1

Introduction to Hydroxyapatite-based Materials in Heterogeneous Catalysis

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1.1 Generality

As recently reviewed by Wisniak [1] and summarized in the book of Zecchina and Califano [2] on the history of the catalysis, the first known work seemed to be carried out in 1552 by Valerius Cordus, for the synthesis of ether from alcohol catalyzed by sulfuric acid. During the next centuries, several examples were recorded [1], such as the hydrolysis of potato starch in water catalyzed by potassium hydrogen tartrate or by acetic acid (1781); hydrogen production from alcohol and concentrated sulfuric acid catalyzed by alumina, silica, or clay without external heating (1796); starch conversion into gum, dextrin, and raisin sugar catalyzed by inorganic acids (1811); and starch fermentation into alcohols via sugar formation (1816). However, the term *catalysis* was only introduced for the first time by Berzelius in 1835 [1, 3], which means "the property of exerting on other bodies an action which is very different from chemical affinity. By means of this action, they produce decomposition in bodies, and form new compounds into the composition of which they do not enter." In 1836, Berzelius stated "the catalytic power seems actually to consist in the fact that substances are able to awake affinities, which are asleep at a particular temperature, by their mere presence and not by their own affinity" [2, 4].

The first large-scale industrial application of the catalysis could be assigned to the production of sulfuric acid over platinum catalyst at the end of the nineteenth century [2]. This process was later improved (around 1920) by replacing platinum catalyst by vanadium pentoxide, which is still used today for sulfuric acid production. The beginning of the twentieth century was also marked by the industrialization of the ammonia oxidation over platinum catalyst to produce nitric acid (Ostwald–Brauer process), ammonia production from direct hydrogenation of molecular nitrogen over iron-based catalysts (Haber–Bosch process), and liquid fuel synthesis from syngas over iron, cobalt, or ruthenium catalysts (Fisher–Tropsch process) [2]. Then, the catalysis passed through its golden period with the petroleum and polymer eras, with the discovery and industrialization of many important

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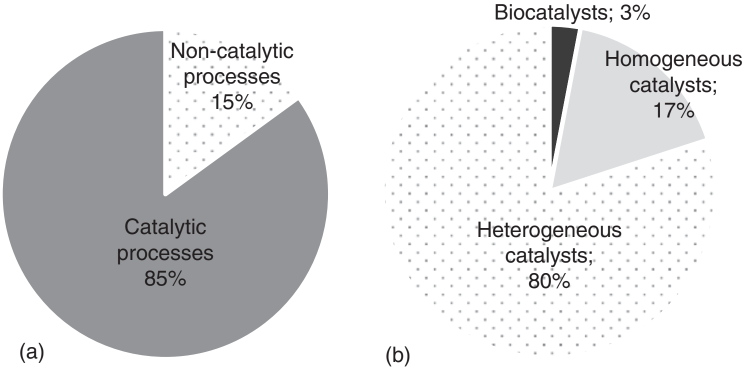

Figure 1.1 Pie charts showing: (a) the percentages of catalytic processes *versus* non-catalytic processes; (b) and the percentages of all industrial processes that entail the use of heterogeneous, homogeneous and bio-catalysis. Source: Adapted from Thomas and Harris [5] with permission of the Royal Society of Chemistry.

catalytic processes such as catalytic cracking, isomerization, alkylation, reforming, hydrodesulfurization, and polymerization [2]. Nowadays, the catalysis has a pivotal role in the modern society, and it is present in ca. 85% of manufacturing processes (Figure 1.1a), as recently reviewed by Thomas and Harris [5].

Generally, three categories of catalysts are distinguished: heterogeneous catalysts that are usually solid materials, homogeneous catalysts that are usually soluble salts or complexes, and enzymatic catalysts. Among them, heterogeneous catalysts occupy an important place in comparison with the counterparts, mostly because of their easy separation from products and their applicability in large ranges of temperature and pressure. Thus, among catalytic processes, heterogeneous catalysts represent up to 80%, much higher than the parts of homogeneous and enzymatic catalysts (Figure 1.1b) [5].

More specifically, other catalyst classifications have been also proposed in the literature. For example, by key properties responsible for their catalytic behavior, the following catalyst families can be classified: redox catalysts, acid-base catalysts, or polyfunctional catalysts [6]. Misono [7] classified catalysts by their main components. Thus, different families of catalysts are classified such as metals, metal oxides, metal salts, metal coordination compounds, organic molecules, organic polymers, and biocatalysts.

