It is easy to see that the TOF will then assume values of x.xx x 10^x, which can be considered as molecules of product formed in one turnover cycle per mol surface metal per time. If we assume that all surface sites (active sites) have equal energetics, i.e., equal heats of adsorption and heats of reactions/activation energy of elementary steps, and thus equal time scale of reaction, this seems to be the more correct way to define TOF.

The last question in this analysis that is intuitively obvious is how does one estimate or even measure the relevant time scales of reaction (assuming equal energetics and one single rate controlling step/mechanism). It is, however, clear that it is the total of all time scales of the sequence of elementary steps, including diffusion in the gas film followed by surface phenomena and back diffusion from the gas film to bulk product (even though one step is rate-controlling). While we want to pose this as an open question to the catalysis fraternity (as to how to select the microscopic quantities to properly define TOF based on microscopic variables alone), we want to state again that the TOF as currently defined is a wrong definition and lacks a physicochemical meaning from the standpoint of 1 catalytic cycle, at microscopic time and length scales (also stated by M. Boudart, one of leading researchers of our field). It is further clear that the TOF as defined originally was for the enzymatic catalysis, as the maximum rate per catalytic site at maximum concentration of enzyme, applied to Michaelis-Menten kinetics. As Boudart writes in one of his papers, "This unfortunate limitation is totally unnecessary and provides another cogent reason to avoid completely the use of turnover number in catalysis."

B.2 New Perspectives on Surface Physicochemical Characterization

Most traditional heterogeneous catalysts consist of an active metal component/metal oxide distributed in an ill-defined way over high surface area supports, with the pore architecture not well-defined as well. In fact, a precise control over the pore architecture, i.e., the dispersity index (or, the centrality of the pore size distribution around a certain pore size), of mesoporous and nanostructured supports is essential, which is now the new and cutting-edge area of research on forefront of heterogeneous catalysis. To this end, several recent studies have focused on the rational (i.e., based on science) synthesis strategies towards a precise pore size control of inorganic (or, amorphous) and zeo-type (crystalline) supports, as well as modeling studies of a given type of pore architecture [29-31]. It is important here also to make a distinction between research catalysts (the type discussed here, which comprise of an active phase and a support phase, mostly an inorganic carrier) and technical catalysts (which are macroscopic and granular forms of the research bodies, which are micron-sized powders). The agglomerated forms or technical catalysts are derived by the process of granulation (or, agglomeration), which is a

complex and multidisciplinary yet still predominantly empirical process at the interface of physics, chemistry, colloidal and surface chemistry, materials science, and chemical engineering [32, 33]. It is not covered in this manuscript as this is focused on newer advances in the synthesis and physicochemical characterization of nanoscale catalysts. A possible new approach for the synthesis of these nanoscale materials is the incorporation of atomic-scale precision and molecular control over the final size and dispersity, shape, and morphology of the catalyst [34-37]. Often times, colloid chemistry techniques in solution, i.e., chemical reduction of metal salt precursors, electrochemical synthesis, and controlled decomposition of organometallic compounds and metal-surfactant complexes, can be used to synthesize metal nanoparticles with a precise control over dispersity and particle size. The use of structure-directing agents, i.e., high molecular weight lipophilic molecules (polymers) who organize themselves in a manner comparable to liquid crystals, is also common in synthesis of nanoporous materials, especially such as MCM, commonly termed both as Mobil Crystalline Material or Mesoporous Crystalline Material, and sometimes also as Mobil Composition of Matter [38-41]. MCM-41 is an example of one such ordered mesoporous silica, initially introduced by Mobil researchers in 1990s. MCM-41 contains an array of hexagonal ordered pores which can range from 15 Å to over 100 Å. It has been usually synthesized in the solution phase with tetramethylammonium silicate, precipitated silica, alumina (usually catapal, as in the original schemes), and a surfactant as the structure-directing agent (SDA - hexadecyltrimethyl ammonium hydroxide – whose chain length determines the pore structure/size and the dimensions). Recently, research group at University of Calif. – Santa Barbara headed by Galen Stucky developed a new synthesis strategy for highly ordered, hexagonal mesoporous silicas, called Santa Barbara Amorphous No. 15 (SBA-15), based on non-ionic triblock and diblock copolymers (such as pluronic 123) and surfactants) [42-44]. The formation of SBA-15 silicas follows the same mechanism as that of MCM-41, a liquid crystal mechanism [45]. These novel siliceous mesoporous materials have been the subject of recent interest as they offer very appealing textural properties, high surface areas, and good hydrothermal and chemical stability. However, selective functionalization of the SBA-15 silicas by inorganic/organic heteroatoms by replacement of framework silicon is necessary to impart the necessary catalytic functionality [38, 46]. The use of other SDAs such as polyamidoamine (PAMAM) dendrimers can also lead to a precise control over the dispersity and particle size of the final nanoscale architectures [47, 48].

In all fields of catalysis, the rational design, synthesis, and characterization of new nanostructured materials is thus a key to future success and indeed the critical underpinning science for a sustainable future. Moreover, to unequivocally describe the nature and function of the active site (<0.1 nm or sub- Å scale), we need a precise control over the final particle size (dispersity) and the inorganic matrix carrier (pore architecture). In addition, for the developments and improvements in catalyst properties, three interrelated pre- and post-synthesis areas need to be considered further:

- The chemical nature of the active center (<0.1 nm (or, even sub-Å scale) that controls the bond-breaking (substrate) and bond-forming (product) actions of the catalyst;
- The local environment, with its hydrophilic or hydrophobic nature, and stereochemistry, that is influenced by processes on sub-nanometer length scales; and,
- The rate of transport molecules and the accessibility of the active sites (<0.1 nm scale) that also controls the local activated complex concentrations (adsorbates or around sites).

If we go back to the traditional systems and focus on newer size-selective methods for synthesis of nanostructured materials, it is important to coin a new term, "Surface Reaction Engineering" or "Surface Kinetics". In the traditional systems, a metal solution of a precursor (aqueous or organic) is used for pore filling, and the deposition of the metal clusters occurs via thermal effects. There are several questions that relate to the kinetics and growth of an active site ensemble. How does the nucleation occur? What are the typical time scales (say, ns or ps scale) for nucleation, i.e., generation of the first atomic "bond" between the active component and the support? Are there tools and techniques available currently (say by ultrafast microscopy or spectroscopy, in a time and space resolved manner) that may allow us to "observe" this phenomena? What is the mechanism of the crystal growth, or the does the deposition occurs at the molecular or the cluster level (less likely) and not on the atomic scale? What governs the morphology of the final cluster? What are the drivers for the cluster heterogeneities and how are these heterogeneities important from the standpoint of catalytic activity? What are also the origins of cluster or morphological defects and the quasi-heterogeneous active sites, such as steps, terraces, kinks, and other vacancies in otherwise regular crystal planes?

