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# Evolution of Catalysts Design and Synthesis: From Bulk Metal Catalysts to Fine Wires and Gauzes, and that to Nanoparticle Deposits, Metal Clusters, and Single Atoms

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## 1.1 The Cradle of Modern Heterogeneous Catalysts

The modern discovery of heterogeneous catalysts stretches as far back as 1800 when Joseph Priestley and Martinus van Marum reported the dehydrogenation of alcohol over a heated metal catalyst, although not too much was thought about the role of the metal catalyst at that time except as a heating source. Then in 1813, Louis Jacques Thénard of École Polytechnique in Paris discovered the decomposition of ammonia to nitrogen and hydrogen over “red-hot metals” and recognized that the phenomenon was due to some catalytic reaction [1, 2]. The concept was followed up by Humphry Davy and Michael Faraday at the Royal Institution of London who, in 1817, reported the flameless catalytic combustion of coal gas and air over heated platinum wire producing bright white ignition. Their results were reproducible when using palladium, but not on copper, silver, iron, gold, and zinc [1, 3]. These experiments made clear that there was some form of catalytic role associated with the different metals. The discovery soon became the basis for the invention of the coal mine safety lamp, also known as the Davy lamp – although mysteriously but rather practically, the use of inefficient steel iron rather than platinum gauze became the standard for Davy lamps. At around the same time, Thénard and Pierre Dulong found that the catalytic ammonia decomposition rates decrease in the following order: iron, copper, silver, gold, and platinum, marking the first recognition of the kinetics of different metal catalysts. The importance of catalytic surface area, as we now know to be one of the most important governing factors in heterogeneous catalysis, was discovered by Edmund Davy (cousin to Humphry Davy) at the University College Cork in the 1820s, who found that finely divided platinum could catalyze the oxidation of alcohol as well as the oxidation of hydrogen at room temperature [4].

In 1831, a little-known gentleman by the name of Peregrine Phillips, Jr., patented sulfuric acid production by oxidizing sulfur dioxide in air over platinum packed in porcelain tubes heated to “strong yellow heat”. The resultant sulfur trioxide forms sulfuric acid fume upon contact with water, hence earning

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its name as the Contact Process [5]. Ironically, despite the high importance of this catalytic process, not much is known about Phillips except that he was son of a tailor and was born in Bristol [1]. A large-scale manufacturing of sulfuric acid using the Contact Process and platinum catalyst was realized many years later in 1875 by Rudolph Messel, a German-born and naturalized English industrial chemist. Messel himself was very much involved in the studies of the kinetics as well as the problematic poisoning of platinum catalysts by arsenic trioxide. In 1913, BASF was granted patents on a new catalyst based on the more versatile supported vanadium pentoxide and alkali oxide on porous silica [6, 7]. The first manufacturing plant based on this new catalyst was commissioned in 1915. Improvement in the activity of the supported vanadium pentoxide catalyst through the addition of potassium sulfate promoter was invented in Germany and the United States between 1916 and 1919. It was only in 1988 that Haldor Topsoe and Anders Nielsen revealed that the addition of cesium or rubidium promoter, rather than potassium, was more efficient in enhancing the activity of sulfur dioxide oxidation. With a typical lifetime of up to 10 years, the industrial catalyst composition for the Contact Process has been largely unchanged even to this day [8].

Going back to 1838, just a few years after the discovery of the Contact Process, Frédéric Kuhlmann discovered the production of nitric acid from the oxidation of ammonia in air over platinum sponge at 300 °C and filed a patent on this [9]. Based on the discovery, he later founded the Etablissements Kuhlmann company, which still exists to this day as part of the Pechiney SA. Despite being an important chemical commodity for the use in fertilizers and explosives manufacturing, the interest in Kuhlmann reaction was not immediately of interest since Chile saltpetre (a naturally occurring mineral of alkali metal nitrate precursor found at the Atacama desert repository) was widely available. In his vision, Kuhlmann stated that “If in fact the transformation of ammonia to nitric acid in the presence of platinum and air is not economical, the time may come when this process will constitute a profitable industry.”

Indeed, the Kuhlmann reaction picked up interest toward the end of the century as part of the solution to “The Nitrogen Problem.” In 1901 and building on Kuhlmann’s earlier findings, Wilhelm Ostwald of the University of Leipzig investigated the production of nitric acid using supported platinum on asbestos before moving to coiled platinum strips that gave higher conversion [9]. A large-scale nitric acid manufacturing plant went into operation at Gerthe in 1908 with an output of 3 tons nitric acid per day using 50 g of corrugated platinum catalyst of 2 cm wide. Given the short catalyst lifetime of no more than six weeks, it was soon realized to be a costly operation. To tackle the problem, Karl Kaiser of Technische Hochschule, Charlottenburg, developed the platinum gauze catalyst in 1909, consisting of 0.06 mm diameter wires woven to 1050 mesh/cm<sup>2</sup>, that gave a higher surface-to-bulk ratio and uninterrupted production of nitric acid of up to six months [9]. But because the source of ammonia at that time was derived from gas works liquors containing impurities such as arsenic and sulfur that deactivate the platinum catalyst, the really large industrial-scale production was only possible after the implementation of the Haber–Bosch process that provided clean ammonia. The present-day nitric acid catalyst is based on rhodium–platinum gauze (5–10% Rh) [10].