Considering the periodical table of elements, the most well-known catalysts are found within the elements of the columns 1–14, which are principally metals and metal-based compounds. Among the most available non-metallic elements (e.g. C, Si, N, P, O, S, F, Cl, Br, I), O is usually present in catalytic materials; C constitutes a large family of catalyst supports such as activated carbon, carbon nanotube, carbon nanofiber, and graphene; Si also builds different types of catalysts (zeolites) or catalyst supports (SiO_2-based materials); F, Cl, Br, I, N, and S have been applied as acid catalysts (in the form of their inorganic acids) or catalyst additives (in the form of their inorganic acids or salts) to modify acid-base properties of another material. On the other hand, P is more particular in comparison with the other non-metallic elements, since it provides a large number of water soluble and insoluble compounds, of simple or complex oligomer or polymer structures, e.g. orthophosphates (PO_4^{3-}), pyrophosphates ($P_2O_7^{4-}$), cyclophosphates, and polyphosphates [8]. Among them, phosphate is the most popular form of phosphorus compounds and also constitutes a large number of materials that have potential applications in the catalysis of various chemical processes such as dehydration and dehydrogenation of alcohols, hydrolysis reactions, oxidation and aromatization reactions, isomerization, alkylation, Knoevenagel reaction, Claisen–Schmidt condensation, epoxidation, nitrile hydration, cycloaddition, Michael addition, water splitting, and conversion of biomass-derived monosaccharides [9–13]. For example, Vieira et al. [13] studied direct conversion of glucose and xylose to HMF (5-hydroxymethylfurfural) and furfural over the niobium phosphates as efficient bifunctional catalysts. The acidity of the catalysts, expressed as the ratio of Lewis to Brønsted acid sites (L/B) could be tuned by varying the molar ratio of P to Nb, which allows controlling the catalyst performance. Thus, both the conversion of monosaccharides (glucose and xylose) and the formation of furans linearly increases with the L/B ratio; the later increases by decreasing the P to Nb molar ratio. In another example, Kim et al. [14] successfully synthesized cobalt pyrophosphate ($CoP_2O_7^{2-}$) and cobalt phosphate ($CoPO_4^-$) based materials as new electrocatalysts for water splitting reaction. High electrocatalytic activity and stability during 100 cycles were observed, explained by the structural stabilities of the investigated materials.

Stoichiometric calcium phosphate hydroxyapatite (chemical formula: $Ca_{10}(PO_4)_6(OH)_2$), denoted thereafter HA, belongs to the family of apatites, which is a category of phosphate compounds. A given apatite has the general chemical formula of $M_{10}(XO_4)_6Y_2$, where M is generally a bivalent metal cation (Ca^{2+}, Mg^{2+}, etc.), XO_4 is generally a trivalent anion (PO_4^{3-}, VO_4^{3-}, AsO_4^{3-}, etc.), and Y is typically a monovalent anion (OH^-, F^-, Cl^-). However, other cations and anions with different valences can also be present in an apatitic compound. For example, carbonate anion (CO_3^{2-}) can partially replace both Y and XO_4 anions, while Na^+, K^+, Al^{3+}, etc., can partially replace M cations. More details on the apatite composition and structure will be discussed in Chapter 3 of this book.

In heterogeneous catalysis, HA-based materials are still considered as a new potential family of catalysts for various applications, as recently reviewed by Gruselle [15], and Fihri et al. [16]. Gruselle [15] focused his review on the catalytic performance of HA-based materials in the organic synthesis, while Fihri et al. [16] enlarges their review to other processes including the photocatalysis, hydration, hydrogenation, hydrogenolysis, transesterification, and multicomponent reactions. On the one hand, HA can be used itself as a solid catalyst. For example, in the Knoevenagel condensation reaction conducted by Sebti et al. [17], undoped HA allowed obtaining high yields (e.g. 80–98%) at room temperature and atmospheric pressure. In many cases, HA-based materials were usually found to be competitive in terms of catalytic performance in comparison with conventional catalysts. On the other hand, HA can be used as a catalyst support to disperse a catalytically active phase, such as metal nanoparticles, or metal cations. For instance, Phan et al. [18] demonstrated the superior catalytic activity of HA supported bimetallic

Co–Ni catalysts in the dry reforming of methane for syngas production. As will be discussed in Chapter 3 of this book, the first publication on HA as catalyst appeared around 1940s, but, research on HA catalysts has only accelerated during the last two decades, with an exponential increase of the annual number of publications. The Section 1.2 will focus on the main reasons making HA-based materials as new promising candidates in the heterogeneous catalysis.

1.2 Hydroxyapatite: A New Family of Catalytic Materials in the Heterogeneous Catalysis

Well-known for their application in the field of biomaterial [19–21], HA and apatite-based materials have gained increasing attention during the last two decades owing to their structural, physicochemical, and thermal properties [15, 16, 22, 23]. The most important properties of HA and HA-based materials are summarized next, which are detailed and analyzed in different chapters of this book.