Apart from these fundamental questions in surface kinetics, other questions also become immediately obvious in a closely related area: Thermodynamics of nucleation and crystal growth. For example, how does one minimize the overall free energy of formation of the catalytic surfaces? If you take the surface particles of the final surface, will large particles have a small free energy of formation (likely) or smaller particles? Another important question on the atomic scale/crystal plane scale is why are some crystal planes turnover planes, while others are not or do not display the same reactivity, as some preferential crystal planes? In light of this issue, does the concept of an active catalytic site (proposed by H.S. Taylor in 1870) need revisions? The issue of accessibility is related to the mechanism, and there are practical examples (typically substrate hydrogenations) where the reaction selectivity is markedly different if the substrate molecule and/or hydrogen adsorb directly on the metal nanoparticle or adsorb first on the support and then associatively or dissociatively migrate back on to the metal nanoparticle. Clearly, the inorganic support should display some adsorption characteristics for the substrate molecules, which can be assessed by the usual H_2- or CO chemisorption techniques. Finally, one could conceive and synthesize novel pore architectures for supports, such as say,

parallel cylindrical pores or spherical pores, from first-principles synthesis methods, and then even arrange molecular scale active sites (say, co-ordinatively unsaturated sites, cus) of one or many types, say, in a "family" of parallel pore system, for single or multiple ("tandem" or sequential, or, consecutive) reactions.

The complementary tools of spectroscopy and computational chemistry make it possible for a catalysis researcher to formulate and unravel reaction mechanisms and to elucidate the working state of nanostructures. Spectroscopic and electron microscopy tools offer unprecedented ways to monitor the structure and function of catalysts at the atomic level [49, 50].

The key challenges in this critical direction are:

- Understanding the molecular-level mechanism of catalytic reactions (in real time, at very fast time scales and to the nm scale),
- Understanding of the transition state and use of the above findings in a more rational design of catalysts, i.e, ligands, particle size, shape, and,
- Development of ultra-high microscopic and spectroscopic space and time resolution with sensitivity to establish structure-function relationships at the atomic and molecular scale.

As examples, super-resolution imaging of an individual molecule in the vicinity of a site is given in Figure 3, along with the SEM and HRTEM micrographs of the surface structure of the catalyst. A scanning transmission X-ray microscopy of a working catalyst is given in Figure 4 [49]. These advances are the first of its kind in high-resolution imaging of working catalyst under practical conditions.

As stated above, the crux of the future research in advanced characterization of nanostructured materials lies in understanding the molecular-level mechanisms around a catalytic site and the structure-function relationships at the atomic scale. Thus, the theme and content here is focused on future directions and advanced characterization including spatiotemporal, i.e., space and time resolved studies, and we have naturally chosen not to include newer developments in some traditional but important methods and those which primarily yield global volume-averaged information (spatially averaged over the entire surface of the catalyst sample, of the order of μm^2), and which can be, in some cases, at a local (surface, to a depth of 5-7 nm) scale. These techniques include optical spectroscopic tools such as IR and DRIFTS, UV-Vis, Raman, and X-ray techniques, such as XRD, small-angle X-ray scattering, XPS, X-ray absorption spectroscopy (in its two common embodiments, XANES and EXAFS, and now the new QEXAFS), and electron energy loss spectroscopy (EELS). There is also an emerging trend in the current literature to "combine" two or more traditional characterization techniques, say, vibrational spectroscopy (IR/DRIFTS) with X-ray methods (such as X-ray diffraction or X-ray absorption spectroscopy), to gather and glean more information in a synergistic way than that could be

gathered using one technique at a time [51]. For example, a combination of IR/DRIFTS and X-ray methods (XAS) can perhaps shed light on active site-adsorbate complexes and intermediates and coordination numbers/interatomic distances of the surface adsorbates, which may provide an additional way to discern between reactive intermediates and spectator species and reaction mechanisms. It is clear than the conventional (ex situ) X-ray absorption spectroscopy, while useful in some regard (in terms of metal-metal coordination numbers and interatomic distances), discerns the atomic-scale environment around a central atom that is a principal scatterer (typically active metal site), but not the active site-adsorbate complex itself.

As mentioned above, combination methods discussed briefly above notwithstanding, the spectroscopic tools are inherently limited in their nature and are unable to offer atomic scale information on working catalysts. These traditional techniques can provide information only on a spatially averaged working volume of a sample, and to a local scale (nm-scale). For example, X-ray photoelectron spectroscopy can provide a global volume averaged information on chemical valence states or oxidation states of surface elements that comprise the sample, typically to a surface probe scan of 5 nm. The atomic-scale and structural information is ideally obtained using high-resolution electron microscopy and imaging of nanostructured materials, which can provide direct working images of active sites/centers or crystal planes (typically at sub-nm scale and even at sub-Å scale). This is important because the typical working surface of a heterogeneous catalyst can consist of many active structures, and which may constitute only a small fraction of the overall proportion of the active sites (or total active sites), such as single atom (with perhaps different crystal planes and orientations), single atom layers, bilayers, and the three-dimensional crystallites (typically of the order of a few atomic diameters, or 1-2 nm), where different geometries (cubes, spheres, pyramids, etc.) configurations can arise. For example, in a recent study [52], the Au/FeO_x system for low-temperature CO oxidation was discerned by aberration-corrected high resolution electron microscopy as to consist of 2-atomic layer thick Au atom structures, ~ 0.5 nm in diameter, which, despite being only a small fraction (<1 at%) of the overall active gold, were postulated to be the active sites for CO oxidation. Based on empirical and calculated atomic radii of gold atoms, of about 135 pm and 144 pm (or, 0.135 and 0.144 nm, respectively), the gold sites in the above study can be construed to consist of 4 atoms.

Several novel areas can be conceived to study the structure-function relationships at the atomic and molecular scales. First, the molecular mechanism of catalytic deactivation, and indeed, the catalytic turnover as a function of number of catalytic cycles can be further studied by advanced tools in microscopy and spectroscopy, such as sum frequency generation (SFG) spectroscopy, femtosecond spectroscopy, and 4-D electron microscopy, popularized by Prof. Ahmed Zewail [53-55]. (Prof. Zewail is the Linus Pauling Chair Professor of Chemistry and Director of the

Physical Biology Center for Ultrafast Science and Technology, and the "Father of Femtochemistry", and Winner of the 2001 Nobel Prize). As further detail and advance, 3-dimensional electron tomography (ET) can be used as a tool to diagnose the atomic structure at the crystallite level and even on the one building block of the crystal ensemble.

With a precise control on the size and shape of the nanoensemble active form (from the atomic-scale synthesis of nanostructured materials, see discussion above in Section 2.1), one can become interested in the molecular and catalytic imaging methods, such as with those with Synchrotron or Neutron Scattering/Diffraction methods [56-58]. In principle, with only one active site (or, say, a few) anchored on to the catalyst support, it is perhaps conceivable to take snapshots of images of a molecule and its motion around the vicinity of the site, the first step of the sequence, molecular (associative) or atomic (dissociative) adsorption, surface reaction, and the subsequent desorption [59-63]. In fact, one could be also interested in the exact speeds or rates of these turnover steps in the turnover cycle, and then assess the rate-limiting step, such as, say, the associative or dissociative adsorption of the first molecule. A technique such as chemiluminescence can be used to artificially "dye" a molecule and use a tracker of sorts to track its trajectory around the active site and identify how and when it attaches to the site.

