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Ceramics for catalysis

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The use of ceramics as heterogeneous catalysts represents an extension of "non-traditional" ceramics applications and is now a burgeoning topic of research. In this Review, the principles of heterogeneous catalysis are presented and discussed in terms of surface reactivity and catalyst structure in general. Catalytic selectivity, rate enhancement and catalyst deactivation are addressed. The critical (bulk and surface) structural features that impact on catalyst performance are identified along with a survey of catalyst characterization techniques. Ceramics applications in catalysis are divided into (i) direct use as catalysts and (ii) use as support materials (substrates) to anchor and disperse a variety of active metals. Practical ceramic catalysts are typically complex metal oxides containing at least two different cations which offer enormous compositional flexibility, as is discussed in the case of perovskite oxides. Taking a broad definition of ceramics as "any inorganic nonmetallic material," there is a wide array of catalysts that can be termed ceramics with disparate end uses. For the purposes of illustration, three established systems are discussed that each illustrates the role of ceramic materials in practical heterogeneous catalysis: (i) catalysis using zeolites; (ii) catalytic converters; (iii) solid oxide fuel cells.

1. Introduction

Ceramics encompass such a vast array of materials that a concise definition is difficult to formulate. As a workable explanation, ceramics can be considered as inorganic, nonmetallic materials and can be crystalline or amorphous (glassy). Ceramic compounds are formed between metallic and nonmetallic elements such as aluminum and oxygen (alumina-Al_2O_3), calcium and oxygen (calcia-CaO), and silicon and nitrogen (silicon nitride-Si_3N_4). Ceramic materials display a wide range of properties which facilitate their use in many different product areas. Modern ceramics include structural clay products such as bricks, sewer pipes, tiles, whitewares (dinnerware, sanitary fixtures, porcelain, decorative ceramics, etc.), refractories, glasses (including fibers for communication), abrasives and cements. The so-called advanced ceramics comprise structural materials used for engine components, coatings, cutting tools and the bioceramics used as bone and tooth replacements. The latter applications require a high resistance to wear/corrosion, features that set ceramics apart from most metals/alloys [1]. While metals weaken rapidly at temperatures above ca. 800°C, ceramic materials retain their mechanical properties at much higher temperatures and such thermal resistance has been put to good effect in a number of applications [2]. Advanced ceramics are used in capacitors, resistors, insulators, piezoelectrics, magnets, superconductors, and electrolytes. Such materials require a level of processing science and engineering far beyond that used in the production of conventional ceramics.

This paper deals with an application of ceramics that is growing in importance, i.e., as catalytic material. The classification of ceramics into "traditional" (clay products, glass, cement, etc.) and "advanced" (carbides, oxides, nitrides, etc.) is now common parlance in the materials research community. The application of ceramics in catalysis certainly falls within the non-traditional category. Heterogeneous catalysis and ceramics overlap in terms of solid state inorganic chemistry but the development of ceramic materials as effective catalyst supports and catalytic agents has meant a closer synergy in terms of research and development. The latter has focused on a tuning of the chemical reactivity of the oxide surfaces to modify the interaction with adsorbed reacting species. It is estimated that 90% of the new processes commercialized in the chemical industry in the last 50 years have been based on catalysis. Catalytic chemistry finds applications in the production of commodity chemicals, fuels, polymers, and pharmaceuticals, as well as in environmental applications for pollution abatement [3]. Given the number of ceramic materials that exhibit catalytic properties, a full enumeration of the associated catalytic applications is beyond the scope of this paper. Three established systems present themselves as suitable case studies to illustrate the role of ceramic materials in practical heterogeneous catalysis: (i) catalysis using zeolites; (ii) catalytic converters; (iii) solid oxide fuel cells.

2. Fundamentals of heterogeneous catalysis

The development of catalysis, from the Greek (*kata*, wholly; *lyein*, to loosen), as a concept has been accorded to Berzelius (1779–1848) who rationalized the "catalytic power" of certain substances as an ability

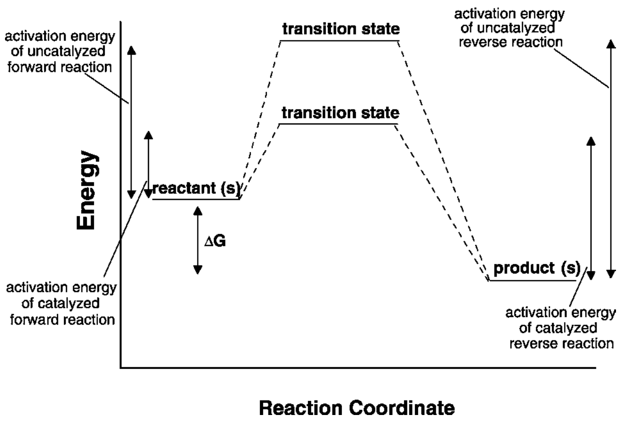

Figure 1 Energy diagram for a catalyzed and uncatalyzed chemical reaction.

to "awaken affinities, which are asleep at a particular temperature, by their mere presence and not by their own affinity" [4, 5]. Various definitions of catalysis have been proposed but an early definition offered by Wilhelm Ostwald in 1895 is still widely in use: "Catalysts are substances which change the velocity of a reaction without modification of the energy factors of the reaction." The latter serves to exclude substances that accelerate the rate of reaction by entering into reaction with a resultant disruption of the reaction equilibrium. A catalyst works by forming chemical bonds to one or more reactants which facilitates their conversion but the catalyst does not significantly affect the reaction mechanism [6]. A more rigorous definition of a catalyst is then "a substance that increases the rate of reaction without modifying the overall standard Gibbs energy change in the reaction." This is illustrated schematically in Fig. 1. In an uncatalyzed transformation collisions between participating molecules must possess sufficient (activation) energy to pass over the energy barrier that is characteristic for that reaction. In terms of the more realistic "transition state theory" originated by Eyring and co-workers, the reactants form a short-lived transition state or activated complex which reacts to give product(s) [7]. Catalyst/reactant interactions serve to lower the energy barrier (transition state is at a lower energy) and facilitate reaction under more moderate reaction conditions. The catalyst reduces the enthalpy of activation for the forward reaction by exactly the same amount as it reduces the enthalpy for the reverse reaction, there is no entropy change and the free energy change/position of equilibrium remains the same for the catalyzed and uncatalyzed processes. The incorporation of catalysts into any reaction system will impact on reaction rate with the result that reaction kinetics is central to catalysis, providing the quantitative framework for an assessment of catalyst activity. The qualitative aspects of catalysis take the form of reaction mechanisms that account for such matters as reaction stoichiometry, nature of the chemical interaction, geometric and electronic effects.

Catalysts can be divided into two broad categories: heterogeneous and homogeneous [6, 8]. Homogeneous catalysis occurs when the catalyst is uniformly dispersed in the reaction mixture, be it a gaseous or liquid solution. Examples of homogeneous catalysts include transition metal ions, transition metal complexes, inorganic acids/bases and enzymes. In a heterogeneous reaction, the catalyst is in a different phase from the reactants, where the reaction occurs at the surface of a solid (catalyst) particle in contact with the gaseous or liquid solution. The main disadvantage associated with heterogeneous when compared with homogeneous catalyst operation is the lower effective concentration of catalyst as the reaction occurs only on the exposed active surface. Catalyst recovery and reuse is, however, far more facile in the case of heterogeneous operation. The prototypical example of heterogeneous catalysis is the formation of hydrocarbons from the reaction of hydrogen and carbon monoxide over a suitable solid catalyst. The simple methanation reaction

$$3H_2 + CO \leftrightarrow CH_4 + H_2O \qquad (1)$$

has an associated $\Delta G^0 = -96$ kJ mol^{-1} at 500 K, which represents a favorable equilibrium ratio. However, the homogenous reaction rate between CO and H_2 in the gas phase is very low and only proceeds to any appreciable degree in the presence of metal catalysts at temperatures in the range 523–723 K [8].