1.2.1 Possible High Porous Volume and High Specific Surface Area

In the heterogeneous catalysis, high specific surface area is generally required since it favors the contact of solid catalyst surface with chemical compounds in both the liquid and gas phases. *It is possible to synthesize HA with high specific surface area and porosity* by different methods, which will be detailed in Chapter 2 of this book. For example, Verwilghen et al. [24] obtained HA powder with a specific surface area of $156\,m^2\,g^{-1}$ by coprecipitation of monoammonium dihydrogen phosphate ($NH_4H_2PO_4$) and calcium nitrate ($Ca(NO_3)_2$) at 75 °C. Starting from calcium acetate ($(CH_3COOH)_2Ca$) and diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) as calcium and phosphate precursors, Nagasaki et al. [25] successfully synthesized HA exhibiting specific surface area up to $90\,m^2\,g^{-1}$ and containing mostly mesopores with mean diameter of around 2.5 nm. It is usually observed that the specific surface area and the porosity of HA strongly depends on a set of multiple factors including the nature of calcium and phosphate precursors, the nature of solvent, the maturation time, the agitation speed, the pH, and the post-treatment by drying.

1.2.2 High Thermal Stability

HA can be heated to high temperature (ca. $>850\,°C$, this threshold temperature being a function of different parameters such as the stoichiometry of HA, the atmosphere of heat treatment, and the pressure of the heat treatment) without significant modification of its chemical composition and structure. *Thus, HA can be used as catalyst or catalyst support in most of the chemical reactions, which are usually performed below this threshold temperature*. Above this threshold, partial dehydroxylation occurs, leading to the formation of oxyhydroxyapatite ($Ca_{10}(PO_4)_6(OH)_{2-2x}O_x$). Then, oxyhydroxyapatite can decompose into tricalcium phosphate (TCP) and tetracalcium phosphate (TTCP). The impact of this dehydroxylation on catalytic

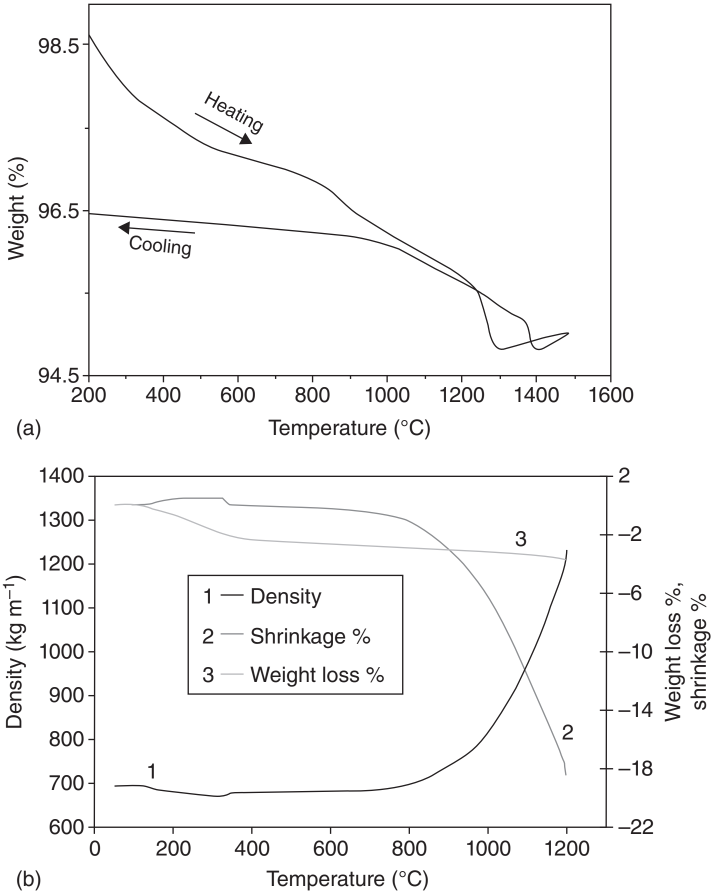

Figure 1.2 (a) Thermal behavior of a commercial stoichiometric HA under the air atmosphere. Source: Liao et al. [26]. Reproduced with permission of Elsevier. (b) Evolution of bulk density, weight loss, and shrinkage during HA heating. Source: Bailliez and Nzihou [27]. Reproduced with permission of Elsevier.

properties also merits to be further studied in high temperature processes. Liao et al. [26] studied the decomposition of a commercial stoichiometric HA under the air (Figure 1.2a). The weight losses below 200 °C and between 200 and 400 °C are assigned to adsorbed water and lattice water, respectively. The latter causes a contraction in the α-lattice dimension. This dehydroxylation seemed to take place progressively up to around 1000–1360 °C. Then, oxyhydroxyapatite decomposed into TCP and TTCP between 1400 and 1500 °C. TCP and TTCP can be partially recombined forming oxyhydroxyapatite and HA by cooling down the material. The flexibility of HA and HA-based materials toward dehydroxylation/hydration makes them more resistant in catalytic systems involving water vapor, which is the case for various chemical processes.

On the other hand, heating HA to high temperature (e.g. 1000 °C) generally leads to a decrease of its porosity and specific surface area by thermal sintering.