In-situ measurements of the chemical (from a turnover standpoint) and spatiotemporal (from isotropic uniformity or nonuniformity and time standpoint) of the catalysts in a working state (i.e., say, for some simple reaction, such as an isomerization of n-pentane to n-pentene) is also an important advance. The conventional hypotheses of the Langmuir-Hinshelwood mechanisms of only one rate limiting step (say, adsorption, surface reaction, gas phase or Ely-Rideal, or desorption) in a overall sequence of elementary steps can be erroneous, particularly if say, 2 steps have a "reaction coordinate" in terms of heats of adsorption or activation energies for surface reaction/gas-phase molecule with an adsorbate, that are similar, and, say, are far-removed than the remaining step. The implications of this "novel" approach for heterogeneous catalysis and the formulation of L-H mechanism is also an important "discovery" and an advancement. Some of these concepts were developed by Prof. Gerhard Ertl (Professor Emeritus, Dept. of Physical Chemistry at the Fritz-Haber Institut der Max-Planck-Gesellschaft in Berlin, Germany) who won the Nobel Prize in Chemistry in 2007, for formulations of chemical reactions on surfaces.

The use of tools of heterogeneous catalysis at a molecular dimension/scale for preparation and characterization of newer nanostructures (based on, say, geometry) should be now possible, with advances in synthesis methods and characterization suites available to researcher. For example, while nanocubes and nanospheres are now well-documented, one could focus on other geometries and polygons, such as, say, pyramids, pentagons, or even hexagons. While a strictly a new concept, with an undeveloped tableau, it can have a practical utility, with a persistent and purposeful development.

B.3 New Paradigms and Future Critical Directions for Research

One of the more interesting avenues and a future critical direction for research is molecular catalysis or "homogenized heterogeneous catalysts", and is the merging homogeneous and heterogeneous catalysts. One key objective here is to be able to prepare molecular-level catalysts anchored onto solid, inorganic supports. As is commonly understood, molecular catalysts in solution (i.e., homogeneously-catalyzed) offer the dual benefits of uniform accessibility and reactivity, of a single catalytic cycle and high selectivity. In contrast, catalyst nanoparticles anchored are on surfaces are non-uniform (both in terms of ensemble size and orientation of crystal planes preferential to catalysis) and thus have an array of reactivities, with non-uniform selectivities. Uniform catalytic sites on surfaces retain the advantages of those in solution, with the added benefits of ease of separation from products, lack of corrosion, and robustness for high-temperature operation. Syntheses of supported molecular catalysts are carried out with precursor compounds that can be anchored to the support with removal of the precursor ligands.

In this molecular design at the interface of homogeneous and heterogeneous catalysts, several interesting areas of discovery can be conceived as follows:

- Highly reactive, coordinatively unsaturated cations isolated on support surface, and arrays of these sites on the supports, arranged even a modular fashion (in a bio-inspired way), for sequential or tandem catalytic processes.
- Precisely constructed clusters of metals, metal oxides, and metal sulfides on supports.

Nanoclusters of metals, oxides, and other materials can have new, undiscovered properties, different from those of the bulk; they represent a new kind of single-site catalyst. Most catalytic transformations occur in a sequential manner in which the substrate undergoes a series of physicochemical changes and processes to the final product. Clearly, the intermediate steps (changes) of isolation, purification, and separation of products are energy-intensive as are the intermediate operations or processes (of, say, distillation, liquid-liquid extraction, chromatographic purification and separation, etc.). It is clearly in the interest of process design that this sequential manner be replaced by some type of tandem reactions. Two such tandem reactions can be thought of: an auto-tandem reaction, in which the disparate catalytic functions are incorporated into a single module and the nanostructures are dispersed on the support surface (one type of arrays), and an orthogonal tandem reaction, in which more than one type of nanostructure is supported on the surface (many arrays). Clearly, it is important to understand that these materials are a new class of single-site catalysts, and that we can have multi-component catalysts (for multi-step synthesis, kind of "one-pot" synthesis), that process multiple feedstocks into a single product, and those which can process one feedstock into multiple

products. We can also incorporate component switchability (kind of an on-off mechanism, say, to process one of different types of feed) or even tunability (kind of a trigger mechanism to activate selectively more of one component of the modular design). These one-pot processes allow for multiple reactions in the same sequence to be carried out in a single reactor vessel, thereby avoiding stop-and-go processes and purification steps, which can lead to environmental and economic benefit [64-68]. An example scheme for tandem reactions for one-pot processes with multiple reactions is given in Figure 5 [65, 66]. These processes incorporate the concept of artificially-engineered DNA of single or multiple arrays of modular/molecular catalysts, for parallel/sequential reactions. These new materials, modular in nature — tailored molecular catalysts on tailored supports— offer the prospects of entirely new catalytic properties, combined with the following two advantages:

- They can be characterized invasively, even in the working state, by methods available at modern facilities offering high-flux sources of photons and neutrons and by spatially resolved, atom-specific microscopy and spectroscopy.
- They can be modeled accurately with modern theoretical/computational methods.

Research needs also clearly exist in the areas of photocatalysis, electrocatalysis, and photoelectrocatalysis for more sustainable processes. Photocatalysis and photocatalytic reactions are inspired by natural photosynthesis processes in plants, which harness solar energy and carbon dioxide, to photochemically reduce water to glucose and oxygen, by electron transport chains. In artificial photocatalytic processes (artificial photosynthesis), chemical reactions in presence of light (artificial or solar) are accelerated by the use of a catalyst. Electrocatalysis deals with the catalysis of redox reactions and is a key discipline for the development for energy storage, fuel cells, solar fuels, and all other electrochemical devices. The economic pressures have always dictated that the energy-intensive chemical conversions such as ammonia synthesis and chlor-alkali process are the traditional choice of researchers. The processes based on photocatalysis and photoelectrocatalysis (say, photoelectrochemical generation of hydrogen visible light-induced splitting of water) are carbon-netural but suffer from an adverse energy output/energy input and thus may not be economical (compared to energy-intensive chemical processes, which are clearly economical but not carbon-neutral and come with a huge environmental burden). The photo- and photoelectrocatalysis processes are thus perhaps more benign from the standpoint of a carbon footprint (the photocatalytic processes can be more sustainable as they are more selective, due to different chemistry and/or lower process temperatures), but clearly, "life-cycle" or "cradle-to-grave" analysis is needed to arrive at any definitive conclusions. A case in point is the known adverse energy output/energy input ratio of biological routes (more so in case of corn- or other foodstock-based sources like sugarcane, and less so in other non-foodstocks based routes wood or switchgrass) to ethanol, a practice which results in less volumetric energy output than energy input. Nevertheless, it is incumbent upon human endeavor to practice sustainability.

Studies on photocatalysis for solar fuels promise to generate novel devices that produce hydrogen from electrochemical or photoelectrochemical splitting of water [69]. An example of an artificial leaf – a solar fuels device - for water splitting is given in Figure 6. Pt (a) of Figure 6 shows the working model with triple-junction amorphous/crystalline Si system and Pt (b) shows the wired configuration for the PEC system for water splitting. The second example in Figure 7 also shows a solar fuels device, as proposed by Joint Center for Artificial Photosynthesis (University of Calif. – Berkeley), a design based on light harvesting nano-/micro-wires embedded in a proton conduction polymeric membrane coated with nanoscale catalysts for H_2 and O_2 evolution reactions [69].