Catalysis involving ceramics falls within the remit of heterogeneous systems used to enhance reactions between reactants in the gas and (to a lesser extent) liquid phase by use of a solid catalyst. Any discussion of the role of ceramics in heterogeneous catalysis must be preceded by a consideration of surface reactivity and catalyst structure in general.

2.1. Catalysis on surfaces

Any reaction that is promoted by heterogeneous catalysis involves the following steps:

Step 1: reactant + catalyst
Step 2: reactant/catalyst complex
Step 3: product/catalyst complex
Step 4: product + catalyst

The surface reaction is facilitated by reactant/catalyst interaction(s) that generates a reactive reactant/catalyst complex. These interactions may be weak, of the 'non-bonding' type with the reactant staying intact while sticking to (or absorbing on) the surface. Alternatively, the interactions may involve the formation of new chemical bonds between the surface atoms and the adsorbed molecule, which necessarily involves extensive reorganization of the bonding within the reactant. This reactive type of interaction is generally known as *chemisorption* in contrast to *physisorption*, the term used to describe the weaker unreactive binding of molecules to surfaces [9, 10]. Physisorption involves weak van der Waals interactions and the adsorption energy is typically 5–15 kJ mol^{-1} which is much lower than that associated with chemical bonding. Moreover, the van der Waals interaction(s) between adsorbed molecules does not differ significantly from the van der Waals interaction(s) with the surface, with the

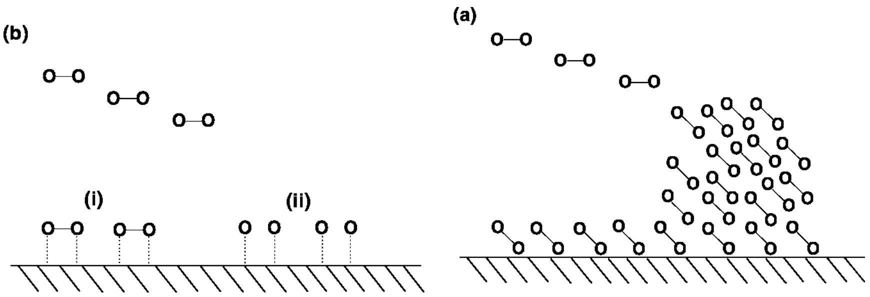

Figure 2 Simple schematic showing (a) physisorption and (b) chemisorption involving (i) associative and (ii) dissociative interactions.

result that many layers of adsorbed molecules may be formed, as shown in Fig. 2. In the case of chemisorption, the reactant may chemisorb intact or it may dissociate (Fig. 2); the chemisorption energy is 30–70 kJ mol^{-1} for molecules and 100–400 kJ mol^{-1} for atoms [3, 9, 11]. The magnitude of the adsorption coefficient depends on the nature of the surface and the chemical identity of the reacting species.

Once the reactant is bound to the surface, it can readily undergo reactions which take place only with difficulty in the gas or liquid phases. This may result from the close proximity of reactant molecules on the surface and/or the changes in bonding consequent upon chemisorption; both are essential features of the catalytic properties of the solid. Bond dissociation is one of the simplest but most effective ways in which surfaces can catalyze reactions. Taking hydrogenation as an industrially significant process that involves the addition of hydrogen atoms to double bond(s) in an unsaturated reactant, reactant/hydrogen collisions will require a high energy input to effect any chemical transformation [12]. However, the adsorption of hydrogen on a metal (Pt, Pd or Ni) surface results in hydrogen dissociation and the formation of hydrogen/metal bonds. These surface hydrogen atoms can now diffuse over the surface and attack unsaturated molecules under less severe reaction conditions. This process is illustrated schematically in Fig. 3 for the hydrogenation of ethylene to ethane. The weakened reactant structure undergoes surface reaction to yield another complex that is essentially the product attached to the catalyst. Finally, this complex breaks down to release the product molecule (i.e., desorption) which leaves the catalyst surface ready to interact with another reactant molecule.

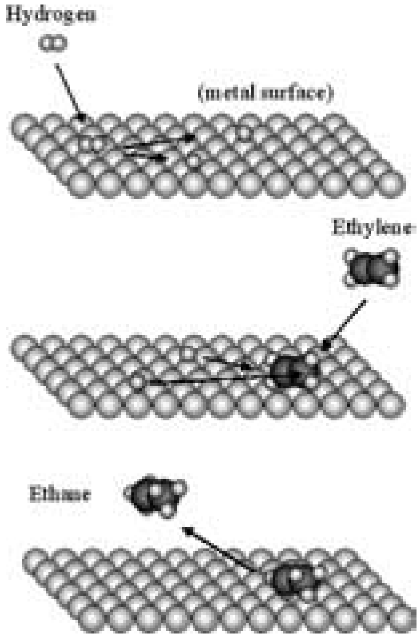

Figure 3 Schematic representation of the surface reaction of dissociatively chemisorbed hydrogen and associatively chemisorbed ethylene to form ethane.

2.2. Catalyst structure

It is unfortunate that, in certain quarters, the science of catalysis is regarded as something of a "black art" largely because of the difficulty in achieving a full catalyst characterization and providing an explicit correlation of catalytic performance with catalyst structure. The choice of a suitable catalyst for a particular reaction depends on the stability of the complexes formed between reactant and catalyst and/or product and catalyst. These must be stable enough to form and provide an alternative pathway to the uncatalyzed reaction but they must not be too stable as this would lead to an increase in the associated activation energy with a consequent lowering of reaction rate. A heterogeneous catalyst is present as separate particles or agglomerates of particles immersed in a fluid medium in motion. Reactants and products diffuse in the gas or liquid phases at the boundary of the solid and in the pore spaces of the aggregates. Catalyst efficiency is assessed in terms of three parameters: *activity*; *selectivity*; *lifetime*. The activity is the extent to which the catalyst influences the rate of change of the degree of advancement of the reaction, i.e., reactant conversion (per unit weight or per unit volume of catalyst) under specified conditions. The activity per unit volume is of practical importance in terms of process economics where a low catalyst bulk density reduces the necessary reactor volume and associated cost. The turnover frequency represents the specific rate and is defined as the number of molecules reacting per active site per unit time. The usefulness of turnover frequency values is dependent on the validity of the method used to measure (or estimate) the number of active sites [7, 13]. A distinction between the total number of surface sites and the fraction that are catalytically active is often difficult while comparison of turnover frequency values is only meaningful where the catalyst surface is saturated with reactant. Very often a reactant or set of reactants may simultaneously undergo several parallel reactions giving different products that may react further in consecutive reactions to yield secondary products. Selectivity is an important catalyst property, serving as a measure of the extent to which a particular catalyst promotes the formation of a "target" product, i.e., the ability of the catalyst to direct conversion to a desired product. The productive lifetime of the catalyst is the period during which the catalyst delivers a product yield in excess or equal to that designated [10].

Catalytic efficiency is influenced by four principal factors which are interdependent:

(i) The exposed area in contact with the fluid;
(ii) The intrinsic surface chemical reactivity;
(iii) Surface topography—geometric and electronic features;
(iv) Occurrence of lattice defects—vacancies, interstitials and dislocations.

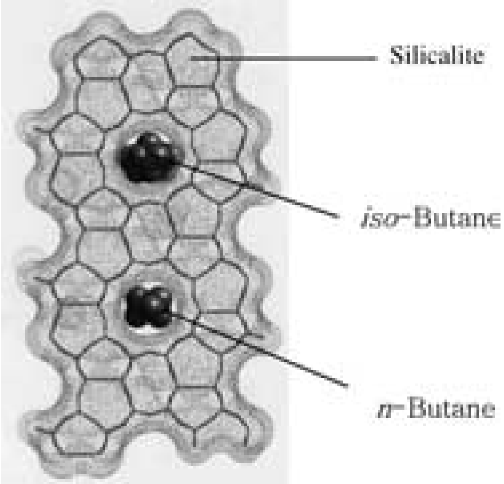

Figure 4 View through two equivalent channels of a silicalite framework showing free and restricted transport of *n*-butane and *iso*-butane, respectively.