Further advancement in the design of bulk metal catalysts was evident from the work of Murray Raney on the synthesis of skeletal nickel, which was granted US patent in 1925 [11]. The Raney catalyst was prepared by first forming a Ni–Al alloy and ground into small particles, followed by the selective leaching of Al in caustic brine (such as NaOH) to yield the skeletal structure. The resultant Raney catalyst is composed of finely divided nickel so fine that it is pyrophoric and hence requiring storage under deionized water. Initially, the Raney Ni was used as an industrial catalyst for the hydrogenation of vegetable oil (to make butter substitutes) but later proved to be useful for a range of other hydrogenation reactions. Other forms of Raney catalysts including those of metallic cobalt, copper, palladium, silver, and ruthenium were later developed and found applications in methanol synthesis, conversion of furfural into furfural alcohol, and the hydrogenation of acrolein to allyl alcohol, among others [12, 13].

## 1.2 The Game Changer: High-Pressure Catalytic Reactions

The implementation of high-pressure reactor technologies pioneered by Robert Le Rossignol (assistant to Fritz Haber) [14] and later by Carl Bosch [15] was one of the most important milestones in the advancement of heterogeneous catalysis. Their breakthroughs enabled a series of high-pressure catalytic reactions that include the ammonia synthesis and methanol synthesis, which to this day rank among the most important industrial catalytic reactions. High-pressure conditions are particularly useful in overcoming reaction dilemma that under ambient pressure could obtain high selectivity but at extremely sluggish rates and vice versa at high temperatures. By carrying out the same reaction under high-pressure conditions, one can shift the equilibrium line to higher selectivity even at high temperatures, thus allowing high yield of the desired product. Chapter 35 is devoted to this topic.

Haber in one of his earlier efforts in synthesizing ammonia by  $N_2$  fixation (through reaction with  $H_2$ ) under ambient pressure could only obtain 0.005% yield when using iron catalysts at  $1000^\circ C$  [16]. A year later, in 1906, Walther Nernst at the University of Berlin reported favorable conversion at  $1000^\circ C$  when using iron catalysts in a ceramic apparatus that allowed him to perform the reaction at 75 bar. Unfortunately, the reactor and the extreme condition were far too impractical for industrial-scale implementation. Haber, who became professor at the Karlsruhe Technische Hochschule, used a steel-based reactor but this time working with Le Rossignol (who actually built the bench-scale high-pressure reactor, equipped with a high-pressure and high-temperature valve, now known as the Le Rossignol valve). With the new reactor, they were able to screen a number of catalytic materials ranging from iron, chromium, nickel, manganese, osmium, and uranium (as uranium carbide) at 200 atm and in excess of  $700^\circ C$ . Osmium and uranium catalysts were found to be active, with the former achieving a 6% conversion. Realizing that the  $N_2$  fixation reaction is limited by its kinetics rather than equilibrium, Haber further developed the feed

recycle system for which he received a patent [17]. BASF AG acquired Haber's patents on ammonia synthesis and, interestingly, also the total world supply of osmium at that time (100 kg) [2]! The amount of osmium was estimated to be capable of producing 750 tons of ammonia per year, although that amount would still be insufficient to cope with the total ammonia demand. Alwin Mittasch, who was tasked by BASF to look for more commercially feasible alternatives, together with his colleague, George Stern, screened more than 2500 catalysts and found that a magnetite ( $\text{Fe}_3\text{O}_4$ ) sample taken from a Swedish mine gave very high yield. Mittasch soon realized that the presence of impurities in the sample was critical before arriving at an optimized synthetic  $\text{Fe}_3\text{O}_4$  catalysts promoted with 2.5–4%  $\text{Al}_2\text{O}_3$ , 0.5–1.2%  $\text{K}_2\text{O}$ , 2.0–3.5%  $\text{CaO}$ , and 0.0–1.0%  $\text{MgO}$  (together with 0.2–0.5%  $\text{Si}$  present as impurity in the metal) [18, 19]. The catalyst formulation was so robust that it has not significantly changed until now.

Meanwhile, the major challenge in high-pressure reactor design shall be described. The diffusion of hydrogen through the standard carbon steel reactor under high pressure and temperature can result in the decarbonization and formation of brittle iron hydride, thus reducing the pressure rating of the reactor [20]. As such, using such reactors would limit the standard operation of ammonia synthesis (200 atm, 500 °C) to a mere 80 hours [17]. The groundbreaking work by Bosch arrived in 1909 when he, after observing Le Rossignol's reactor design, came up with an ingenious design of using a concentric tube consisting of an inner soft (low-carbon) steel tube encased in a pressure-bearing carbon steel outer jacket [16]. Narrow grooves were machined on the outer wall of the inner tube to create small pockets in between the tube and the jacket. During operation, high-pressure and high-temperature hydrogen from the reaction in the inner tube would diffuse out through the soft steel into the pockets while experiencing rapid loss of pressure and temperature. Small holes were drilled on the outer jacket to allow continuous release of the diffused hydrogen from the pockets [21]. With the catalyst formulation and reactor design in place, a pilot test on a 4 m reactor was carried out in 1911, subsequently leading to the commissioning of a full-scale manufacturing plant at Oppau consisting of an 8 m high reactor to produce 20 tons of ammonia per day [16], which is known now as the Haber–Bosch process.