In the photoelectrochemical processes, the most widely used semiconductor catalyst (typically with ultraviolet light) is titanium dioxide (TiO_2), because it is chemically and biologically inert, photocatalytically stable, relatively easy to produce and to use, able to efficiently catalyze reactions, cheap and without risks to environment or humans [70]. TiO_2 absorbs ultraviolet light alone, and not visible light, owing to its large band-bap (difference between conduction band potential and valence band potential) and is thus not very active for solar photons. Other photocatalysts include ZnO, ZnS and CdS, but these are much less active. Among these, ZnO exhibits similar band gap positions as TiO_2 and is thought to have higher electron mobilities, but is less active for photoelectrochemical conversions. Besides TiO_2 and ZnO, some oxide semiconductor photoelectrodes such as $a\text{-}Fe_2O_3$, WO_3, $SrTiO_3$, $KTaO_3$, and $BaTiO_3$ have also been studied extensively [71-73]. They have narrow bandgaps as well as good stability and a low price. By absorbing a photon of energy greater than its bandgap, a semiconductor generates an electron-hole pair followed by the migration of the holes and electrons to its surface to participate in chemical reactions. Charge recombination occurs at defects and grain boundaries and competes with the separation of charges and redox reactions. Small particle size (nanoscale) is preferred to minimize charge recombination. Band edge positions of the photocatalyst play a crucial role in determining the feasibility of the redox reactions [74, 75]. For a semiconductor to act as a catalyst to split water, the top of the valence band (VB) must be more positive than the oxidation potential of H_2O (1.23 V) and the bottom of the conduction band (CB) must be more negative than the reduction potential of H^+ (0.0 V). These principles of semiconductor physics that govern the photoelectrochemical conversions are depicted in Figure 8 [76]. In Figure 9, the energy levels of several semiconductors vis-à-vis the conduction and valence bands are given so as to be able to identify those materials which are suitable for water splitting [77, 78]. Of those (Figure 10), materials with ferroelectric properties and with polarization potential are more suitable – under incident photons, the photogenerated electrons and holes migrate in opposite directions due to the polarization, P, of the ferroelectric material, which results in band bending at the surface, and leads to the two chemical reactions of interest – H_2 formation and H_2O oxidation [78].

There is considerable scope in examining several new bifunctional (metal-semiconductor) catalysts, based on the rationale that semiconductors (small gap, amenable to visible light) in combination with metals having a more positive Fermi level than the seminconductor itself, affords separation of charges and also can provide sites for photoreduction of H^+ to H_2. Thus, Pt, Pd, or Ru can all be used as promoters for a small-gap semiconductor such as CdS or even CdSe. The Fermi levels of these elements are 8.79, 7.69, and 10.82 eV, respectively, and are higher than the Fermi level of Cd (6.45 eV). These elements also display excellent proton reduction activities. Another strategy that has been reported to yield excellent results vis-à-vis hydrogen generation (mmol/cat. g) is to combine a co-catalyst such as graphene (a quasi-2-dimensional, atomic-scale, honeycomb lattice of carbon, of ca. 3 Å layer thickness) with semiconductors such as CdS or CdSe, promoted with Pt. The use of dyes with the semiconductors such as MoS_2, where the dye acts as a sensitizer and provides an electron transfer (or, conduction) channel, to facilitate the flow of electrons, is another strategy that has been reported. The use of semiconductor heterostructures, CdS-CdSe, for example, promoted with Pt, is also reported [79]. These heterostructures are reported to yield a hydrogen activity of 40 mmol g^{-1} h^{-1}, with a quantum yield of 20%. Here, CdS and CdSe are in the form of nanorod and quantum dot respectively and Pt in the form of nanoparticles. In this system, CdS absorbs the light and generates electrons and holes, electrons are transferred to Pt nanoparticles to carry out the reduction of protons while holes are transferred to CdSe. The results obtained with CdS-CdSe-Pt, ZnO-Pt-$Cd_{1-x}Zn_xS$ and am-TiO_2/Pt/$Cd_{1-x}Zn_xS$ are the best reported so far.

The obvious limitation of the photochemical processes is the photocatalytic reactor efficiencies, currently limited to about $0.05 - 0.1$ mol/$m^3_{reactor}$-s, which need to be increased by a factor of 100-1000 before a commercial application is deemed feasible [70]. Apart from the clearly adverse potential energy diagrams with a high barrier for both activation and reaction at the surface of an active site of a photocatalyst (say, the photoreduction of a proton, which comes from the solvation of the electrolyte, H^+, with an electron) and low turnover frequencies, when compared to a conventional heterogeneous catalyst), there are reactor design and engineering-centered barriers, which limit the photocatalytic processes and their industrial applications. The primary among these are low efficiency of illumination or photon transfer (activation of catalytic sites) and limited contact between catalyst surface and reagents (mass transfer limitation). The mass transfer limitation is intuitively less serious (especially in the liquid phase, where the entire pore structure can be construed to be completely wetted by liquid), and has been shown to be overcome to a large extent by recent introduction of innovative reactor designs, such as slurry reactors for fine particles [80, 81], spinning disc reactors [82-84], and monoliths [85-87]. For external mass transfer, the reactor operational variables such as linear velocity and/or Reynolds number can be suitably chosen. The internal mass transfer (i.e., within the pore structure) is also likely to be minor, as most photoelectrodes under active research investigations are mostly non-

porous, with low pore volumes/surface areas. The presence of another fluid phase, i.e., a gas phase, within the photoreactor can introduce additional mass transfer problems and solubility issues, as the gas phase must first dissolve into the continuous liquid medium, a problem that can arise in the electrochemical conversions of specific substrates, such as carbon dioxide. Other factors such as post-reaction separation of the catalyst from the solution (in case of slurry reactors), and enhancement of adsorption (of reactive substrates) and desorption (of products) to and from catalytic sites are also important. Microreactors have also been recently investigated for photochemical and photocatalytic reactions [88-91]. The main advantage of microreactors is the high surface-to-volume ratio, which leads to a more efficient illumination (increased photon transfer). The small size of the flow channels also provides a greater control over variables such as temperature control and flow rates, fast heat and mass transfer, and the presence of laminar flow. The light source itself can also be UV-LED, which can miniaturize the photocatalytic set-up.

Apart from electrocatalytic splitting of water (as discussed above), photocatalytic and electrocatalytic (photoelectrocatalytic) reduction of carbon dioxide is the other area of interest to researchers.

Clearly, the challenges for the next generation of research will have a firm focus on sustainability and on the development of green technologies which are only minimally invasive to our environment, in keeping with the spirit of the principles and practice of green chemistry.

To this end, the needs of the future are newer carbon management methodologies that lead to a reduction of carbon dioxide emissions and carbon content of the earth, and it is imperative that apart of end-of-the-pipe solutions, we must focus our attention on reduced carbon content sources like natural gas and renewable sources such as biomass. We obviously need to diversify our energy sources, but also make these chemical transformations more atom- and energy-efficient. Atom efficiency reflects a more efficient use of chemical feedstocks (or, atom economy), and minimization of wastes and byproducts that leads to lowered separation costs and reflects energy efficiency. This is the new wave of the future, which embodies the principles of green chemistry and engineering (and sustainability).