Commercial catalysts must possess sufficient mechanical strength to resist losses as a result of crushing (in packed bed operation) or attrition (in reactors involving vigorous agitation). High surface areas can be attained either by fabricating small particles or clusters where the surface-to-volume ratio of each particle is high, or by creating materials where the void surface area (pores) is high compared to the amount of bulk support material. Many catalysts are porous solids of high surface area that is both "external" and "internal," the former represented by the envelope surrounding discrete particles. The internal surface comprises the walls of the pores/channels/cavities and the total surface area equals the sum of the external and internal areas. Gas adsorption methods, notably the Brunauer-Emmett-Taller (BET) approach, are widely used to determine surface areas [14, 15]. Porosity is a measure of the fraction of the bulk volume that is occupied by pore or void space. Pore size distribution is an important characteristic of porous catalysts where pores of diameter in excess of 50 nm are considered macropores, those less than 2 nm are termed micropores and pores of intermediate size are denoted mesopores [7, 16]. It must be stressed that a wide range of pore sizes, spanning both mico- and macro-porosity is characteristic of standard solid catalysts. The pore size distribution is an important factor in controlling diffusion of reactants/products within any catalyst pore network and is an essential characteristic property of the catalyst. A distinction must then be drawn between the true catalyst density (solid mass to volume ratio excluding all pores and voids) and bulk or packing density. The location of the catalytically active component within the porous structure and the manner in which pores interconnect can have a profound effect on the accessibility of reactants to the catalytically active site, and to the removal of products. This effect is illustrated in Fig. 4 where *n*-butane can be seen to have ready access to the internal silicalite matrix while the movement of the more bulky *iso*-butane isomer is hindered.

The catalyst particle can be a complex entity composed of a porous solid serving as a support for one or more catalytically active phases. The latter may comprise clusters, thin surface mono- or multi-layers or small crystallites where interaction with the support can impact on surface reactivity. The major active component is typically expressed on a percentage weight basis (e.g., 10% w/w Pd/Al_2O_3) where the crystallographic form of the support (e.g., γ-Al_2O_3) should be given. Secondary components or additives are included (or doped) and serve as promoters where this modification may be directed towards enhancing activity/selectivity, poison resistance or textural properties. The determination of the surface chemical composition and structural properties, as opposed to bulk characteristics, can call upon a range of complimentary surface science techniques: established techniques with the pertinent obtainable information are identified in Table I. The structures of catalyst surfaces are notoriously difficult to elucidate due to the involvement of microscopic and even macroscopic regions with different compositions, phases and structures, each bearing a diversity of imperfections. A detailed discussion of each of the techniques listed in Table I is outside of the scope of this Review. It should, however, be noted that each surface analytical technique typically employs high vacuum conditions and catalyst structure under standard operating (reaction) conditions is often impossible to determine. Adsorption/desorption measurements provide indirect structural information while transmission electron microscopy is applicable for surface analysis down to tenths of a nanometer. In terms of catalysis, the atomic scale structure is critical, i.e., the arrangement of atoms involved in chemical bonding with reactants. X-ray diffraction is applicable to measurement of crystallite sizes and identification of the crystalline phases present. Electron spectroscopies, notably AES, XPS and SIMS, facilitate measurement of the chemical composition of reactive surfaces. Each technique involves bombardment of the surface with high energy (electron, X-ray or ion) beams with an energy analyzer (or mass spectrometer in the case of SIMS) as detector. Instrumentation developments are directed towards detection of finer detail, i.e., atomic spacial resolution, ever smaller energy resolution and shorter time scales. A comprehensive characterization

TABLE I Common experimental analytical techniques used to characterize catalyst surface structure

Technique	Surface property	References
Chemisortion/temperature programmed desorption (TPD)	Active site concentration/adsorbate binding energies	[17–19]
Fourier transform infrared spectroscopy (FTIR)	Adsorbate/surface interactions, bonding geometry and strength	[20, 21]
Transmission electron microscopy (TEM)	Imaging technique, active site distribution, surface structure	[22–24]
X-ray diffraction (XRD)	Bulk diffraction and diffraction at extreme glancing angles, bulk and surface structure	[25, 26]
X-ray photoelectron spectroscopy (XPS)	Near surface composition, oxidation states	[17, 27–29]
Auger electron spectroscopy (AES)	Near surface composition	[17, 27, 30, 31]
Secondary ion mass spectrometry (SIMS)	Surface composition	[27, 32, 33]
Ultraviolet photoelectron spectroscopy (UPS)	Bonding of surface species	[17, 31, 34]
Scanning tunneling microscopy (STM)	Surface topology, surface electronic structure	[27, 35, 36]
Low energy electron diffraction (LEED)	Surface atomic structure	[37–39]
Extended X-ray absorption fine structure (EXAFS)	Local surface structure, coordination numbers	[17, 38, 40, 41]
Atomic force microscopy (AFM)	Surface structure/topology	[42, 43]
Electron energy loss spectroscopy (EELS)	Electronic structure	[17, 34, 44]

(atomic, molecular and electronic) of catalyst surfaces will result from a combination of the tabulated techniques. In those cases where experimental characterization techniques are impractical, theoretical calculations (*ab initio*, semi-empirical and force field methods) can be instrumental in gaining a better understanding of catalyst structure and the feasible transition states/reaction pathways.

Certain catalytic reactions proceed at the same rate regardless of the nature of the reactive surface and are deemed to be structure insensitive, whereas other reactions exhibit an appreciable structure sensitivity where the rate can vary by orders of magnitude from one crystal face to another [7]. Masel has noted [45] that all catalytic reactions exhibit some degree of structure sensitivity under certain reaction conditions. Heterogeneous catalysts cannot be regarded as representing a "model" uniform reacting surface but display a distribution of interaction energetics associated with the different exposed crystal faces, occurrence of dislocations, defects and other disturbances [46]. The simplest surfaces can be regarded as "flat" surfaces (see Fig. 5) and deviations from this ideal arrangement include "ledges," "kinks," "adatoms" and "vacancies." Ledges are the steps formed at the borders of the pristine flat surface while a kink is a defect formed at the end of a ledge; a kink can viewed as a ledge on a ledge. The growth of "terraces" of parallel atomic planes is largely due to a small mismatch of atomic planes, i.e., a dislocation [47]. An adatom is a single atom sitting on a terrace and a vacancy is a single atom missing from a terrace. Ledges and kinks are termed "line defects" to distinguish them from vacancies and adatoms, which are denoted "point defects" [13]. Solid surfaces are heterogeneous on the atomic scale and the relative concentration of atoms in the ordered domain (flat surface), in line defects and in point defects depends on surface preparation/pretreatment. Variation in catalytic particle size can result in a change in the distribution of sites and preponderance of a particular defect which may be the source of observed structure sensitivity.

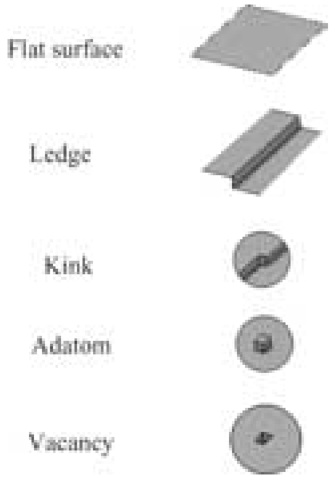

Figure 5 Diagram showing an ideal flat surface and ledge, kink, adatom and vacancy arrangements.