The triumph in ammonia synthesis in Germany caught on with the industrial production of methanol (from syngas). As early as 1921, George Patas in the neighboring France patented a high-pressure process for the synthesis of methanol using copper as well as nickel, silver, and iron catalysts [22]. BASF has again sought the help of Mittasch to search for suitable catalysts. This resulted in the discovery of zinc chromite ( $\text{Cr}_2\text{O}_3$ – $\text{ZnO}$ ) catalyst that was used in its industrial methanol production plant at Leuna in 1923. The catalytic reactor operated at 300 atm and 300–400 °C [23, 24]. Although iron-containing (as well as nickel) catalysts also show methanol synthesis activity, they were later excluded from the catalysts screening due to the formation of iron carbonyl (from the reaction with carbon monoxide in the syngas) during the reaction that further decomposes to metallic iron (or iron carbide) [25]. Instead of catalyzing

the methanol synthesis, these iron phases are more efficient at producing hydrocarbons (the basis for Fischer–Tropsch synthesis!), which is a more exothermic reaction. For the same reason, high-pressure steel reactors were lined with copper, silver, or aluminum [26].

In 1947, Polish chemist Eugeniusz Błasiak patented a highly active methanol synthesis catalyst containing mixed copper, zinc, and aluminum prepared by coprecipitation [27]. Using the same catalyst, the Imperial Chemical Industries (ICI) developed a low-pressure methanol synthesis process that only required operation at 30–120 atm with sufficient kinetics at 200–300 °C and selectivity of over 99.5%. The process along with the upstream high-pressure steam reformer was patented in 1965 [28], followed closely by another landmark patent on the synthesis of mixed oxide of copper–zinc catalyst with promoter element from groups II–IV [29]. The catalytic process and catalyst formulation have remained largely unchanged.

Using Bosch's high-pressure reactor, Franz Fischer and Hans Tropsch of Kaiser Wilhelm Institute for Coal Research (now known as Max Planck Institute of Coal Research) found the formation of high-molecular-weight hydrocarbons when using iron filings at 100 atm and 400 °C. As mentioned earlier, this was an undesirable reaction during the methanol synthesis, but Fischer understood the importance of this reaction. While continuing to work on this direction, they routinely assessed a range of metal oxides, hydroxides, and carbonates and in 1926 reported that reduced iron and cobalt catalysts yielded gasoline fuels from coal-derived syngas [30, 31]. The reaction is known as the Fischer–Tropsch synthesis (FTS), which in 1935 marked the first FTS plant commissioned by Ruhrchemie using the cobalt catalyst. By 1938, there were nine such facilities within Germany with a manufacturing capacity of 600 000 tons/annum. The cobalt catalyst (100 Co/100 SiO<sub>2</sub>/18 ThO<sub>2</sub>) used by Ruhrchemie was developed by Fischer with Meyer and later with Koch by rapidly coprecipitating hot solutions of cobalt and thorium nitrate on SiO<sub>2</sub> (Kieselguhr diatomaceous earth) suspended in an ammonia-containing solution [32, 33]. The irreducible thorium oxide restricts the crystallization of the cobalt metal to maintain a high dispersion. The slightly radioactive thoria has been replaced by zirconia, titania, or manganese oxide in the present-day catalysts.

While cobalt is known to produce a large fraction of diesel and paraffin wax, the iron catalyst results in higher content of short-chain olefins when carried out at high reaction temperatures (~340 °C) or paraffin wax at much lower temperatures. As the reaction proceeds, the iron metal is gradually converted into iron carbide, which is an even more active phase [24, 34]. Compared with crude oil–derived fuels, the FTS-derived diesel and gasolines are characterized by their exceptionally high cetane and octane ratings due to the high yields of straight-chain paraffins for cobalt-derived diesel and olefins/isomers in the iron-derived gasoline, respectively. Although nickel and ruthenium catalysts are also active in FTS, they are rarely used as stand-alone catalysts. Nickel, which forms carbonyl and decomposes to the metallic phase (like iron), has a high tendency to form methane instead of liquid fuels. Ruthenium, which is the most active FTS catalyst, is far more expensive than cobalt and iron to justify its bulk

usage except as a promoter to cobalt catalysts. Incipient wetness impregnation is by far the most common technique for the synthesis of FTS catalysts [35].