For example, heating an HA to 1200 °C decreased its specific surface area from ca. 105 to ca. 5 m^2 g^{-1} and led to the formation of non-porous and dense HA (Figure 1.2b) [27]. For high temperature catalytic processes, this evolution of textural properties of HA can provoke a catalytic deactivation. Alternative solution can be a stabilization of HA by thermal treatment, as demonstrated by Rego de Vasconcelos et al. [28]. In this work, HA support was sintered at 1000 °C for 5 hours, before the deposition of Ni nanoparticles by a conventional impregnation method. This allowed limiting the catalyst deactivation due to the thermal sintering during the chemical reaction at high temperature (dry reforming of methane). Nevertheless, this also caused a decrease of the initial catalyst activity due to the reduction of the specific surface area and the suppression of the porosity of HA support. *A compromise between the activity and the thermal stability must be found for catalytic applications of HA and HA-based materials at high temperatures.*

1.2.3 Exceptional Ion Exchange Capacity

Calcium cations, phosphate, and hydroxyl anions of a given HA can be partially replaced by other cations and anions [23]. Cation exchange capacity of HA with various metallic cations such as alkalis, alkaline earth metals, or transition metals in aqueous media differentiates it from other catalyst supports, at the exception of zeolites. The cation exchange usually takes place quickly on HA surface (few seconds to few minutes), with higher sorption capacities (Q_e) in comparison to reference materials such as activated carbon, ion exchange resins [29, 30], or even zeolites [31]. For instance, it was found that the Q_e of an HA powder synthesized from calcium carbonate and orthophosphoric acid reached up to 625 $mg_{Pb^{2+}}\ g_{HA}^{-1}$ for Pb^{2+} removal from an aqueous solution, which was much higher than that obtained with activated carbon, resin, or biochar (15–250 $mg_{Pb^{2+}}\ g_{adsorbent}^{-1}$) [32]. High cation exchange rate and high Q_e offer the flexibility to improve metal deposition and metal loading for the preparation of HA supported catalysts. *This is an important advantage of HA, in comparison with the conventional catalyst supports, particularly when highly dispersed metal supported catalysts are targeted.* For example, bimetallic Ru–Zn/HA could be easily obtained by cation exchange method by setting in contact an HA powder with an aqueous solution of $RuCl_3$ and $ZnSO_4$ at room temperature under stirring for two hours [33]. After drying and activation under H_2 at 300 °C for 1 hour, nanoparticles of Ru smaller than 2.4 nm were formed on HA surface, which were found to be active and particularly stable in the selective gas-phase hydrogenation of benzene at 150 °C and 50 bar. Kaneda's group [34–36] performed the deposition of monomeric Zn, Ru, or Pd species on HA-based supports, for selective alcohol oxidation, using a simple ion exchange approach, in which HA-based supports were set in contact with an aqueous solution of $RuCl_3$ or $Zn(NO_3)_2$, or an acetone solution of $[PdCl_2(PhCN)_2]$. No further activation was applied to these catalysts, leading to the dispersion of isolated metal cations on HA surface. In fact, extended X-ray absorption fine structure (EXAFS) analysis proved that the active phase existed as monomeric species, and no metal–metal bond was detected. These catalysts were found particularly active in alcohol oxidation. More recently, Akri et al. [37] have reported the preparation of

Ni_{SA}/HA catalysts by strong electrostatic adsorption method. This method consists in the cation exchange of Ca^{2+} with Ni^{2+} at a controlled pH in an aqueous solution. A mixture of isolated Ni species, small Ni clusters, and Ni nanoparticles could be obtained, and the contribution of each Ni species depended on the Ni loading and the thermal treatment (e.g. drying or H_2 reduction). At low Ni loading (0.5 wt%), only isolated Ni atoms were deposited on HA surface after the drying step, while the reduction under H_2 at 500 °C mainly led to a deposition of Ni isolated atoms (ca. 94%) and small amounts of Ni clusters (ca. 6%). The synthesized catalyst exhibited high specific activity in dry reforming of methane to produce syngas at 750 °C and 1 bar.

It is worth noticing that ion exchange is usually carried out in an aqueous solution. HA generally has a very low solubility product in water. However, in the literature, different values were reported, because the solubility depends on various parameters such as the pH, the synthesis method, and the stoichiometry of HA [38]. As examples, at a pH of 8.25, Bell et al. [39] found a mean value of the solubility product of $1\,830\,000 \times 10^{-58}$ for a stoichiometric HA, while at a pH of 4.90, the solubility product strongly decreases to 3.15×10^{-58}. Ito et al. [40] reported much lower values of solubility product for a carbonated apatite, which varied from 10^{-119} at pH of 4.9 to 10^{-130} at pH of 4.1. Despite this inconsistency, it is important to take into consideration the high sensitivity of HA and HA-based materials to pH values in order to design catalytic formulations meant for aqueous-phase processes. In fact, a solution presenting a very low pH such as that of 1 M HNO_3 acid can completely dissolve an HA powder.