2.2.1. Catalytic properties of ceramics

As ceramic materials withstand high temperatures, exhibit chemical durability and wear resistance, they have unlimited potential as catalytic materials for use in a diversity of reactor configurations and over a range of operating conditions. Ceramics applications in catalysis can be divided into (i) direct use as catalysts and (ii) use as support materials (substrates) to anchor and disperse a variety of active metals. Taking a broad definition of ceramics as "any inorganic nonmetallic material," there is a wide array of catalysts that can be termed, although it is not common practice in the catalysis community, ceramics. Ceramic catalysts and catalyst supports constitute the largest market segment outside the electronic ceramics, estimated to be $1.43 billion in 1998 with an expected increase to $1.84 billion by the year 2003 [48]. Practical ceramic catalysts are typically complex metal oxides containing at least two different cations which offer enormous compositional flexibility. The redox chemistry of these materials in the bulk and at the surface may be very different from that expected in solution, with the result that certain cations may be held in unusually high oxidation states [49]. A selection of ceramic oxide catalysts that have been subjected to rigorous characterization and/or catalytic (principally oxidation) reactions are provided in Table II. The surface redox behavior and defect structure is of crucial importance in determining catalytic activity and

TABLE II Representative ceramic oxide catalyst systems

Catalyst	Reference
V_2O_5/SiO_2	[50]
$CeO_2/MgAl_2O_4$	[51]
CeO_2/ZrO_2	[52]
V_2O_5/TiO_2	[53]
CeO_2/Al_2O_3	[54]
$BaO/SrTiO_3$	[55]
Sr/La_2O_3	[56, 57]
SrO/Nd_2O_3	[58]
Sm_2O_5/MgO	[59]
N_2O/MgO	[60]
La_2O_3/CaO	[61]

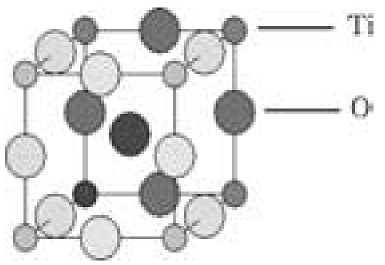

Figure 6 Perovskite unit cell structure with Ti atoms at the corners, O atoms at midpoints of the edges and a Ca atom in the center; dark shades are used to indicate a layered effect.

selectivity [62]. Electron defects may arise either in the form of ions present with charges deviating from the normal lattice ions or as a consequence of the transition of electrons from normally filled energy levels (valence band) to normally empty levels (conduction band) [63]. Over the past decade, research on nanocrystalline materials has been greatly accelerated by the advances in the ability to manipulate structures on the molecular or atomic level. As catalysts, nanometer-sized active clusters have been examined for some long time, but largely limited to supported metal systems. Direct synthesis and successful stabilization of nanocrystalline ceramic materials has only recently been investigated in detail for some catalytic applications [64]. When a ceramic is fabricated from "nano" powders, the resulting advanced nanophase material has dramatically improved properties, in that it may conduct electrons, ions and heat more readily than conventional materials, features that will impact on catalyst efficiency.

One notable case of catalyst development based on ceramic materials with a definite commercial application (particularly in oil refining) is represented by zeolites [65], the subject of Section 3.1. Perovskite oxides are another branch of ceramic materials that exhibit significant potential as heterogeneous catalysts. Perovskites are a large family of crystalline ceramics that derive their name from a specific mineral known as perovskite, first described in the 1830's by the geologist Gustav Rose, who named it after the famous Russian mineralogist Count Lev Aleksevich von Perovski. Perovskites are oxides having the same crystalline structure as the natural mineral $CaTiO_3$, which is usually expressed as ABO_3. They form a technologically important class of compounds now finding widespread use [66] as multilayer capacitors ($BaTiO_3$), piezoelectric transducers ($Pb(Zr,Yi)O_3$, thermistors ($BaTiO_3$), switches ($LiNbO_3$), actuators ($Pb(Mg,Nb)O_3$, superconductors $Ba(Pb,Bi)O_3$ and ferromagnets $(Ca,La)MnO_3$. In terms of catalytic processes, perovskites (combinations of Sr, Mn, La, Ca, Mn, Ni, Co, Cu, Fe, Ba) have served as oxidative agents [67–71] and as substitutes for noble metals in electrocatalysis [72, 73]. An ideal perovskite has a structure in which A (cation) is located at the center of the cubic unit cell, B (cation) is located at each apex and O (anion) is located at the center of each side; the perovskite unit cell structure is shown in Fig. 6. Perovskites are often characterized by large covalently bonded, closely packed cubic structures; the A atoms have twelve O neighbors while the B atoms have six closer neighbors. The smaller atom at the center of the cube has the freedom to shift slightly within the lattice without breaking any bonds. The perovskite structure possesses a very high degree of compositional flexibility, being able to tolerate a wide variety of cations on both the A and B sites. Variations in the relative size and charge of the A and B cations can be accommodated in a number of ways. Some involve distortions of the ideal cubic structure (usually with a tilting of the B-site octahedra), and others result from the introduction of face-sharing octahedra into the network of vertex-sharing octahedra which is found in the cubic compounds [74]. Both the A and B sites may be occupied by more than one cation species in a particular compound. In the case of the B sites this can involve cations of more than one element, or it may involve two oxidation states of the same element. The introduction of vacancies onto the anion sublattice is another method by which chemical reactivity can be varied. Indeed, the chemical properties of perovskite can be readily tailored by altering the valence state of the structural transition metal ions, the binding energy and diffusion of O in the lattice, the distance between active sites and the conductive properties of the solid. A recent development in catalysis by ceramics has seen the application of ionic and conducting oxides as either the electrode or solid electrolyte material in solid oxide fuel cells (SOFC), a novel and topical development that is discussed in Section 3.3.

Ceramic substrates have found widespread use in catalytic converters, the topic of Section 3.2, which are employed in the clean up of exhaust gases from petrol and diesel engines through the conversion of CO, hydrocarbons and NO_x. In this application the ceramic substrate possesses a very large surface area, enhanced filtering efficiency, as well as high thermal-shock resistance. Catalyst overall morphology is an important issue with a need to balance performance, strength and pressure drop across the catalytic material. Many catalysts are employed as randomly packed fixed beds of small particles (e.g., extrudates, granules or spheres) typically in the millimeter size range. Ceramic supports can adopt a structured "monolith" or a "honeycomb" configuration (see Fig. 7) that possesses appreciable mechanical strength, vibration resistance, a low thermal expansion coefficient and limited

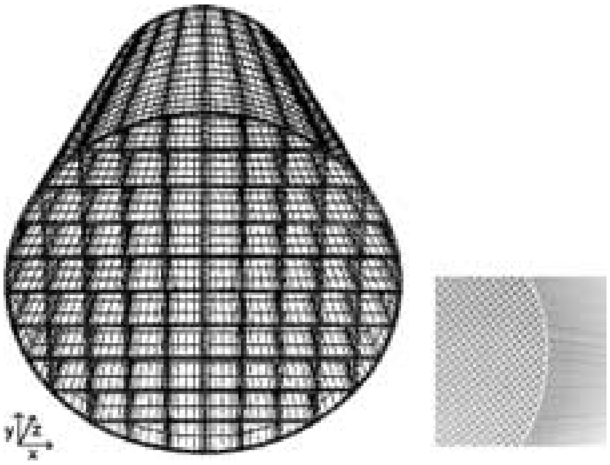

Figure 7 Three dimensional structure for a typical honeycomb ceramic catalyst.

resistance to reactive fluid flow, i.e., low associated pressure drop [75]. Honeycomb structures are typically made of cordierite ($(\text{MgO})_2(\text{Al}_2\text{O}_3)_2(\text{SiO}_2)_5$) by means of a precise extrusion process, which allows the production of various cell shapes and sizes [76] with differing rheological characteristics [77]. Ceramic foams possess structural characteristics that make them, in turn, suitable as substrates for heterogeneous catalysts. These features include high porosities with a significant degree of interconnectivity that results in low pressure-drop while convection in the tortuous mega-pores provides enhanced mass and heat transfer [78].