### 1.3 Catalytic Cracking and Porous Catalysts

One of the earliest applications of heterogeneous catalysts in the modern petrochemical industries (crude oil refineries) can perhaps be traced to the catalytic cracking process. In the early 1920s, French engineer Eugene Jules Houdry, E. A. Prudhomme (the pharmacist who discovered the reaction) and their team developed the catalytic lignite-to-gasoline process, whereby lignite was first pyrolyzed to high-boiling-point liquid hydrocarbons, followed by vaporization and catalytic conversion to the gasoline fractions [36]. The latter step is similar to noncatalytic, high-temperature, and high-pressure cracking of the heavier fractions of the crude oil to produce (low octane rating) gasoline developed by Standard Oil Company in the United States a few years earlier. Efforts were made to boost the octane rating of the synthetic gasoline including trial using aluminum chloride as the cracking catalyst but was found to be economically unfeasible. Thomas Midgley and Charles Kettering of General Motors patented the addition of tetraethyl lead to gasoline to improve its octane rating substantially, which was rather successful commercially but was banned worldwide many years later due to the release of toxic exhaust fumes [37]. Houdry discovered a more environmentally benign solution, that is, use of Fuller's earth, a naturally occurring aluminosilicate layered clay, as a cracking catalyst to produce extremely high-quality gasoline from heavy crude.

Despite not having found much success in France, where the process was deemed not commercially viable, Houdry brought his catalytic cracking process to the United States in the 1930s for further development with Sonoco Vacuum Oil Company (later Mobil Oil Corporation and now ExxonMobil) and adapting the technology to the petrochemical processing. Upon overcoming various reactor engineering challenges to cope with the rapid catalyst coking during the cracking reaction, the Houdry process became a phenomenal success that revolutionized the petrochemical industry. His inventions paved the way for the development of the modern fluidized catalytic cracking (FCC) process, where catalysts were fluidized for continuous looping between the catalytic cracking reactor and adjacent regenerator unit (to remove coke by air oxidation). The Houdry process was so successful that the production of synthetic silica–alumina and magnesia–silica catalysts was commenced in the 1940s to meet the needs for catalytic cracking reaction [38]. In fact, the silica–alumina catalyst is still used to this day in industrial FCC, but in the form of synthetic zeolites, which have a much higher surface area than the clay minerals.

Synthetic zeolites, which constitute crystalline microporous (0.3–2.0 nm pores) aluminosilicates, have been actively developed since the late 1950s by the Union Carbide and Mobil Oil Corporation, resulting in the discovery of zeolites A (Linde Type A) and X (Linde Type X) in 1959 [39], zeolite Y (Linde Type Y) in 1964 [40], and ZSM-5 in 1972 [41, 42]. These landmark catalysts continue to find important applications not only in FCC but also in the isomerization

of hydrocarbons, synthesis of specialty chemicals, methanol-to-hydrocarbon conversions, and catalytic  $deNO_x$ , with a great deal of advancement achieved in the last decade in the conversion of biomass, among many others. Excellent accounts on the fundamentals as well as the state-of-the-art progress in some of these topics are highlighted in Chapter 33 (on the conversion of lignocellulose to biofuels), Chapter 34 (on the conversion of carbohydrates to high-value products), and Chapter 38 (on the abatement of  $NO_x$ ). In fact, the discovery of new zeolites has been thriving since the 1980s, with a unique set of material compositions, frameworks, and pore dimensions being discovered annually. A large database of zeolites is maintained by the International Zeolite Association since 1977 through the Atlas of Zeolite Structure Types [43]. While silicate and aluminosilicate zeolites dominate a large extent of the database, other zeolites based on aluminophosphates, metallosilicates, germanosilicates, aluminoborates, and so on also exist. Among them, some of the most widely used zeolites in industrial catalysis besides zeolite Y and ZSM-5 include zeolite X, MCM-22 (Mobil Composition of Matter No. 22), MCM-49, SAPO-34, Beta zeolite, and SSZ-13.

The most common approach to the synthesis of zeolites involves interfacing sol-gel chemistry with organic structure-directing agents (SDAs) as soft templates. In a classical sol-gel process, precursors especially those of alkoxides such as tetraethyl orthosilicate (TEOS) are first hydrolyzed to form alkoxysilanol and/or orthosilicic acid. Subsequent cross-linking reaction through the dehydration of the hydroxyl moieties results in the formation of nuclei, and further polymerization yields amorphous silica particles that appear either as sol (well-dispersed particles in solution medium) or gel (continuous network formed by particles throughout the solution medium). The physical sizes of these amorphous particles are strongly influenced by concentration, pH, and temperature of the reaction medium. In the presence of SDAs, typically amines or quaternary ammonium surfactants but in some cases inorganic ions, the cationic head of SDAs will bind strongly to the silicate anions. Under such situations, there exist concerted interactions between (i) the silicate and surfactant (functioning as structural stabilization and blocking agents), (ii) surfactant and surfactant (functioning as structural template for the micropores), and (iii) silicate and silicate (assembly of silicate network) during the self-assembly of the crystalline zeolites. The term "crystalline" refers to the repeated assembly of the basic unit cells of the microporous silicate network. Studies have shown that the slow crystallization process takes place during the hydrothermal aging after the formation of the amorphous silica particles. The surfactant SDAs can be removed by simple calcination, leaving behind well-ordered micropore channels within which catalytic reaction can take place. These micropores range from 8-membered ring (8-MR) (ultrasmall pore  $\sim 4 \text{ \AA}$ ), 10-MR ( $\sim 5 \text{ \AA}$ ) to 12- ( $\sim 7 \text{ \AA}$ ) and 14-MR (ultralarge pore,  $\sim 8 \text{ \AA}$ ) or above. Channels of 6-MR or less are too narrow to allow molecules to pass through and hence considered nonporous.