Carbon dioxide capture and control is one important area of application. The steam reforming of natural gas leads to formation of one mole of carbon dioxide, which is either captured or released to the environment. Carbon dioxide accumulations in the atmosphere thus have continued to rise, due to human endeavor (fossil fuels, such as petroleum crude, coal, natural gas, and even biomass), leading to greenhouse effect. We should perform the capture at the power plants, but ideally, we should control this at the source (i.e., in the oil wells or in coal seams), and the challenge then is to gasify coal/oil at lower temperatures at which gasification can occur (as

carbon dioxide is a product of complete combustion) and run these gasification in sub-stoichiometric fashion, with less than stoichiometric quantities of oxygen. One other way is to be able to increase the efficiency of the transformation and shift the equilibrium of the conversions, possibly using co-catalysts or membrane technologies. It is clear that the reforming process is an equilibrium reaction and thus product removal by membranes or co-catalysts will shift the equilibrium to the right, and concomitantly increase efficiency.

In the area of electro-catalysis, electrochemical splitting of water is another way to produce hydrogen, but the process is not energy-efficient, and about 30-40% energy is lost in the process. The focus is thus needed on energy efficiency. The production of electricity from hydrogen using fuel cells (proton-exchange membrane fuel cells or also termed as polymer electrolyte membrane fuel cells) is limited due to the high cost of platinum for electrode materials, and also the very limited availability of platinum. New catalytic chemistry is thus needed to find substitutes for platinum, which is costly.

In the area of liquid fuels and chemicals, the current energy sector is primarily based on petroleum crude, and petroleum refining derives the light olefins, alkanes, gasoline- and diesel-boiling range hydrocarbons, and aviation fuels, for our transport and chemical/petrochemical sector. The abundance of domestic coal makes it an attractive option to make liquid fuels, however, the processes are not energy-efficient. For example, the coal gasification process with steam is not energy-efficient, but can be improved to increase hydrogen yield, for example. In the second case, the Fischer-Tropsch process converts the coal-derived syngas into liquid hydrocarbons, but the process is highly unselective. Syngas can also be made from natural gas, but again, the steam reforming process is endothermic.

We can also skip the syngas step completely and convert methane directly into chemicals and also ethane (coupling or homologation). This has been a hotbed of academic and industrial research for over 30 years, although the commercial application is still elusive. Some other competing routes for existing technologies are to use n-butane to maleic anhydride and maleic acid, instead of benzene or butenes. This is now practiced successfully on a commercial scale by Huntsman Petrochemical Corporation in the United States (Pensacola, FL, Neville Island, PA, Neal, WV) and at its licensees in Europe and Asia. Some facilities in Europe still continue to use benzene-based feedstocks. Another few possibilities are the direct conversion of propane to acrolein and acrylic acid, oxidative dehydrogenation of propane, and the direct synthesis of ethanol and light alcohols from syngas. In fact, selective oxyfunctionalization of alkanes to olefins and aromatics is one area that has received considerable attention. Currently, these chemical precursors are made from energy-intensive endothermic processes, starting from petroleum crude or natural gas. The typical selectivities of these processes are 50-70%, and carbon dioxide is generated as a by-product. In addition, there are copious emissions of carbon

dioxide from the burning of fuels to supply the energy needed for the reactions. Selective oxyfunctionalization technologies offer the dual advantages of reduced carbon dioxide emissions and better energy management, and steam/electric power can be generated from the overall process exothermicity. While there are a few commercial examples of these processes, most are currently at research or pilot scale. Thus, oxyfunctionalization of methane to syngas and methanol, ethane to ethylene and acetic acid, propane to propylene, propylene oxide, acrylic acid, and acrylonitrile, and n-pentane to phthalic anhydride are all topics of interest to academic and industrial researchers. There is a research trend to use the alkane-based feedstock versus the corresponding alkenes (say, n-propane vs. propylene for propylene oxide synthesis), as the cost of the alkane feedstocks is about 20% lower (than corresponding alkenes) and the feedstock cost constitutes about 65-70% of the overall manufacturing cost.

Biomass conversion is a hot topic for researchers [92-95]. There are three main components to biomass, cellulose, hemicellulose, and lignin. Researchers are developing gasification and pyrolysis processes for the cost-effective thermochemical conversion of biomass to biofuels. Gasification - heating biomass with oxygen produces a mixture of carbon monoxide and hydrogen, known as syngas. Pyrolysis - heating biomass in the absence of oxygen—produces a liquid bio-oil. Both syngas and bio-oil can be used directly or can be converted to clean fuels and other valuable chemicals. Alternatively, biochemical conversion of biomass entails the steps of pretreatment of cellulose (basically sugars comprising of glucose and fructose) to remove the protective coating of lignin and hemicellulose (which are inactive), development of enzymes for enzymatic hydrolysis, and the final step of fermentation (using microorganisms).

Chemical and biochemical routes for biomass conversion have recently attracted a flurry of attention. The development of processes and catalysts for conversion of glucose, fructose, and aldose sugars into so-called platform chemicals include conversion of glucose into levulinic acid, isomerization of glucose (to fructose), transformation of aldose sugars into furans, dehydration of D-fructose into 5-hydroxymethyl furfural (5-HMF), and conversion of sugars to lactic acid and succinic acid (so-called platform chemicals, amenable for further conversion into value-added products), conversion of hemicellulose to sugars and sugar alcohols, conversion of glucose and cellobiose to sorbitol, and glycerol hydrogenation and hydrogenolysis. Finally, it is important to note that catalysis and biocatalysis play a major role and are drivers for rate control, selectivity control, and stereo control, and sustainable, atom- and energy-efficient processes. Chemical transformations for platform chemicals, lactic acid, succinic acid, and 3-hydroxypropionic acid into valuable products are given in Figure 11 [94].

Notwithstanding the increasing maturity of catalytic science/technology for most bulk and commodity chemicals, one can still recognize and identify limits for most current processes, and also identify avenues for a few major advances. The major advances in the future will require

technical discontinuities. These discontinuities and the accompanying advances, as opposed to incremental improvements in existing technologies (which are also important and offer cost savings), offer real opportunities for catalysis to have an impact. Each such advance constitutes a latent opportunity to shift to a lower-cost feedstock or to a simpler, less-capital-intensive route. The cost of the feedstock often constitutes to about 70% of the overall manufacturing cost, thus a shift to a lower-cost feedstock often leads to great financial impact and cost savings. For example, the Monsanto process for making acetic acid (CH_3COOH) via methanol (CH_3OH) carbonylation involved a feedstock change—a shift from ethylene (C_2H_4), used in the previously dominant Wacker process, to methanol (CH_3OH). Since its launching in 1970, the Monsanto process has captured most of the world's new capacity for making acetic acid. The synthesis of ethylene glycol via the oxidative coupling of methanol rather than the standard process based on ethylene as feedstock has also been a subject of significant research in academia and industry. Significant progress has been made in the oxidative dimerization of dimethyl ether to dimethoxyethane. Dimethoxymethane, in turn, is readily hydrolyzable to ethylene glycol. Oxidative coupling of dimethyl ether readily proceeds at about 200° C with a mixed magnesium-tin oxide catalyst, and as against methanol as the source, there are no side reactions. The use of dimethyl ether is thus more selective (low operating temperature and feedstock) and more efficient.