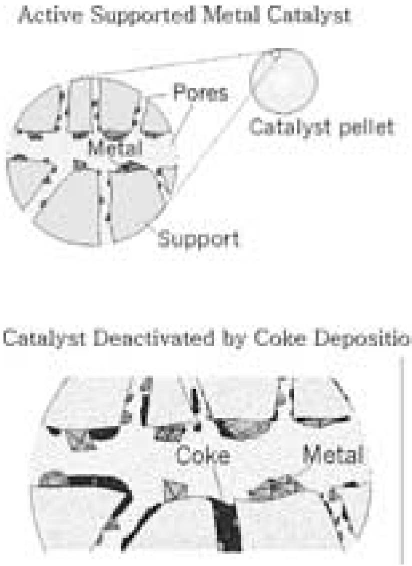

Figure 8 Catalyst deactivation by coke deposition.

2.3. Catalyst deactivation

One of the major problems that have bedeviled the operation of heterogeneous catalysis is a progressive loss of activity with catalyst use. Catalyst deactivation as a function of time is often unavoidable and the deactivated catalyst must either be regenerated or replaced [79]. The causes of catalyst deactivation are numerous but they can be conveniently grouped into three general categories [80]: *sintering, poisoning and coking*. Sintering refers to a diminution of active site dispersion and can apply to all phases present in the catalyst, i.e., active phases, modifiers and support. The overall effect of sintering is a reduction in active surface area per unit volume of catalyst and is normally the result of excessively high reaction temperatures [81]. Ceramic monoliths [82] and foams [83] exhibit far superior properties in terms of thermal stability when compared with more conventional catalyst systems and are resistant to deactivation by sintering. The presence of deactivating species in the reactant feed (as impurities) or formed during reactant conversion (transformation of an intermediary and/or product) can induce a partial or total loss of activity. Catalyst poisoning can be irreversible (true poisoning), reversible or transient (inhibition) or may involve fouling agents which induce a mechanical inhibition. The latter refers to non-covalent bonding (van der Waals interaction, hydrogen bonding, ionic interactions etc.) that serve to physically impede access of reactants to the active sites. True poisoning involves strong chemical interaction with the active sites where catalytic activity cannot be recovered without a drastic change in the operating conditions [84, 85]. The time dependent loss of activity can be linked to a migration of active species into the catalyst pellet, morphological changes of surface crystallites of a given phase, change in the number of steps, kinks and vacancies on the surface and modifications to the surface/bulk composition ratios.

Activity loss due to coke formation is typical of reactions involving hydrocarbons and is due to reactant or product degradation that produces a carbonaceous residue on the surface which is inactive for catalysis. Coke that accumulates on a catalyst may cause deactivation either by covering active sites or by physical blocking of the pores in the catalyst, as shown in Fig. 8. Coke deposits can amount to 15–20% w/w of the catalyst, depending on the operating conditions and the nature of the catalyst and reactant(s) [86]. Moreover, carbon deposition on reactor tubes and heat exchanger surfaces can adversely affect the performance of an array of unit operations associated with catalytic processing. Such deposits invariably contain both carbon and hydrogen with H/C ratios varying from almost zero up to 2 [87]. The carbonaceous byproduct deposits are a complex mixture of amorphous, filamentous and graphitic structures [88–90]. Forzatti and Lietti [86] and McCarty and Wise [91] have identified up to seven forms of "carbon" associated with hydrocarbon processing, notably "encapsulated" hydrocarbons, filamentous carbon and pyrolytic carbon. Considerable effort (use of promoters/catalyst regeneration) is expended to minimize carbon deposition and extend the productive lifetime of the catalyst [87, 92, 93]. The catalyst regeneration strategy depends on the causes of deactivation [94, 95]. Deactivation due to carbon deposition can be reversed by heating the spent catalyst in air/oxygen which serves to "burn off" the carbon deposit. This oxidative (highly exothermic) treatment must be carefully controlled in order to avoid any possible sintering due to excessive high temperature fluctuations.

3. Ceramic based catalysts

3.1. Zeolites

Zeolites represent a commercially important branch of advanced ceramic catalytic materials. They are aluminosilicates that are structurally unique in having cavities or pores with molecular dimensions as part of their crystalline structure [96, 97]. Zeolites occur naturally as minerals and are extensively mined in many parts of the world. They are often formed where volcanic rock of specific chemical composition is immersed in water with a resultant leaching of certain components—the precise composition is dependent on the kind of rock minerals involved. The Swedish mineralogist Cronstedt is accredited with the discovery of naturally occurring zeolites when he isolated a selection of natural minerals which, when heated produced copious amounts of steam. This unexpected behavior prompted Cronstedt to name these minerals "zeolites" from the Greek zeo(to boil)-lithos(stone). Indeed, zeolites are often described as materials that are "hard as a rock but work like a sponge," the latter a reference to the water release upon heating. The zeolite materials that find widespread use in the chemical industry are synthesized with a global market of several million tonnes per annum [98]. Industry has, in effect mimicked the natural zeolites with a controlled synthesis that is targeted at a specific zeolite structure tailored for a particular application.

The zeolite aluminosilicate framework is composed of oxygen tetrahedrons, each encasing either a Si or Al atom. The oxygen atoms can be shared by only two tetrahedra, and no two Al atoms can share the same oxygen atom, with the resultant restriction that the Al/O ratio ≤ 1. The zeolites finding the greatest application on a commercial scale belong to the family of faujasites and include zeolite X and zeolite Y. The framework structure of zeolites X and Y is shown in Fig. 9a and is based on a regular arrangement of truncated octahedral and sodalite cages to generate a high surface area microporous structure. Zeolite Y is synthesized by a gelling process, is characterized by a void volume fraction of 0.48, with a Si/Al ratio of 2.43 and thermally decomposes at 793°C. [99]. The geometrical crystalline features associated with zeolite Y are evident from the scanning electron micrograph (SEM) presented in Fig. 9b. Zeolite crystal structures are complex three dimensional frameworks with long range crystalline order and pore sizes of sub-nano dimensions. Access to the intracrystalline Y zeolite sites is *via* an interconnecting, three dimensional network of cavities, i.e., the accessible supercages of internal diameter 1.3 nm that are linked by shared rings of twelve tetrahedra (free diameter = 0.7–0.8 nm) and the less accessible sodalite units that are linked through adjoining rings of six tetrahedra which form the hexagonal prisms (free diameter = 0.20–0.25 nm).

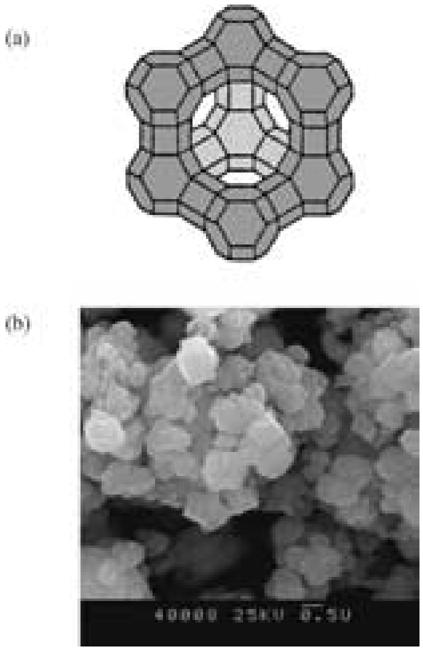

Figure 9 (a) Structure of faujasite and (b) SEM micrograph showing topographical features of a Na-Y zeolite.