The signature strong acidity of silicate-based zeolites originates from the partial substitution of the silicate ( $SiO_4^{4-}$ ) building block with that of the aluminate ( $AlO_4^{5-}$ ). The additional charge deficiency brought about by the latter can be readily neutralized by a labile proton, i.e., Brønsted acid. The Brønsted acid site can be conveniently used as an ion-exchange site to immobilize other cations for

single-atom catalysis (discussed below). Interestingly, ion-exchanged  $\text{Ca}^{2+}$ ,  $\text{Y}^{3+}$ , and  $\text{La}^{3+}$  sites are efficient catalytic sites for the pyrolytic carbonization of ethylene and acetylene. This produces homogeneous graphene-like layers within the micropores that upon the removal of the zeolite template produce faithful carbon replica of the microporous framework [44]. Such zeolite-templated carbon (ZTC) is interesting not only because of the electrically conductive and well-ordered microporous framework that can now be utilized for electrochemical and fuel cell-related reactions but also because the carbon, which can be easily removed by calcination, can potentially serve as secondary templates to synthesize other nonzeolite microporous catalysts.

Care should be taken not to confuse zeolites with well-ordered mesoporous catalysts (e.g., MCM-41, SBA-15, KIT-6), which belong to a different class of porous materials and, by definition, consist of pores in the range of 2–50 nm. The MCM-41 (tunable pore size of 2–9 nm) and SBA-15 (tunable pore size of 5–10 nm), discovered by Charles T. Kresge et al. at the Mobil Oil Corporation in 1992 [45] and Galen D. Stucky and coworkers at the University of Santa Barbara in 1998 [46], respectively, are arguably the gold standards for this class of catalytic materials. These mesoporous catalysts are templated through the addition of bulky micelles such as those formed by cetyltrimethylammonium bromide (CTAB) surfactant and Pluronic P123 triblock copolymer, and sol-gel silica particles will precipitate in between these self-assembled soft templates. Because the micelles serve as long-range structural templates (and none at short range like those used for the synthesis of zeolites), well-ordered mesopores can be obtained, but the silica walls are basically amorphous. These glassy walls are catalytically inactive, in stark contrast with the crystalline walls of zeolites. Nevertheless, the mesoporous materials are attractive as high-surface-area supports with mesoporous channels large enough for the deposition of a wide range of active metals without pore blocking and at the same time accessible to bulky reactant molecules that otherwise could not penetrate the zeolite micropores. Because there is no requirement for short-range ordering, these surfactant templates can be flexibly used to fabricate a plethora of other mesoporous metal oxides including  $\text{TiO}_2$ ,  $\text{WO}_3$ , and  $\text{Al}_2\text{O}_3$ . Furthermore, the mesoporous silica can be used as hard templates for the synthesis of mesoporous carbon and metal oxide nanorods [47]. An area that is actively being pursued is the synthesis of hierarchical zeolites, where mesoporous channels are introduced in zeolites, in such a way that the wall of the mesoporous catalyst is no longer amorphous silica but that of catalytically active, microporous crystalline silicate. This allows the accessibility of acid sites by large reactant molecules while overcoming the mass diffusion limitation associated with the narrow micropores of zeolites during catalytic reactions. More details on the design and synthesis of such hybrid micro-/mesoporous catalysts are presented in Chapter 7.

Metal-organic framework (MOF) is a term first coined by Omar Yaghi in 1995 to describe a class of crystalline porous solids formed by a continuous network of multivalent metal cations/clusters and organic linkers of at least two coordination positions [48]. It is analogous to the zeolites, except with different set of building blocks. The elegance of MOFs arises from the simplicity of the template-free synthesis, and the micropore size can be easily tunable by adjusting the length of the organic linker. A classic example is the fabrication



of UiO-66 that involves the simple hydrothermal reaction between zirconyl chloride and 1,4-benzenedicarboxylic acid (BDC) linker. By replacing the BDC with a longer 1,4-biphenyldicarboxylic acid (BPDC), one can obtain UiO-67 and an extension of the pore size from 7.5 and 12 Å to 12 and 16 Å, respectively. In fact, the design of MOFs is so flexible that it can be extended to fabricate mesoporous catalysts by manipulation of the linkers or using SDAs [49]. The catalytic active sites of MOFs may originate from the active metal atoms or compounds covalently functionalized on the linkers or the framework metal cation centers if made coordinatively unsaturated (without affecting the rigidity of the MOF structure). An elegant account on the different strategies in designing MOF catalysts can be found in Chapter 8. To date, MOFs find wide applications in organic synthesis, biomass conversion, photocatalysis, and electrocatalysis, among others. Because of their organic frameworks, MOFs are normally used in mid- to low-temperature applications below 500 °C. A more recent sister class of compound is the covalent organic frameworks (COFs), first discovered by Yaghi in 2005, that are built entirely based on nonmetal centers [50]. In their pristine forms, some COFs are effective in catalyzing photocatalytic and electrocatalytic reactions, while their tunable porous structures can also be functionalized with the desired metal catalysts similar that of the mesoporous silica structure to catalyze a wider range of reactions, e.g., the Suzuki–Miyaura coupling reaction when deposited with the Pd<sup>2+</sup> single-atom catalyst.