1.2.4 Tunable Acid-base Properties

The possibility of tuning the acid-base properties of HA and HA-based materials is another interesting advantage that justifies their use in various catalytic processes. HA bears both acidic and basic sites on its surface. Acidic sites are principally attributed to PO–H from $HPO_4{}^{2-}$ species (Brønsted sites) and Ca^{2+} cations (Lewis sites), while basic sites are due to surface $PO_4{}^{3-}$ and OH^- groups (and possibly other phases such as CaO, $Ca(OH)_2$, and $CaCO_3$) [41, 42]. Particularly, the acido-basicity of HA can be tuned by controlling the Ca/P molar ratio [41–43]. Globally, calcium-deficient HA ($Ca_{10-Z}(HPO_4)_Z(PO_4)_{6-Z}(OH)_{2-Z}$, with $0 < Z < 1$), with a Ca/P molar ratio smaller than 1.67, behave as acid materials. Stoichiometric HA (Ca/P = 1.67) and calcium-surplus HA (global Ca/P > 1.67, with the presence of other phases such as CaO, $Ca(OH)_2$, and $CaCO_3$), which depend on the synthesis conditions, behave as basic materials. Moreover, the acido-basicity of HA-based materials can also be controlled by promoter addition (Mg^{2+}, Ba^{2+}, Sr^{2+}, etc.) while keeping their apatitic structure [43–45]. *The tunability of the surface chemistry of HA and HA-based materials is an important property, suitable for various processes,* since the acid-base catalysis covers a large number of chemical reactions such as isomerization, alkylation, esterification, hydration, dehydration, oligomerization, cracking, and acylation. For example, Silvester et al. [41] synthesized different HA-based materials having different Ca/P molar ratios by using the precipitation method under controlled conditions of temperature (Table 1.1). Expectedly, increasing the Ca/P molar ratio leads to an increase in basicity and a decrease in acidity. The insertion of Na^+ and CO_3^{2-} also modified the acidity and basicity of the materials. In another work, Tsuchida et al. [46] also demonstrated the dependency of the acidity and basicity of different HAs on the Ca/P molar ratio. These catalysts were evaluated in the transformation of ethanol into other valuable chemicals. At the iso-conversion of ethanol of 10 and 20% (by varying the reaction temperature and keeping other conditions unchanged such as gas hourly space velocity [GHVS]), the acidity and basicity strongly impacted the selectivity of the reaction, where different mechanisms pathways were found to be involved. Ethylene was the main product over strongly calcium-deficient HA, exhibiting high acidity that favors dehydration reaction, while 1-butanol was predominant over stoichiometric HA possessing high basicity that favors the Guerbet condensation.

1.2.5 High Affinity with Organic Compounds

HA and HA-based materials are efficient not only for the fixation of metallic cations but also for the immobilization of organic compounds on their surface [47]. Adeogun et al. [48] synthesized HA from poultry eggshells (calcium source) and ammonium dihydrogen phosphate (phosphate source). In the removal of reactive yellow 4 dye from the liquid phase, the resulting materials showed a high sorption capacity of $127.9\ mg\ g^{-1}$. Sebei et al. [49] investigated the sorption of catechol on an HA synthesized from $CaCO_3$ and KH_2PO_4. Interesting sorption capacity of $24.6\ mg\ g^{-1}$ could be obtained. HA synthesized from $Ca(NO_3)_2$ and $NH_4H_2PO_4$ was also found to be efficient for the removal of fulvic acid in the liquid phase, and its sorption capacity ($90.2\ mg\ g^{-1}$) was even much higher than that of other materials such as zeolite, activated sludge, chitosan hydrogen beads, carbon nanotubes, and vermiculite [50]. In the gas phase, HA deposited on a polyamide film also presented interesting reactivity in the removal of formaldehyde [51].

High affinity of HA and HA-based materials to organic compounds will be beneficial for the design of efficient catalytic systems employing these molecules. Moreover, the reactivity of the surface of HA and HA-based materials can be improved by different routes (e.g. mechanical treatment, chemical modification). As examples, HA doped with Zn^{2+} was more efficient than a bare HA in the sorption of catechol in the liquid phase [49], while HA activated by mechanical treatment, which led to the creation of surface defects and oxygen vacancies, was more efficient than untreated HA in the oxidation of volatile organic compounds [47].

1.2.6 Formulation of HA-based Materials

HA can be synthesized by different routes as will be detailed in the Chapter 2 of this book. Depending on the synthesis conditions, fine micro- and/or nanoparticles of HA can be formed [52, 53]. Laboratory investigations of HA and HA-based materials in the catalysis can be performed using fine HA powders. For an eventual scale-up, HA powders must be processed to obtain materials of controlled form

Table 1.1 Quantification of the density and nature of acid and basic sites of various HA-based materials as functions of the Ca/P molar ratio.