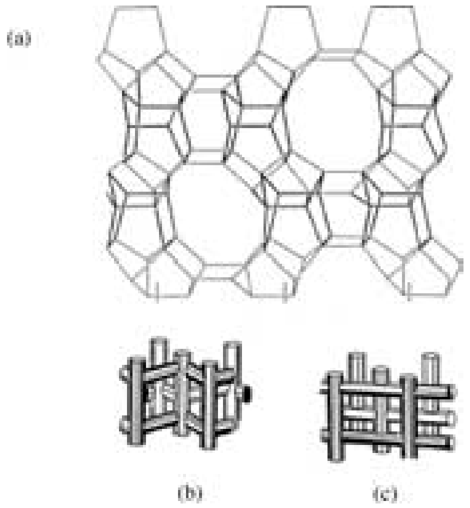

Figure 10 Typical zeolite structures depicting: (a) the positions of the O atoms at the vertices, (b) three dimensional and (c) two dimensional channel structure.

A representative three-dimensional zeolite cage structure is shown in Fig. 10 together with a depiction of the straight and ziz-zag channels and a two-dimensional zeolite with channels only in 2 directions. The vertices in Fig. 10a denote the position of the O atoms in the crystalline lattice; this particular zeolite has ten atoms in the zeolite "window." The size of the zeolite window is determined by the number of oxygens in the ring, as revealed in Table III. This makes for a molecular "sieving" effect where molecules can pass freely through the zeolite matrix or transport can be severely restricted or blocked depending on the relative

TABLE III The relationship between the number of ring oxygens and zeolite "window" dimensions

Number of ring oxygens	Window diameter (Å)
4	1.2
5	2.0
6	2.8
8	4.5
10	6.3
12	8.0

dimensions of the incoming molecule and the zeolite cavities. For example, normal hexane with a kinetic molecular diameter of about 5.1 Å can pass through a 10-membered ring (or larger), whereas cyclohexane with a kinetic molecular diameter of 6.9 Å would experience severe transport limitations. This size/sieving property is put to good effect in separation applications. The void spaces in the crystalline structure of zeolites present a high capacity for adsorbates and the internal surface area typically provides the predominant contribution to the overall uptake. Adsorption in zeolites is, as a direct consequence, strongly dependent on the molecular dimensions of the adsorbate and configurational diffusion is often an important consideration where mass transport control predominates.

Recent developments have focused on materials virtually identical to the classical zeolite i.e., oxides of metals other than silicon and aluminum which have stretched the range of materials that are "zeolitic" in nature [100]. The vast majority of oxide structures with a well defined porous structure are now lumped together and classified as zeolites—the term "zeotypes" has emerged as a generic description.

Zeolites are unique among inorganic oxides because of their uniform microporous character, high internal surface area, high thermal stability and their ability to develop internal acidity. Zeolites are structurally resistant to temperatures in excess of 723 K, can operate over a range of acid/alkaline conditions, are unaffected by ionizing radiation and can be used in the uptake of radioactive cations [101, 102]. The latter application draws on the ion exchange properties of zeolites. Silicon is tetravalent and aluminum is trivalent, which results in negatively charged zeolite framework structures where each mole of aluminum produces one equivalent of cation exchange capacity for the zeolite framework. The net negative charge is balanced by an exchangeable cation (typically Na^+), as shown in Fig. 11. Zeolites are proven ion exchange materials where the indigenous charge balancing (sodium) cations are not fixed rigidly to the hydrated aluminosilicate framework and are readily exchanged with metal cations in solution [96]. In environmental remediation applications, both synthetic [103–105] and naturally occurring [106, 107] zeolites have been used to remove a range of toxic heavy metals from water. Solution pH has a significant impact on zeolite exchange properties where a sufficiently low pH can cause structural damage while metal hydroxide precipitation/deposition may predominate at high pH [105]. Zeolite addition to water is accompanied by an immediate solution pH increase as a result of a hydrolysis of the zeolite [108], which in the case of zeolite Na-Y can be shown as

$$\text{Na-Y} + (\text{H}_2\text{O})_x \rightleftharpoons \text{H-Y} + (\text{H}_2\text{O})_{x-1} + \text{Na}^+ + \text{OH}^- \tag{2}$$

The ion exchange of divalent metal (M^{2+}) ions with Na-Y can be represented by the equilibrium [96]

$$\text{M}_\text{S}^{2+} + 2\text{Na}_\text{Z}^+ \leftrightarrow 2\text{Na}_\text{S}^+ + \text{M}_\text{Z}^{2+} \tag{3}$$

where S and Z represent the solution and zeolite phases, respectively. The degree of divalent ion exchange is dependent on the zeolite composition (Si/Al ratio), size of the exchanging hydrated metal ions, metal ion concentrations and temperature [109]. The use of zeolites for the sorption (separation) of non-electrolytes has been covered to a more limited extent in the literature but there are a number of reported accounts of the adsorption of organic compounds on zeolites [110, 111].

Metal ion exchange serves as a synthetic route to supported metal catalysts where a reduction (in hydrogen) of the divalent metal exchanged zeolite generates a supported zero valent metal phase according to the equilibrium [112, 113]

$$\text{M}_\text{z}^{2+} + \text{H}_2 \leftrightarrow \text{M}_\text{Z}^0 + 2\text{H}_\text{Z}^+ \tag{4}$$

Zeolite supported transition metal catalysts have found widespread use in a range of hydrogenation/dehydrogenation, hydroisomerization, dehydrocyclization and hydrogenolysis reactions [114–117]. Two surface hydroxyl groups (Brønsted acid sites) are generated for each reduced divalent metal and these impart a surface acidity that can be employed to promote catalytic transformations that require acid sites, e.g., alkylation and dehydration [118, 119]. Brønsted acidity can also be introduced through hydrolysis (as shown in Scheme (2) above) and by zeolite exchange with NH_4^+ followed by thermal treatment [118, 120]. The ability of zeolites to preferentially sieve molecules can be put to good effect in catalytic applications in that the production of a chemical of particular size and/or shape may be preferentially promoted [121], as is depicted in Fig. 12. Where a reactant is sterically hindered in accessing the active sites located within the zeolite pore network, then the product resulting from that reactant will also be restricted, as shown in Fig. 12a for the case of a branched hydrocarbon feed. Alternative, if a "bulky" product is formed within the zeolitic cavities, its intracrystalline diffusional transport will also be restricted, as arises

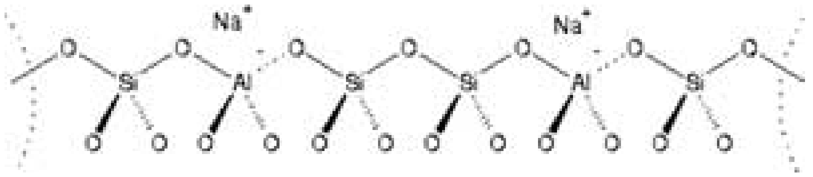

Figure 11 Neutral sodium (charge) balanced zeolite framework.

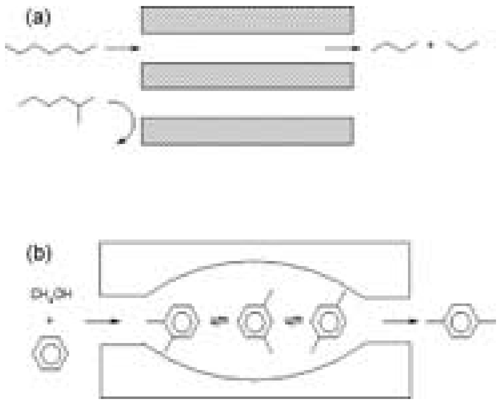

Figure 12 Schematics illustrating shape selectivity in zeolite catalysis: (a) rejection of branched chained hydrocarbons, (b) preferential production of *para*-xylene during benzene methylation.

in the case of (acid site catalyzed) methylation leading to xylene isomer formation (Fig. 12b). The molecular sieving properties of zeolites, in consort with the dual functionality (metal and acid sites) of the zeolite surface place these ceramic materials in a unique category of highly efficient, selective and widely applicable catalysts.