The synthesis of porous anisotropic catalysts received significant interests since 2005 or so, especially for photocatalytic reactions such as solar water splitting, abatement of environmental pollutants, and CO<sub>2</sub> reduction. Photocatalysts are composed of semiconductor materials, that is, they can photoexcited with photons equal to or larger than their bandgaps to produce usable charges for surface redox reactions. Photocatalytic reactions can be carried out in two ways: particulate photocatalysis where the redox reactions as mediated by the electron–hole pairs take place on the same photocatalyst particle/aggregate (see Chapter 11 on the art of photocatalysts design) and photoelectrocatalysis where the photocatalyst is made into a photoelectrode and connected with a counter electrode in such a way that the electron–hole pairs are separated across the two electrodes (see Chapter 36 on the basics of photoelectrocatalysis) [51]. One-dimensional (1D) photocatalysts such as nanorod and nanotube arrays are particularly attractive to capitalize on the high surface-to-bulk ratio as well as the much sought-after vectorial charge transport for efficient photocharge separation during photoelectrocatalytic reactions. A variety of synthesis techniques to obtain such structures have been developed, ranging from chemical vapor deposition, spray pyrolysis, and hydro/solvothermal synthesis to electrochemical anodization, producing efficient anisotropic photocatalysts of TiO<sub>2</sub> nanotubes, WO<sub>3</sub> nanosheets, Nb<sub>2</sub>O<sub>5</sub> nanorods, Ta<sub>2</sub>O<sub>5</sub> nanotubes, α-Fe<sub>2</sub>O<sub>3</sub> nanotubes, etc. The electrochemical synthesis of these fascinating array photocatalysts can be found in Chapter 3. In recent years, the interest has expanded to two-dimensional (2D) photocatalysts such as the graphitic carbon nitride, molybdenum disulfide, tungsten disulfide, and MXenes. Besides maximizing the surface-to-bulk ratio, these materials exhibit unique quantum electronic properties seen only when made into atomic-thin layers [52].

## 1.4 Miniaturization of Metal Catalysts: From Supported Catalysts to Single-Atom Sites

A core criterion in the design of catalysts is to maximize the active metal dispersion (the ratio of surface atom to bulk), such that the highest reactivity per amount of metal loading on the catalyst can be achieved. This is especially relevant when precious metals are used, which is indeed the case for a large number of catalytic reactions. In the abovementioned historical overview, the strategies for maximizing dispersions include making metal sheets into metal sponges and gauzes of fine wires, as well as depositing active metals onto high-surface-area supports to make very fine deposits or thin atomic layers.

The synthesis of supported catalysts capitalizes on the strong interfacial interactions between the active metal and the (usually oxide) support to allow the former to exist as stable and small size deposits. Without the strong interfacial interactions, the initially small deposits tend to diffuse on the support surface and coalesce with another deposit until its surface energy (i.e., a function of surface area) decreases to that of the interfacial energy. Incipient wetness impregnation is by far the most common procedure for the preparation of supported catalysts, where metal precursor solution is drawn into the pores of the support by means of capillary effect. To prevent overflowing of the solution to the external surface of the support, the solution volume introduced in each impregnation step should not exceed that of the pore volume (typically maintained at 80–90%). More liquid solution can be introduced repeatedly upon complete drying of the liquid solvent, leaving behind more metal salt within the pore during each repetition. The advantage of the incipient wetness impregnation is that it does not require very strong interactions between the oxide support surface and the coordinated metal cation from the precursor to reach the desired loading amount. On the contrary, wet impregnation is when the porous support is immersed in the metal precursor solution and the amount that penetrates the pores depends on the metal precursor–support interactions. If the interaction is strong, the impregnated concentration would be higher than that of the bulk, and vice versa. Further drying to remove the solvent from the pores and calcination yield the supported catalysts in both cases of impregnation. To minimize coalescence between the metal deposits during the calcination step, it is essential to remove moisture and oxygen by flowing inert gas and introducing a small amount of NO, respectively [53]. Other techniques such as deposition–precipitation, chemical vapor deposition, and the one-step flame synthesis (see Chapter 10) have also become popular alternatives for producing supported metal catalysts. The ability to produce small Pt deposits on carbon support has been one of the major breakthroughs that led to popularity of low-temperature H<sub>2</sub>-polymer electrolyte membrane (PEM) fuel cell. In fact, the amount of the ~3.5 nm Pt used is so small (0.2 mg/cm<sup>2</sup> of fuel cell, compared with 28 mg/cm<sup>2</sup> in the early days) that it significantly reduced the device cost and thus popularising the H<sub>2</sub>-PEM fuel cell [54]. Chapter 32 introduces the design of electrocatalysts for PEM fuel cell applications, while Chapter 4 complements nicely the strategies of using carbon supports for such purpose.