As stated above, the new wave of the future is a focus on principles of green chemistry and sustainability, in chemical manufacturing. Green chemistry embodies the design of chemical products and processes to reduce or eliminate byproduct wastes and other toxic/hazardous substances. The 12 principles of green chemistry, as originally introduced by Anastas and Warner, are design criteria or guidelines that provide the framework for a sustainable design. They provide an overarching construct for design of safer processes and chemical transformations [96, 97]. Since about 1999, the Environmental Protection Agency (EPA) has instituted the Presidential Green Chemistry Awards, to inspire and reward innovative manufacturing processes and practices in the chemical and pharmaceutical industry that emphasize and incorporate the principles of green chemistry. A few very noteworthy examples among these are the 2009 Green Chemistry Award to Eastman Chemical Company for the development of new, innovative route to enzymatic transesterifications (based on biocatalytic protein molecules), 2006 Award to Merck for the development of a new process for the manufacture of Sitagliptin, a chiral β-amino acid molecule that is a valuable Type 2 Diabetes drug (based on novel asymmetric catalytic hydrogenation of unprotected functional groups in enamines, that was proven to be more efficient (higher yields) and thus cost-effective), and the 2004 Award to BMS for the development of Paclitaxel, a substitute for the active ingredient in the anti-cancer drug currently in use, Taxol. The current process for synthesis of paclitaxel is based on some 11 synthesis steps in series, with 10-decaacetylbaccatin (10-DAB) and with environmental risks. The new strategy for synthesis of paclitaxel is based on extraction from plant cell cultures, and avoids the use of all solvents and additional steps in synthesis.

The progress in the synthetic chemistry and practice can thus be traced from early, stoichiometric methods (based on reagents and homogeneous solvents) to catalytic and biocatalytic routes to the current green chemistry alternatives. These developments have mirrored societal development and progress and an emergent understanding of the critical need for environmental protection/environmentally conscious manufacturing and venerable adherence to sustainability. In keeping with these trends, a shift in the practice from organic reactions that involve covalent bond-breaking and bond-forming (which are energy intensive, unselective, and thus costly) to non-covalent, weak-force interactions and imparting chemical functions and properties through these interactions is likely to become very popular, as these provide a less energy-intensive option which also reduce byproduct wastes. In fact, mastering these weak-force interactions (electrostatic interactions, for example) and the accompanying chemical transformations can result in achieving sustainability at the atomic level. Some of these newer concepts and synthesis schemes are termed as chiral (or, enantioselective) or asymmetric catalysis and more specifically, asymmetric counterion directed chiral catalysis (or, ACDC, for short). Although catalytic transformations with anionic intermediates with chiral, cationic catalysts have been realized, the equivalent versions of inverted polarity (cationic intermediates with chiral, anionic catalysts) with reasonable enantiomeric selectivity have only recently become a reality. The concept, referred to as ACDC catalysis, above, has a wide applicability in organo-catalysis, transition metal catalysis, and Lewis acid catalysis. One illustration of this new concept in chemistry of organic reactions is given in Figure 12. For further information on this emerging area, the reader is referred to some recent works in this area [98-102].

The field of computational catalysis and computational chemistry is now firmly on the forefront of new advances in heterogeneous catalysis and is a critical new direction for catalysis research. The most popular among computational catalysis tools, Density functional theory (DFT), is a quantum-mechanical (QM)/quantum-chemical method widely used in chemistry and physics to calculate the electronic structure of atoms, molecules and solids. The importance of DFT in computational materials science, biological sciences, and chemistry is evidenced by the award of the 1998 Nobel Prize to Walter Kohn for his development of the density-functional theory [103].

There are 2 major types of QM/QC methods that constitute the field of Density Functional Theory: The first, classical molecular dynamics methods that use "pre-defined potentials", either based on empirical data or independent electronic structure calculations, are well established and are used to investigate many–body condensed matter systems. At the heart of any molecular dynamics scheme is the question of how to describe – or how to approximate – the interatomic interactions. The traditional route followed in classical molecular dynamics is to determine these potentials in advance. These "fixed-potential models" have serious drawbacks and are not applicable to many chemically complex systems, especially where electronic structure changes can occur. Among the most delicate ones in these are systems where (a) many different atom- or

molecule-types can give rise to a myriad of different interatomic interactions that have to be parameterized and /or (b) the electronic structure and thus the bonding pattern changes qualitatively in the course of the simulation [104].

The range of traditional molecular dynamics and electronic structure methods was greatly extended by the family of techniques that are termed as "ab-initio molecular dynamics". Other names that are currently in use are: Car-Parrinello, Hellmann-Feynman, First Principles, Quantum Chemical, On–the–Fly, Quantum-Mechanical, and Direct. The basic idea underlying these ab-initio molecular dynamics methods is to compute the forces acting on the nuclei from electronic structure calculations that are performed "on–the–fly", as the molecular dynamics trajectory is generated. In this way, the electronic variables are considered as active degrees of freedom, as against fixed-potential models in traditional methods. In other words, the approximation is shifted from pre-selecting the model potentials (fixed potentials) to pre-selecting a particular approximation for solving the time- and space-dependent Schrödinger equation.

A further level of complexity in molecular modeling arises due to newer discoveries in nanomaterials, macromolecular systems, and bio-molecular assemblies which present us with phenomena that are multiscale in nature (i.e., microscopic and mesoscopic time and length scales), and are even more challenging than that amenable by classical or ab-initio molecular dynamics methods, as above. Examples of phenomena with an inherent multiscale character include protein translocation and signal transduction within complex cellular environments, charge transport through polyelectrolyte membranes, enzymatic catalysis, surface chemistry, fracture propagation in polymers, and self-assembly in complex fluids [105, 106]). A schematic diagram of these multiscale molecular simulation methods, at different time and length scales, is given in Figure 13. The methods range from very highly accurate but computationally demanding Quantum Mechanical/Quantum Chemical (QM/QC), which are used for dynamic electronic structure calculations of a system of a few 100 atoms at picosecond scales, to computationally more tolerant stochastic models at the other end of the diagonal, and, in between, we find the atomistic simulations based on classical molecular dynamics (MD/MC) and coarse-grain methods.

Models with extended time and length scales are very relevant for the design of optimum catalytic systems.

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Table 1. Process Trends in Heterogeneous and Homogeneous Catalysis

Traditional Chemistry [Force]	Traditional Catalysis [Hammer]	New Catalysis [Knife]	Biocatalysis [Scalpel]
Industrial feedstock, ores	Petroleum crude	C1-C4 feedstock, Natural gas	Renewable, Ag products
Strong acids; organic solvents	Inorganic catalysts	Site-specific materials	Enzymes
Nonselective; incomplete	Racemic products	Chiral and Stereoselective	Stereoselective
Hazardous byproducts	Some byproduct concerns	Minimal byproducts	Clean
Capital and energy intensive	Energy intensive	Knowledge intensive	Knowledge intensive
-	-	Rational design	Bioengineering

Table 2. Some conventional and modern techniques for physicochemical surface characterization of nanomaterials [37].