3.2. Catalytic converters

The involvement of ceramics in the automobile industry is far ranging. Indeed, without ceramics, one would not recognize or even be able to operate a modern automobile. The windows, mirrors, spark plugs, lights and electronics that control every function of a car's operation have some ceramic component. Moreover, removal of ceramics would result in a malfunctioning air conditioner, water pump, loud speakers, seat belt buzzer, motors for the windshield wipers and power seats, radio/tape/CD deck; even the airbag would no longer function. Ceramics are used in a hundred different ways in the construction of the modern car but it is the role that ceramics play in the catalytic converter that is the focus of this Section.

In the last sixty years, world vehicle usage has increased from about forty million vehicles to over seven hundred million and each is a source of pollution; this figure is projected to increase to nine hundred and twenty million by the year 2010 [122]. Air quality, particularly in large cities remains grave cause for concern due to the excessive motor traffic. As a means of addressing these issues, cities, states and the federal government have put in place "clean air" laws that restrict the amount of pollution that cars can produce [123]. The legislation imposed by the regulatory bodies is certain to become increasingly more restrictive. This has prompted automakers to redesign car engines and fuel systems where the incorporation of a catalytic converter represents a major automobile refinement. Engine exhaust gases consist of a complex mixture, the composition depending on such factors as type of engine (two- or four-stroke, spark- or compression (diesel)-ignited), driving conditions (urban vs. highway), vehicle speed, acceleration/deceleration, etc. Located just downstream of the engine's exhaust manifold, the catalytic converter processes the exhaust gases by chemical reaction to treat pollutants such as carbon monoxide (CO), nitrous oxides (NO_x) and hydrocarbons [124]. Sulfur oxides (SO_x), although polluting, are not normally removed by post-combustion treatment and the preferred approach to minimize sulfur emissions is to lower the sulfur content in the fuel. In order to reduce toxic emissions, modern car engines carefully control the amount of fuel that is burnt, keeping the air-to-fuel ratio very close to the stoichiometric point. During engine operation the fuel mixture deviates significantly from the ideal stoichiometric ratio where the mixture can be "lean" (higher air content) or "rich" (higher fuel content). The main emissions of a car engine are:

(a) Nitrogen, present in the air inlet feed;
(b) Carbon dioxide, product of combustion;
(c) Water vapor, product of combustion;
(d) Carbon monoxide, product of incomplete combustion;
(e) Hydrocarbons (HC)/volatile organic compounds (VOCs), unburnt fuel and products of incomplete combustion;
(f) Nitrogen oxides (NO_x)

The first three emissions are relatively benign although carbon dioxide emissions have been linked to global warming and added CO_2 emissions compound the environmental burden. The latter three emissions contribute to smog and acid rain and are the main regulated emissions, which catalytic converters are designed to reduce. NO_x emissions at less than ppm levels can affect persons with respiratory complaints while exposure to 3 ppm NO_2 can cause healthy persons to experience breathing difficulties [125]. Modern catalytic converters are designated as "three-way converters" in reference to the three regulated emissions that are treated (CO, HC and NO_x). The action of the three-way converter is shown in Fig. 13. A typical unit consists of either a ceramic honeycomb monolithic structure (see Fig. 7) or ceramic beads coated with precious metals (Pt, Pd and Rh). As the relative movement of parts results in considerable attrition due to friction, ceramic monoliths (typically cordierite based) have now displaced the original bead structure. The term monolith comes from the Greek "mono lithos" (single stone) and as the monolithic catalyst consists of one piece, there is no attrition due to moving particles. The catalytic metal component can be deposited on the surface of the monolith, directly or via an intermediate step, termed washcoating [126]. The latter involves an initial deposition of a layer of high-surface-area oxide(s) onto the monolith. The active catalytic component is incorporated into this layer either during the washcoating step or after the washcoat has been applied using such established techniques as impregnation, adsorption, ion exchange, precipitation/co-precipitation, deposition/ precipitation, sol-gel, slurry dip-coating and in situ crystallization [127]. In every case, the formation of a strong bond between the support and the active phase is a key factor in avoiding catalyst

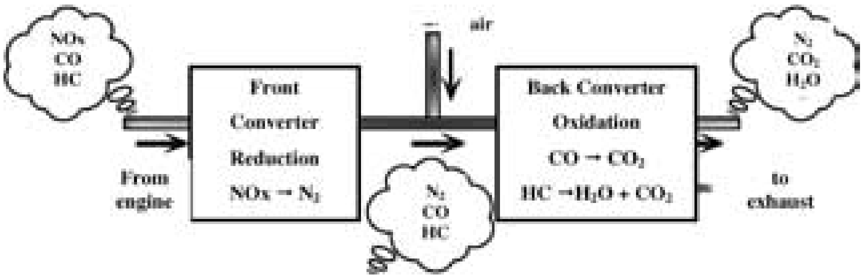

Figure 13 Action of the "three-way converter" to treat CO, NO_x and HC (hydrocharbons) in automobile exhaust.

deactivation. State-of-art washcoating composition can include [128–131]:

(i) Al_2O_3, which is employed as a high surface area support;
(ii) CeO_2–ZrO_2 mixed oxides, principally added as oxygen storage promoters;
(iii) Rh, Pt and Pd as active phases;
(iv) Barium and/or lanthanide oxides as alumina surface area stabilizers.

The geometrical characteristics of the honeycomb monolith can have a significant impact on catalytic converter performance and high conversions are normally achieved under conditions of severe mass and heat transfer limitations [128].

The converter draws on two distinct catalytic actions, i.e., "reduction" and "oxidation" steps, promoted at the precious metal active sites. The use of a ceramic substrate facilitates the exposure of maximum catalytic surface area to the exhaust stream, while also minimizing the amount of (expensive) catalytic material that is required. The exhaust gas flows through the coated ceramic channels and contacts the deposited metal phase. The monolith is surrounded by an insulating element (ceramic fiber mat) which serves to insulate the catalyst and also to secure it mechanically. The thermally durable ceramic component allows the converter to be mounted close to the engine. The reduction catalyst represents the first stage of the catalytic converter, employing Pt and Rh to reduce the NO_x where

$$2NO \rightarrow N_2 + O_2 \quad \text{or} \quad 2NO_2 \rightarrow N_2 + 2O_2 \qquad (5)$$

The oxidation catalyst forms the second stage of the catalytic clean-up and serves to convert the unburned hydrocarbons and CO by oxidation over the supported Pt and Pd

$$2CO + O_2 \rightarrow 2CO_2 \qquad (6)$$

The control system is an integral part of the overall catalytic converter, monitoring the exhaust stream in order to control the fuel injection. An oxygen sensor located upstream of the catalytic converter detects variations in the exhaust stream oxygen content. The engine computer can increase or decrease the amount of oxygen in the exhaust by adjusting the air-to-fuel ratio. This control scheme ensures that the engine is running at close to the stoichiometric point while there is sufficient oxygen to facilitate an oxidation of unburned hydrocarbons and CO.

3.3. Solid oxide fuel cells

Fuel cells employ the same electrochemical principles as conventional cells with the distinguishing feature that the reacting substances are continuously feed into the system. As a direct consequence, fuel cells, unlike conventional cells, do not have to be discarded when the chemicals are consumed. The recent revival in interest in fuel cells has been "fuelled" by energy shortage and air pollution concerns. Indeed, energy generation can be considered the most ubiquitous cause of pollution with appreciable environmental damage associated with coal mining, petroleum extraction/ refining and fossil fuel combustion [132]. Even allowing for steady improvements in energy efficiency, future generations will draw on massive quantities of energy. If the current trends prevail and this demand is met by burning fossil fuels, the environmental implications are grave. Energy technologies drawing on renewable energy serve to minimize the negative environmental impacts associated with the fossil fuel cycle. Such technologies, which are either reasonably well established or in the formative stage, convert sunlight, wind, flowing water, the heat of the earth and oceans, certain plants and other resources into useful energy. The use of renewables can still impact on the environment but the effect is far less than the present dependence on deployment of non-renewable resources. Fuel cell devices can make a valuable contribution to future power generation [133]. Fuel cells that operate on pure hydrogen (as fuel) only produce water as byproduct, thereby eliminating all emissions associated with standard methods of electricity production. However, hydrogen production/storage remains a technological obstacle that must be surmounted [134].