Besides maximizing the metal dispersions, further miniaturization of metal deposits to or approaching the quantum-related level can result in altered electronic properties not otherwise seen in larger particles. Gold catalysis is an intriguing example of such a phenomenon, which was led notably by the independent efforts of Graham J. Hutchings and Masatake Haruta since the mid-1980s. They showed that gold, which was classically believed to be almost inactive, can be made extremely active in the hydrochlorination of acetylene [55] and the oxidation of carbon monoxide (at  $-77^{\circ}\text{C}$ !) [56], respectively, when made less than 25 nm. The latter, which gold size was  $4.5 \pm 1.6$  nm, was first prepared by the coprecipitation technique but was later superseded by the deposition–precipitation technique in which dissolved gold precursor was precipitated by raising the pH of the medium in the presence of suspended oxide support. Over time, the commercial flame-synthesized P25  $\text{TiO}_2$  became the preferred support. Many new reactions by gold catalysis followed in the next three decades, ranging from the oxidation of aqueous polyalcohols to carboxylic acids, selective oxidation of cyclohexane to cyclohexanol and cyclohexanone, epoxidation of propylene, water-gas shift, to the selective hydrogenation of 3-nitrobenzene and the hydrogenation of alkynes to alkenes. Size-dependent turnover frequencies (i.e., conversion rate per active site) is typically observed due in part to the variation of electronic interactions, with the optimum gold deposit size for CO oxidation in the range of 2–4 nm [57, 58]. The size-dependent activity is a general phenomenon as observed readily on different metal deposits including cobalt for FTS [59], palladium for Suzuki coupling [60], and platinum for propane dehydrogenation [61].

Synthesizing ultrasmall size deposits of less than 2 nm (<100 atoms), or so-called metal clusters (or nanoclusters as a more appealing terminology), can be quite challenging because of their high surface energies. At such a size, the surface energy can become so overwhelming that even when deposited onto high-surface-area supports, the metal deposits prefer to exist as larger sizes so as to minimize the exposed surface area (and hence the total energy). In such cases, stabilizing ligands such as glutathione, cetyl trimethyl ammonium bromide (CTAB), and poly(vinylpyrrolidone) (PVP) that bind to the surface of the small deposits can be added during the synthesis procedure. With the ligands being exposed and having lower surface energy than the bare metals, they protect the metal clusters from coalescing or dissolving. Metal clusters are so called not just to distinguish them from the larger nanosized particles, but importantly they reach a state where they no longer behave like metals. As a result of the size quantization effect that gives rise to the discrete orbitals and formation of an energy gap, they essentially behave more as semiconductors. The effect is not unlike the size quantization phenomenon commonly observed for semiconductor photocatalysts with the diameter smaller than the Bohr excitonic radius. Although the term quantum dot (commonly abbreviated as Q-dot) refers exclusively to such semiconductor particles, by the same definition, metal clusters should also be termed quantum metals! [62]. In that respect, Chapter 5 readily lays out the physics as well as the design principles of different metal clusters catalysts. Metal clusters, with or without ligand bound, have been shown to exhibit catalytic properties different from that of larger nanoparticles,

for example, the highly selective oxidation of cyclohexane to cyclohexanone over  $\text{Ag}_6/\text{graphene oxide}$ , 100% selectivity of 4-nitrobenzaldehyde to 4-nitrobenzyl alcohol over  $\text{Au}_{99}(\text{SPh})_{42}/\text{CeO}_2$ , and electrocatalytic reduction of carbon dioxide to carboxylic acid  $\text{Cu}_{32}\text{H}_2\text{OL}_{12}$  ( $\text{L}$  = dithiophosphate ligand). Because of the semiconductor nature of metal clusters, they can even function as photocatalysts, for example, in the photocatalytic degradation of aqueous organic micropollutants over glutathione-protected gold clusters [63, 64].