Technique	Property
Transmission electron microscopy (TEM), bright and dark fields (high angle annular diffraction pattern (HAADF))	Size, shape, crystalline nature
X-ray diffraction (XRD) with Rietveld refinement	Crystal structure
UV-vis spectroscopy (UV-vis)	Light absorption and scattering
Ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS)	Chemical composition and oxidation states (surface science techniques under UHV conditions)
Chemisorption	Particle size and surface area
Scanning electron microscopy (SEM)	Shape and structure
Energy dispersive X-ray analysis (EDX)	Atomic composition of surface elements and alloys
Scanning Tunneling Microscopy (STM)	Shape, size, and surface structure
Near-edge X-ray absorption fine structure (NEXAFS)	Chemical composition and oxidation states
Extended X-ray absorption fine structure (EXAFS)	Chemical composition, coordination numbers, and interatomic distances
Temperature-programmed desorption spectroscopy (TDS), Temperature-programmed reaction spectroscopy (TPRS)	Desorption patterns of adsorbates from surfaces, Desorption of a second adsorbate in presence of a pre-adsorbed or intermediate species to discern reaction mechanisms.
Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS), Infrared reflection absorption spectroscopy (IRAS), attenuated total reflectance (ATR) spectroscopy	Chemical state of the surface including adsorbed species, gas phase species (or, liquid phase), and reaction mechanisms including spectator species.

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Figure 1. Transmission electron microscopy images of a silica-supported model catalysts for Fischer Tropsch synthesis. Left: the silica spheres. Center and right: the reduced Co/SiO_2 catalyst (taken from [4]).

Figure 2. (a) HAADF-STEM image of gold particles on iron oxide. The letters indicate the gold atoms used for intensity calibrations of line scan on C and D to estimate gold atoms in the column, (b) Superposition of SEM (green) and STEM (red) images of hollow graphite spheres loaded with ca. 4 nm platinum particles [34].

Figure 3. Superresolution imaging of nanocatalytic processes. (*a*) Fluorescence image of a single molecule. (*b*) 3D representation of the image in panel *a*, and fitting it with a 2D Gaussian function, yielding the center position of the molecule (*red cross* in panel *a*). (*c, top*) Representative scanning electron microscopy (SEM) image of a zeolite needle sample and (*bottom*) a scatter plot of locations of product molecules generated from a single needle during furfuryl alcohol oligomerization. (*d*, *top*) SEM image of a Ti.O2 crystal with macroscopic defects (*circles*) and (*bottom*) localized positions of product molecules generated on {001} (*blue*) and {101} (*red*) facets in catalyzing boron-dipyrromethene dye reduction. (*e*, *top*) SEM image of a single mesoporous silica-coated Au nanorod and (*bottom*) localized positions of product molecules from the nanorod in catalyzing an oxidative *N*-deacetylation reaction. Each dot represents one product molecule. The inset shows a transmission electron microscopy image of the sample [49].

Figure 4. (*a*) Schematic of the scanning transmission X-ray microscopy (STXM) setup. X-rays are focused on the sample using a Fresnel-type zone plate lens. An order-sorting aperture filters out higher-order diffraction orders. The sample is supported on the ~10-nm-thick SiNx windows within the nanoreactor (~500×500×50 μm^3 in dimension). An image is acquired by moving the sample position with ~35-nm precision in *x*, *y*, and *z* and collecting transmitted X-rays with an X-ray detector. (*b*–*e*) Nanoscale STXM of a working catalyst. (*b,d*) STXM images of a 400 nm×750 nm region of a Fischer-Tropsch synthesis catalyst particle (*b*) before and (*d*) after 4 h in synthesis gas (a mixture of H2 and CO) at 250°C. The black boxes in panels *b* and *d* indicate specific sampling regions for XAS spectra shown in panels *c* and *e* of the Fe L2 and L3 edges, all normalized to a maximum absorption of 1. (*f,g*) 3D full-field imaging. Snapshots of an X-ray nanotomography video of an individual fresh catalyst particle. Red represents Fe (the species Fe2O3, Fe3O4, and Fe2TiO5); green represents Zn (ZnO), and white/yellow/orange represent Ti + K (TiO2 and K2O), with white used for the highest concentration [49].

Figure 5. Scheme for tandem reactions for one-pot processes with multiple reactions [65, 66].

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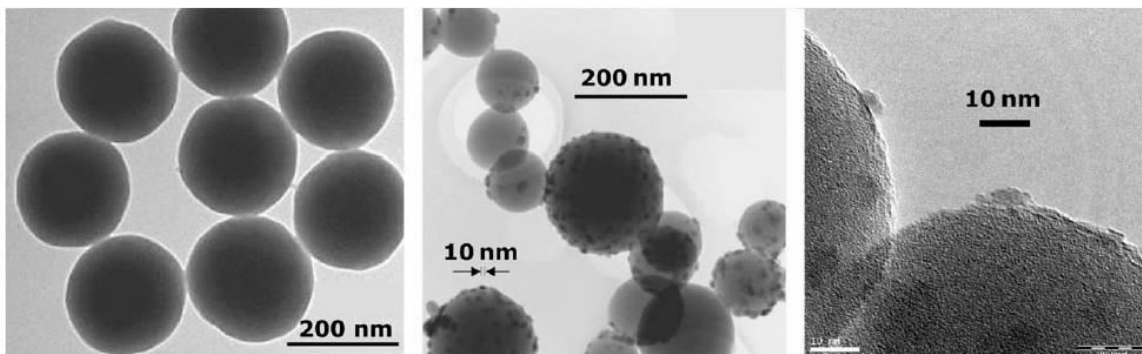
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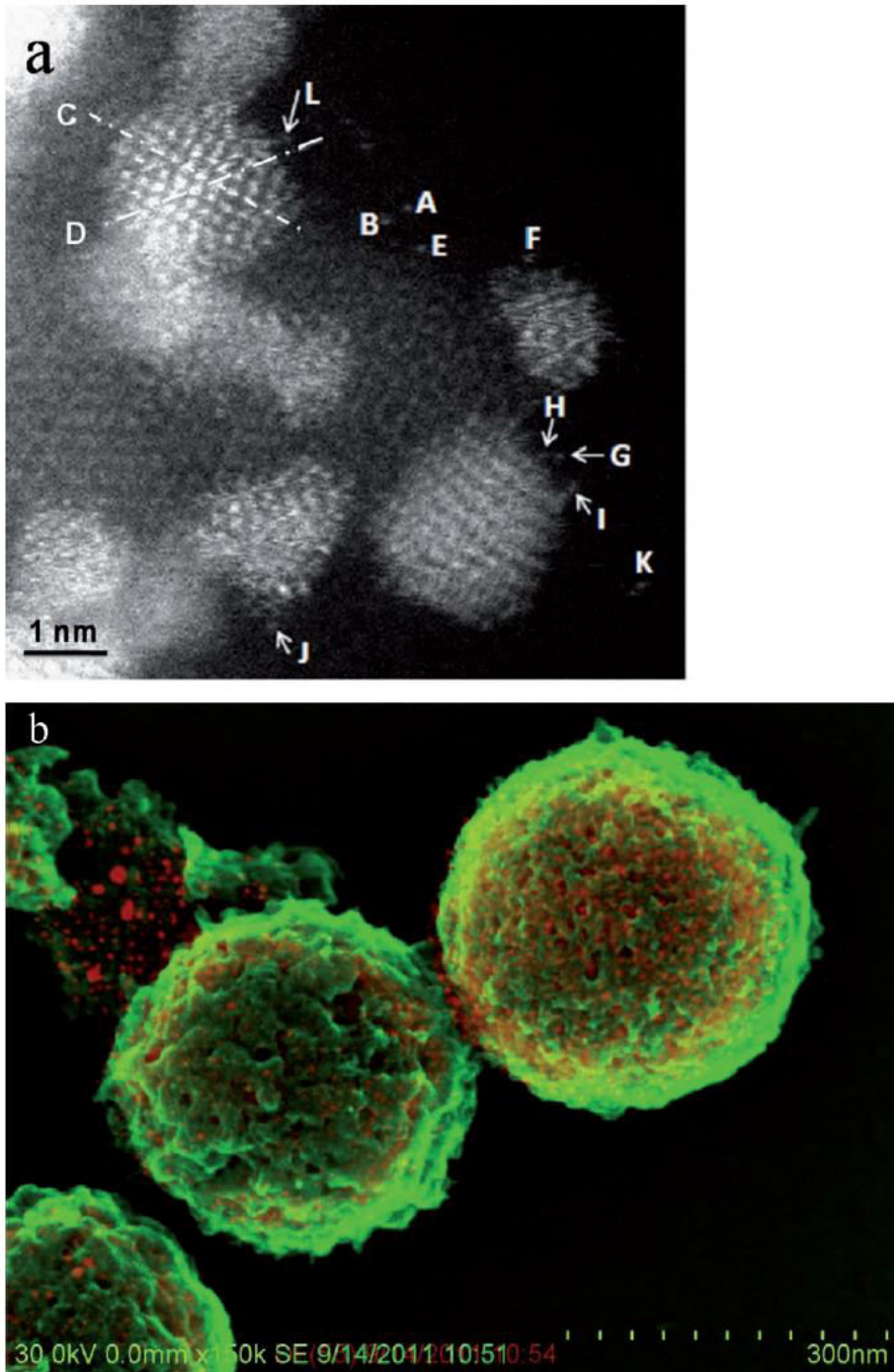
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$$A \xrightarrow{\text{cat 1}} [B] \xrightarrow{\text{cat 2}} C^*$$