Fuel cells are generally categorized on the basis of the electrolyte, the characteristics of which determine the optimal operating temperature and the fuel used to generate electricity. All fuel cells incorporate a barrier that selectively allows ions to pass, ultimately forcing electron flow through an external circuit to create electricity. One type of leading fuel cell system that is constructed from commonly available ceramic materials, such as zirconia, is the solid oxide fuel cell (SOFC). SOFCs represent the one fuel cell technology expected to span all traditional power generating markets (residential, commercial, industrial/distributed generation, utility) and are also likely to penetrate niche markets,

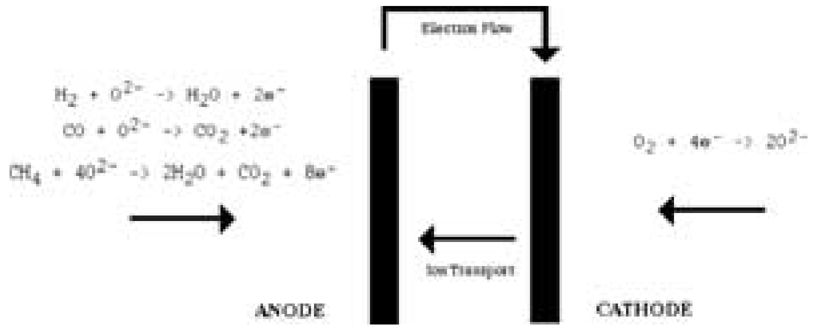

Figure 14 Basic schematic showing SOFC operation.

such as small portable generators, and remote and premium power applications. The basic SOFC unit comprises three oxide ceramic units: a fuel electrode; an air electrode; a solid electrolyte. A simple schematic outline of SOFC operation is shown in Fig. 14. Oxygen in the air supply accepts electrons from the external circuit to form O^{2-} ions at the cathode that travel through the electrolyte to the fuel electrode (anode) to generate H_2O and/or CO_2 (depending on the fuel used), releasing electrons to the external circuit [133]. Many advanced ceramics display electrical properties superior to (or unattainable in) their metallic and polymeric counterparts; these materials are known as electroceramics. One group of electroceramics, referred to as "fast ion conductors," "rapid ion conductors" or "superionic conductors" are able to support a high flux of ions in the solid state. Ceramics that can rapidly conduct oxygen ions (O^{2-}) are potential candidates in SOFC developments.

Today's technology employs several ceramic materials as the active SOFC components. The anode is typically formed from an electronically conducting nickel/yttria-stabilized zirconia (Ni/YSZ) cermet (i.e., a ceramic/metal composite). The cathode is based on a mixed conducting perovskite, lanthanum manganate ($LaMnO_3$). Yttria-stabilized zirconia (YSZ) is used for the oxygen ion conducting electrolyte. To generate a reasonable voltage, fuel cells are not operated as single units but as an array of units or "stack," with a doped lanthanum chromite (e.g., $La_{0.8}Ca_{0.2}CrO_3$) interconnect joining the anodes and cathodes of adjacent units. SOFCs based on a YSZ electrolyte have been developed for operation in the temperature range 900–1000°C. SOFCs can in principle operate by direct electrochemical oxidation of a hydrocarbon fuel. Operation at elevated temperatures enables O^{2-} diffusion through the electrolyte and facilitates C—H bond activation in the hydrocarbon reactant. However, the Ni component in the composite catalyzes hydrocarbon decomposition to solid carbon at such temperatures, leading to fouling [135, 136]. Such anodes are not suitable for use with logistic fuels, i.e., kerosene, JP8, diesel or gasoline. A reduction of the SOFC operating temperature would serve to broaden the choice of materials of construction and lower the manufacturing costs. Recent developments have resulted in an SOFC unit that runs directly on hydrocarbon (methane, ethane, *l*-butene, *n*-butane and toluene) fuels and employs a YSZ anode with a Cu/Ce content [137, 138]. Copper provides enhanced electrical conductivity while Ce promotes hydrocarbon oxidation and also exhibits high ionic conductivity.

Further advances in SOFC performance must now focus on materials development to elevate the electrical conductivity and catalytic performance of the anode. Enhanced SOFC performance must include higher energy conversion efficiency, lower chemical and acoustical pollution, fuel flexibility, cogeneration capability and a rapid load response. While SOFCs now perform adequately in terms of efficiency and fuel flexibility, the high temperatures required for operation have limited the application options. The high temperature also demands that the system include significant thermal shielding to protect operating personnel and to retain heat. While such requirements are acceptable in a utility application, they are not consistent with the demands of most transportation applications nor do they lend themselves to small, portable or transportable applications. Ceramic materials have a decided role in the development of lighter and more compact electrical power sources for emerging applications.

4. Concluding remarks: A look to the future

Until quite recently, ceramics were viewed as being solely of artistic and domestic value. The industrial potential of ceramics has yet to be fully exploited but future advances in ceramics will undoubtedly widen the potential applications. Taking the field of electronics and communication, further developments will be directed towards device (micro) miniaturization where a generation of new ceramic materials for component manufacture with micro-applications in superconductors, sensors and memory storage devices represents a myriad of applications. Indeed, the burgeoning interest in nanotechnology will undoubtedly change the way materials, in general, and ceramics, in particular, will be produced. Potentially, ceramics will have improved mechanical, electrical and optical properties, and be lighter, stronger and cheaper to produce. Developments in the medical field will see ceramic applications in diagnostic instruments, bioceramics for bone replacement, use in chemotherapy release capsules and advances in tissue engineering.

In terms of catalysis, the use of ceramics is still in a formative stage but the most far ranging viable application will be in the field of energy conservation and environmental protection as catalytic materials/reactors and fuel cells. Developments in heterogeneous catalysis have always required an understanding of reactivity at the nano-scale with the result that nanotechnology as applied to ceramics production should lead to improved catalyst support properties. The latter can impact on catalytic converter performance that will meet increasing more stringent air quality demands. The ceramic monolith unit that forms the core of the converter requires further optimization in terms of application (and composition) of the active phase and improvements in mass/heat transport properties to improve gas/surface contact, achieving uniform flow within the honeycomb while minimizing the occurrence of hotspots. Incorporation of advanced ceramic materials in combustion engines and combustion power systems in general can lead to increased fuel efficiency, greater power output and reduced toxic emissions. There are endless possibilities regarding developments of zeolites and zeotype catalysts, largely dealing with modifications to the intrinsic acid and metal site activities and an engineering of the micropore structure to modify the sieving effect associated with shape selectivity. Fuel cells have yet to make a serious impression on the energy market and mass-market zero-emission automobiles are far from realization. The potential for ceramic applications in fuel cells is, however, enormous. For instance, the most expeditious route to lowering SOFC operating temperatures must draw on ceramic composite electrodes/electrolytes with enhanced ionic transport capabilities. On-going developments, still at an early stage, are focusing on doped bismuth oxides, perovskites and apatites. The efficient use of logistic fuel in SOFCs will require a fine tuning of the catalytic/conducting properties of the ceramic components. Ceramic materials will also have increasing application as membranes in attendant fuel cell applications (e.g., extracting hydrogen from methane) and as components in other fuel cell configurations, e.g., PEMs.

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