Single-atom catalysts (SACs) represent the ultimate extreme end of catalyst miniaturization. First demonstrated by John Meurig Thomas of the Davy-Faraday Research Laboratory in 1988 by surface grafting Ti (from titanocene) onto the silanol sites of mesopores of MCM-41, the SAC of Ti showed high catalytic oxidation activities, albeit, rather short-lived [65]. Other forms of SACs include ion-exchanged zeolites or mesoporous silica, unsaturated framework metal sites, coordinated metal ions around the pyridinic sites graphene or carbon nitride, unsaturated metal centers in MOFs, supported organometallics, and isolated surface-exposed metal atoms dispersed in the form of alloy or supported on metal oxide. The physical criterion of SACs requires the catalytic site (usually referring to a metal atom) exists in full isolation from another metal atom of the same type. The ability of SAC to function *in silo* as a catalytic site reminisces that of freestanding homogeneous organometallic catalyst. In that sense, catalysis on SACs is often touted as a convergence of heterogeneous and homogeneous catalyses [66]. Although the research on SACs has progressed reasonably since the report by Thomas, explicit interest picked up substantially since the mid-2010s in conjunction with the advancement of aberration-corrected high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) that enabled the direct visualization and interrogation of SACs. Producing SAC sites is particularly meaningful for precious but otherwise highly active metals (e.g. Pt, Ir, Rh, Ru, Os) since the unity dispersion means that every single atom is on the surface and thus can be utilized for reactions. Elegant account on the synthesis of SACs is well covered in Chapter 6, while the carbon-supported SACs are partly covered in Chapter 4. Compared with the metal clusters and their nanoparticle counterparts, SACs tend to have lower coordination numbers (i.e., less neighboring atoms that are directly bonded with the SAC), although the extent of which depends greatly on their syntheses. At the same time, the effects of quantum confinement and metal-support interactions are amplified in SACs [67]. These effects contributed to the unique catalytic properties of SACs as demonstrated for CO oxidation, water-gas shift reaction, photocatalytic hydrogen evolution, electrochemical oxygen reduction reaction, etc. [68]. Intriguingly, by using a similar surface grafting technique as that reported by Thomas but using paired heteroatoms, e.g.  $\text{Co}^{2+}/\text{Zr}^{4+}$ ,  $\text{Cu}^+/\text{Zr}^{4+}$ ,  $\text{Cu}^+/\text{Ti}^{4+}$ ,  $\text{Cr}^{3+}/\text{Ti}^{4+}$ , and  $\text{Co}^{2+}/\text{Ti}^{4+}$  on MCM-41, Heinz Frei created a class of new photocatalytic system based on metal-to-metal charge transfer (MMCT). In MMCT, each binuclear unit is composed of a photoexcitable donor cation and an acceptor cation connected by an oxo bridge, e.g.,  $\text{Co}^{2+}-\text{O}-\text{Zr}^{4+} + h\nu$  (light)  $\rightarrow \text{Co}^{3+}-\text{O}-\text{Zr}^{3+}$ . When loaded with cocatalysts such as Pt, Cu, and  $\text{IrO}_2$  clusters, these MMCT systems show extremely high activities in water splitting and carbon dioxide reduction under visible-light activations [69].

## 1.5 Perspectives and Opportunities

In the course of 120 years since the discovery of modern heterogeneous catalysis, almost the entire physical length scale of catalyst design with compositions across the periodic table has been explored. From the use of bulk metals in the form of wires and metal strips during the Faraday era to metal nanoparticles and metal clusters and all the way to SACs, the primary objective has always been to identify the most active, selective, and durable catalysts and at the same time economically feasible (not necessarily low cost) and environmentally benign ones. While the classical techniques for catalyst preparation such as impregnation, precipitation, sol–gel, hydro/solvothermal syntheses, and solid-state sintering continue to be relevant to this day, both industrially and fundamentally, many new syntheses and design strategies have since emerged. They include electrochemical anodization, supramolecular assembly, microwave synthesis, vapor deposition, spray pyrolysis, flame and plasma synthesis, etc. At the same time, design strategies including those with soft and hard templating to induce highly ordered pore structures, engineering of crystal facets and anisotropy (see Chapter 2 on how they can be creatively used to manipulate the target catalytic reactions), ligand-capping to obtain well-defined metal clusters, and surface grafting of single-atom sites were developed to tune the physicochemical characteristics and hence the reactivities of catalysts. It is such a process of continuously pushing the boundaries of catalyst design that led to many new catalytically usable properties, e.g., size and spatial selective pores, localized surface plasmon resonance, size quantization effects, non-Newtonian metal–support interactions, and low coordination active sites. The ability to uncover and utilize these new catalytic properties for targeted reactions is what constitutes the frontier in the field.

The discovery of new catalysts is often a challenging but highly rewarding task that requires significant amount of trial-and-error and optimization (recalling the accomplishments of Alwin Mittasch in discovering the ammonia and methanol synthesis catalysts), even with some high degree of rational design approach. To some extent, it is inevitable because the range of optimum performance is at times quite narrow especially for multicomponent catalysts. Some of these tasks can be alleviated by employing advanced computational screening techniques to streamline the search for targeted catalysts. The coupling of physical screening with machine learning is another highly anticipated technique for the discovery of new and better catalysts. In a way or another, the advancement of computational catalyst design helps to push the boundary of the synthesis techniques in identifying new active sites. This may involve the synthesis of crystal phases or alloys that did not previously exist, new pore topologies, new crystal facets orientation, the engineered spatial deposition of two or more active sites, the creation of particular defects adjacent to the active site, etc.

One may question if it would be possible to move away from the use of precious metals, which, as mentioned, appear to be the favored active sites in many heterogeneous reactions. There is certainly some progress being made in carbon-based and 2D catalysts, as well as those searching for light transition metal alternatives or the creation of SAC sites of the precious metals. An underlying consideration that often arises is whether the new catalyst solutions are economically feasible,

not only from the synthesis point of view but whether the reaction output (or earnings) per cost of catalysts is justifiable to the overall chemical process. This includes the environmental costs in the removal of unwanted byproducts when using less selective catalysts and the disposal (or recyclability) of spent catalysts with toxic elements, e.g., chromium. By any means, a truly modern design of catalysts should as much as possible circumvent the production of byproducts (within the bound of thermodynamics) and the use of toxic elements.

As the value of catalysts changes over time depending on the importance of reactions, one needs to be visionary in terms of the type of catalysts to design and their target functions that cannot yet be achieved with existing catalysts. Among the more recent reactions of interest are those that involve the production of sustainable fuels and food (recalling the Nitrogen Problem in the 20th century), mitigation of global warming and climate change, and the abatement of microplastics and new micropollutants lurking in the environment.

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