		Basic sites						**Acid sites**			
		TPD-CO_2		**Benzoic acid adsorption**						**Number and distribution of acid sites**	
Materials	**Ca/P atomic ratio (ICP)**	**Total basic sites (μmol g^{-1})**	**Specific basicity (μmol m^{-2})**	**Total basic sites (μmol g^{-1})**	**Specific basicity (μmol m^{-2})**	**Strong basic sites (μmol m^{-2})**	**Weak basic sites (μmol m^{-2})**	**Number of acid sites (μmol g^{-1})**	**Specific acidity (μmol m^{-2})**	**Lewis (μmol m^{-2})**	**Brønsted (μmol m^{-2})**
HapD	1.62	41.33	0.33	259.9	2.09	1.88	0.21	956	7.73	5.16	2.57
Hap	1.69	100.67	0.87	194.3	1.70	1.45	0.25	763.3	6.73	5.43	1.30
Hap-CO_3	1.70	136	1.27	499.5	4.66	4.66	0	658	6.13	5.58	0.54
HapNa-CO_3	1.72	155.33	1.4	134.7	1.24	0.83	0.41	604	5.53	5.17	0.36
HapE-CO_3	1.90	112.67	1.47	310.4	4.08	3.60	0.48	324	4.27	4.01	0.26
HapE-Na-CO_2	2.39	104	1.47	351.6	4.88	4.29	0.59	141.3	1.87	1.78	0.09

HapD: calcium-deficient hydroxyapatite; Hap: stoichiometric hydroxyapatite; Hap-CO_3: carbonated apatite; HapNa-CO_3: sodium-containing carbonate apatite; HapE-CO_3: sodium-free carbonate-rich apatite; HapE-Na-CO_3: sodium-containing carbonate-rich apatite; TPD: temperature programed desorption.
Source: Silvester et al. [41]. Reproduced with permission of the Royal Society of Chemistry.

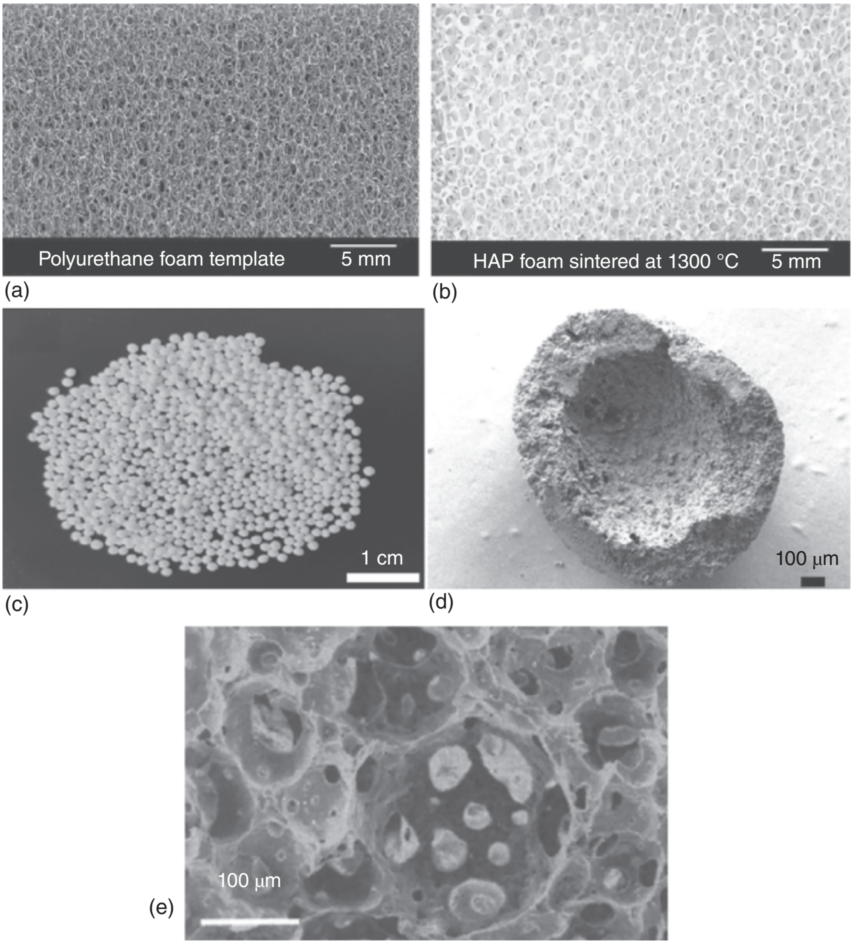

Figure 1.3 (a and b) Initial polyurethane foam and HA foam sintered at 1300 °C, respectively. This HA foam was obtained by impregnating polyurethane foam in an HA slurry followed by drying and sintering. Source: Munar et al. [58]. Reproduced with permission of The Japanese Society for Dental Materials and Devices; (c and d) optical image of beads, and SEM image of hollow structure of a Cu/HA catalyst prepared by a rapid gelling process, using guar gum as gelatinizing agent, and sintered at 1100 °C. Source: Hui et al. ([59]. Reproduced with permission of Elsevier; (e) HA foam obtained from HA powder, polyacrylate derivatives (Dispex A40) as a dispersing agent, acrylic monomers as gel agent, and a nonionic surfactant (Tergitol TMN10) as foam stabilizer. Source: Sepulveda et al. [54]. Reproduced with permission of John Wiley and Sons.