$$A + B \xrightarrow[\text{cat 2}]{\text{cat 1}} C^*$$

$$A + B \xrightarrow{\text{cat 1}} [C] \xrightarrow{\text{cat 2}} D^*$$

$$A + B + C \xrightarrow[\text{cat 2}]{\text{cat 1}} D^*$$

$$A + B + C \xrightarrow{\text{cat 1}} [D] \xrightarrow{\text{cat 2}} E^*$$

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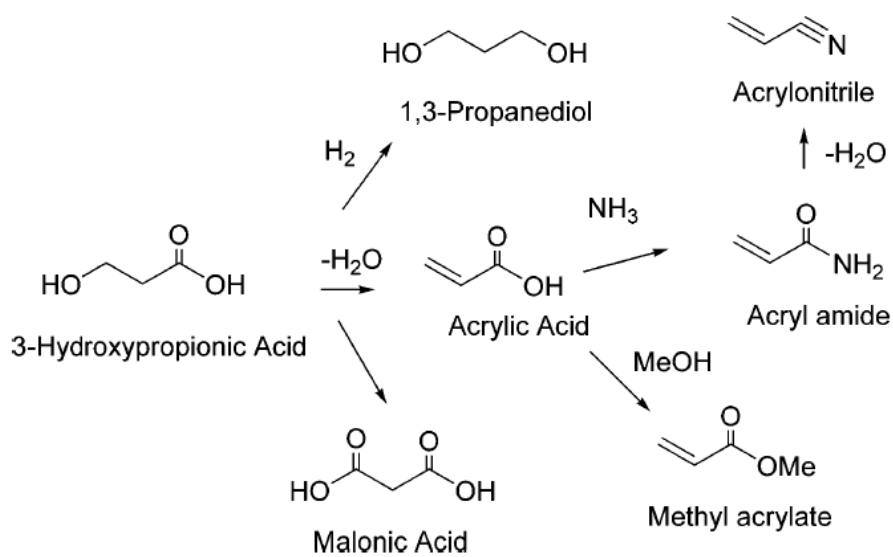
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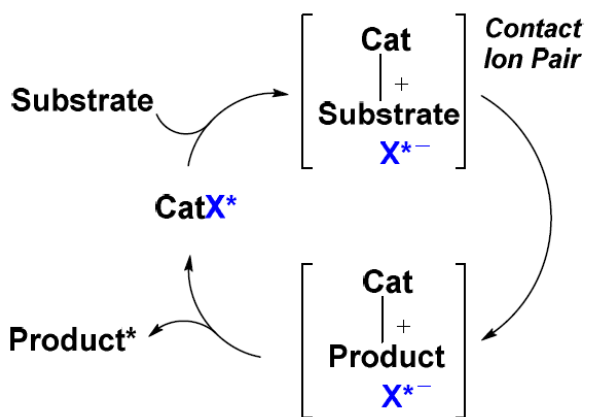
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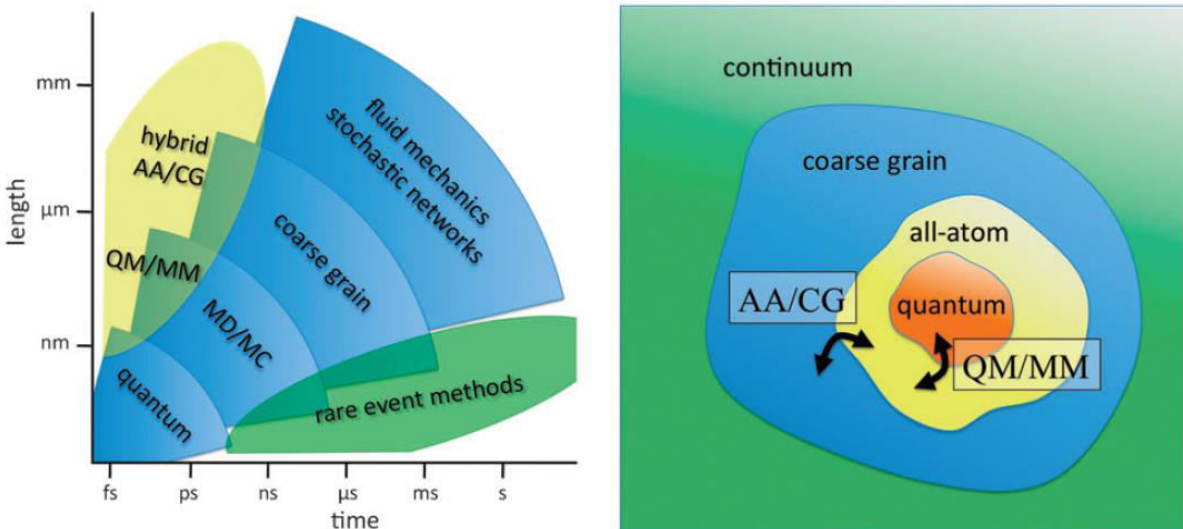
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