and size, such as beads and pellets. To date, macro-porous HA ceramics have been largely reported in the literature for application in the field of biomaterials [54–57]. The global approach is to use fine HA powder and at least a foaming agent and a stabilizer to perform the gelation step, usually in the aqueous medium. Then, the gel is dried and the resulting solid is sintered at high temperature ($> 1000\,°C$) to burn out organic components, leading to the formation of macro-porous materials. Figure 1.3a, b shows examples of macro-porous HA ceramics reported in the

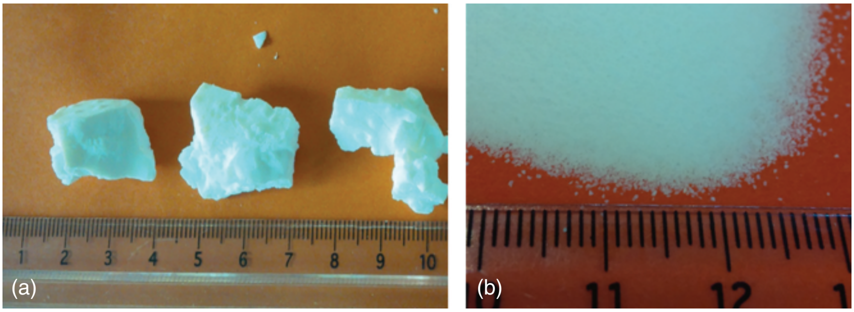

Figure 1.4 Examples of HA blocks after drying (a) and after sieving to 125–315 μm fraction (b). Source: Phan [43]. Reproduced with permission of Phan Thanh Son.

literature. Using this approach, beads of a Cu/HA catalyst could also be obtained as illustrated in Figure 1.3c, d [59].

However, HA foams prepared by this approach generally lose specific surface area, which negatively impacts their catalytic activity. An alternative solution can be the control of HA synthesis conditions to directly obtain HA large particles [43]. In a recent PhD work, conducted by Phan [43], HA was synthesized by the conventional precipitation method using $Ca(NO_3)_2$ and $NH_4H_2PO_4$ at 40 °C for 48 hours under vigorous stirring. Fine particles of HA were formed, which were carefully filtered on filter paper to form large blocks of HA. The latter were dried at 105 °C overnight, crushed, and sieved into particles of desired size (125–315 μm in this case), as illustrated in Figure 1.4. By this way, the resulting HA materials maintain their initial textural properties including meso-porosity (mean pore diameter: 19.3–20.4 nm) and specific surface area (66–90 $m^2\ g^{-1}$), which were suitable for the deposition of nickel nanoparticles for the reforming of methane at high temperatures (700–800 °C) [43]. Another possibility is to simply pelletize HA powders into pellets [60–62]. However, this pelletization step can provoke a partial loss of catalytic performance in comparison with the corresponding powders. For example, Thrane et al. [60] compared the catalytic activity of the powder and pellets of 10 wt% MoO_3/HA in the oxidation of methanol to formaldehyde. A loss of catalytic activity of 10–23% was observed when the HA support was pressed into industrial-sized pellets with different densities (1.18–1.76 $g\ cm^{-3}$).

1.3 Opportunities and Challenges

The global catalyst market was valued at $33.9 billion in 2019 and can reach $48 billion in 2027 (with CAGR – compounded annual growth rate – estimated at 4.5%) [63]. The prime factor driving the catalyst market growth is still the rising demand for petrochemicals from various end-use industries. However, demand for clean and green fuels has shifted the trend of the energy field with focus on clean resources and processes. Moreover, emission regulation is expected as a strong driver for a wide range of application sectors, and the use of catalysts for environmental and chemical applications is anticipated to have the highest market growth in medium and long terms [63]. Thus, new breakthrough scientific findings in the development of efficient catalysts for the production of intermediates, chemicals, and energy carriers (e.g. syngas, biomethane, renewable hydrogen, and biofuel) from renewable resources (e.g. biomass and biowastes), or even from harmful molecules for environment such as CO_2 [64, 65] are currently of crucial importance. Chemical conversion of CO_2 into useful products is strategically important worldwide for limiting global warming, but to date, the number of chemicals produced industrially using CO_2 is still very limited [65]. Moreover, nowadays, catalytic processes also have their place in pharmaceutical and fine chemical industries, since catalytic coupling reactions (C–C and C–N coupling), C–H bond activation, hydrogenation of C=C, C=O, and C=N groups, etc., are efficient for the synthesis of new substances [66, 67]. *Multicatalysis*, term employed by Martínez et al. [68], including cooperative, domino, and relay catalysis, is also an emerging research, in which multiple catalysts enable chemical transformations that cannot be performed through classical approaches. Downsizing metallic particle sizes up to the isolated metal atoms also constitutes a very hot topic (single atom catalysis – SAC) during the past 10 years, which opens new prospects in the catalysis [69–72]. Strong impact on the catalyst market is expected in the upcoming decades by the development and deployment of new catalysts and catalytic processes of high efficiency and low environmental impact. Consequently, HA and HA-based materials, having suitable physicochemical and thermal properties, as presented earlier, and still being considered as a new family of catalytic materials, have great opportunities to be developed in this field, either as catalysts or as catalyst supports. The capacity and flexibility of HA structure to incorporate one or several metals is a major advantage in the design of new catalytic materials. Recent works on HA-based nanocatalysts (metal nanoparticles supported on HA) reported their superior catalytic performance in comparison with reference materials in various reactions. For instance, Rego de Vasconcelos et al. [28] compared the catalytic performance Ni/HA with Ni/$MgAl_2O_4$ in dry reforming of methane to produce syngas. The catalysts prepared on non-sintered support showed comparable catalytic performance, while Ni supported on sintered HA was more active than that supported on sintered $MgAl_2O_4$. Similarly, Munirathinam et al. [73] evidenced the large superiority of a Co/HA catalyst versus a Co/Al_2O_3 catalyst in the Fisher–Tropsch synthesis under the same reaction conditions (Figure 1.5). More generally, Fihri et al. [16] reviewed recent works related to HA-based catalysts and pointed out the versatility and efficiency of these materials in many chemical reactions.

Despite the numerous advantages of HA-based catalysts as mentioned earlier, research conducted on HA and HA-based materials still faces several challenges [16]:

- High sensibility to the acid medium: HA can be partially or completely dissolved by an aqueous solution at low pH (see Section 1.2.3). This limits the utilization of HA-based catalysts in strong acid media.

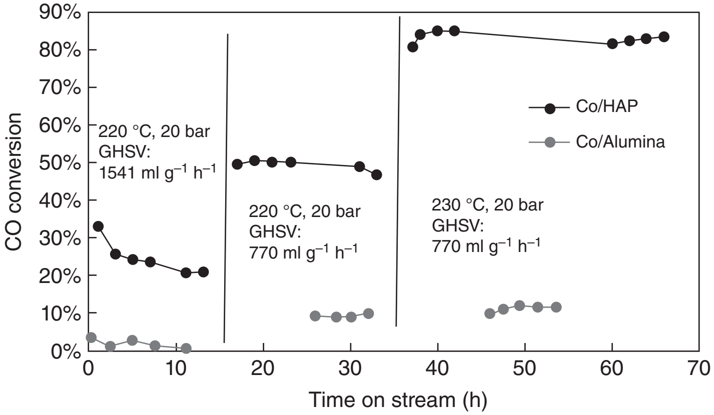

Figure 1.5 CO conversions in Fisher–Tropsch (FT) synthesis using Co/HAP and Co/Alumina catalysts reduced at 350 °C under reaction conditions of 20 bar pressure with different gas hourly space velocities (GHSV: 1540 or 770 ml g^{-1} h^{-1}) and temperatures (220 or 230 °C). Source: Munirathinam et al. [73]. Reproduced with permission of Elsevier.

- Low mechanical resistance: The formulation of HA powders into HA monoliths is possible as discussed in the Section 1.2.6. Pure HA powders usually result in ceramics of low mechanical resistance. The latter can be improved by using additives, usually metal oxides such as bio-glass (a mixture of SiO_2, Na_2O, K_2O, MgO, CaO, P_2O_5, B_2O_3) [74]. However, the presence of additives can negatively impact the catalytic properties of the modified materials, particularly for selectivity control.
- Strong dependence of the textural and structural properties on the synthesis conditions: many synthesis routes can be applied for the synthesis of HA. However, textural and structural properties of the final HA strongly depend on synthesis conditions: nature of calcium and phosphate precursors, solvent, precursor concentration, method of the precursor addition (calcium precursor to phosphate precursor, or phosphate precursor to calcium, or simultaneously both precursors), pH, maturation time, temperature, pressure, washing protocol, drying protocol, presence or not of dissolved oxygen and carbon dioxide in the synthesis medium, etc. This issue will be discussed in Chapter 2 of this book.
- High reactivity of HA surface: though the apatitic bulk structure of HA is generally well known, the structure of the first surface layers of HA is difficult to be determined because of high reactivity and sensibility of HA surface with the environment (such as the presence of humidity and CO_2). Especially, for nanocrystalline nonstoichiometric apatites, highly reactive amorphous surface layers generally exist, of which the composition is usually different from the bulk composition [75]. This feature will be discussed in Chapter 3 of this book. To date, few reports have been devoted to the impact of the surface composition of HA and apatite compounds on their catalytic properties or on the preparation of supported catalysts.

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