

dissociation of H₂ molecules on the metal surface shows high reaction probability on different surface sites [23].

Physico-chemical properties of nano-sized metal particles mainly change as a function of their size. Thus, the most significant consequence of decreasing the particle size is the increase in the surface/volume ratio (i.e. surface atoms of a 2 nm particle constitute about 60% of the total) [25]; the rise in the fraction of surface atoms is responsible for some changes in the structural character. Notable changes typically include: i) a decrease in the melting temperature and ii) a lowering of the interatomic separation. Indeed, small metal clusters (i.e. ranging from ca. 2 to 30 atoms) are close to molecular in their behaviour with electronic states (DOS) that are discrete or approaching discrete behaviour. On the contrary, metal nanoparticles (i.e. containing 10³-10⁷ atoms) have a continuous band of electronic energy levels and a well-defined Fermi surface [25]. These features partially explain some of the fundamental differences in the chemical reactivity between metal clusters and nanoparticles.

Typically, small particles are more reactive than larger ones, since the electronic state and defect density may change markedly at a critical size around 2 nm [26]. As a whole, a decrease in particle size will increase the number of surface atoms having low-coordination numbers, such as corners (CN = 4,5,6) and edges (CN = 7) for all particle shapes. Theoretical studies indicate that surface atoms having low coordination number (such as edges and corners) are the seat of increased chemical reactivity and are therefore the preferred active centres [27]. For instance, the relative fractions of atoms at corners (CN = 6) and edges (CN = 7) in a truncated octahedron Au nanoparticle increase significantly as the particle sizes become smaller than 3-4 nm (Fig. 1A) [17]. Moreover, the relative amounts of edge, corner and terrace sites are particle shape dependent (Fig. 1B), and hence distinct geometries may lead to different chemical reactivities.

As already noted by Langmuir [28] “the surface atoms are not rigid but tend to arrange themselves so that the total energy will be a minimum. In general, this will involve a shifting on the positions of the atoms with respect to each other”. Thus, the displaced atoms must return to their initial state when the reaction cycle is completed. Inward relaxation and reconstruction of catalytic surfaces are much more marked at low-coordination sites, which are more “flexible” and self-repair the sites at higher rates [29].

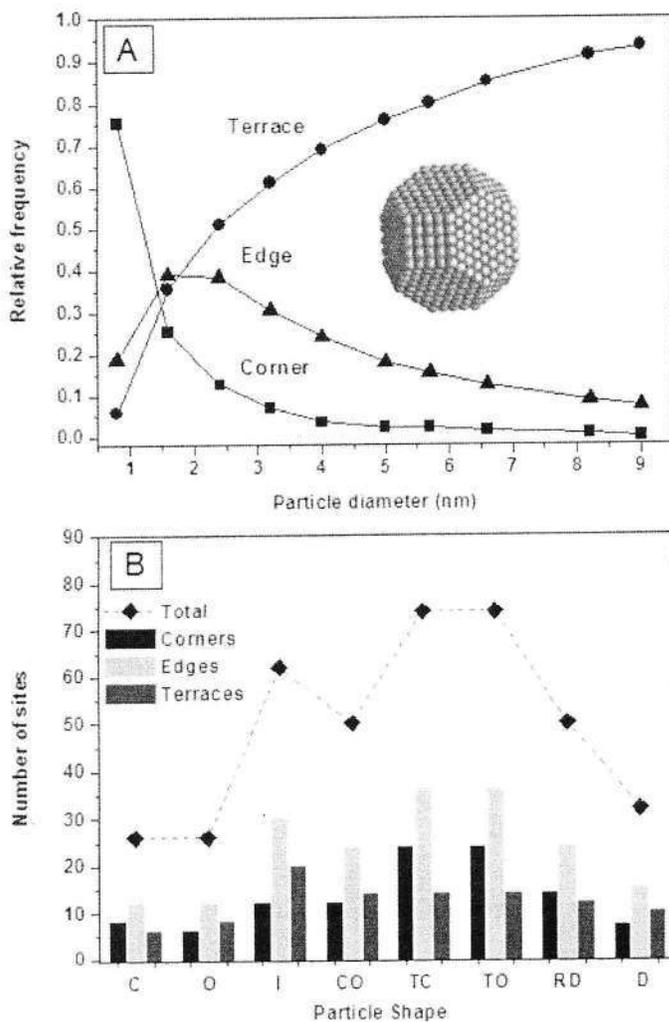


Fig. 1: Dependence of relative amounts of surface sites (normalized to exposed atoms) as a function of Au particle diameter (section A) [17]. Values calculated from ref. [25] Total numbers of edges, corners and terraces of particles having different convex shapes: (C) cube, (O) octahedron, (I) icosahedron, (CO) cuboctahedron, (TC) truncated cube, (TO) truncated octahedron, (RD) rhombic dodecahedron, (D) decahedron (Section B).

Self-repairing phenomena reflect the intrinsic property of any effective catalyst to “regenerate” the sites once the catalytic cycle has been concluded. Such mechanisms occur locally at each active site and represent the lowest level of self-organization at solid surfaces [10]. For instance, the marked ability of isolated Ti(IV) sites inside the silicalite framework (Ti-Silicalite-1 catalyst) to self-repair in a reversible (or nearly reversible) way their local environment upon interaction with adsorbates is probably the key to the reactivity of this important material used for a range of low-temperature catalytic oxidation processes with hydrogen peroxide [30].

In small metal clusters, atoms are often packed into polygonal (2-D) or polyhedral (3-D) shapes, having several planes of symmetry and high packing efficiency with characteristic numbers, namely magic numbers.

For instance, three, four, six and eight atoms are often packed into triangular, tetrahedral, octahedral and cubic arrays, respectively. The formation of a sequence of cluster magic numbers is closely related to the mechanisms of cluster formation (nucleation) and growing, which are kinetically and thermodynamically controlled and hence sensitive to experimental conditions [27]. Therefore, it is natural to expect that metal clusters with magic numbers are more abundant than others, likely because they are particularly stable, as a result of packing of atoms according to precise rules determined by electronic and/or steric principles. As the cluster size increases, the force governing their formation may switch from bonding (electronic) to packing (steric) in nature. Consequently, the assemblage of atoms to form energetically stable clusters/nanoparticles of relatively efficient packing and high symmetry reflects the presence of well-defined concentration patterns, as result of self-organization phenomena.

Depending on the surface energy of the $\{hkl\}$ planes and on the adsorption bond strength of molecules from the surrounding gas-phase, metal nano-sized particles often form convex polyhedral shapes, having the Euler characteristic of the sphere ($X = 2$). Thus, several convex polyhedral geometries, as the regular Platonic solids, the semi-regular Archimedean solids and their dual Catalans, and other semiregular convex polyhedra (i.e. prisms, dipyramids, antiprims and trapezohedra) are frequently found in the cluster chemistry [27]. These solids are dominated by crystallographic faces, which exhibit different surface atom densities, electronic structures, bonding, chemical reactivities and thermodynamic properties [31-33].

In recent years, many studies have investigated the equilibrium shapes of fcc metal nanoparticles, such as gold, platinum and palladium showing several convex polyhedral shapes, including icosahedron and truncated icosahedron, decahedron, truncated octahedron and cuboctahedron [31-33]. For instance, Fig. 2 shows an ideal Pt nanoparticle (~ 2.5 nm) with a truncated octahedron shape, exhibiting corner, edge and terrace sites. This geometrical structure is typical for many metal nanoparticles, as achieved with Pt20C nanoparticles (the inset of Fig. 2).

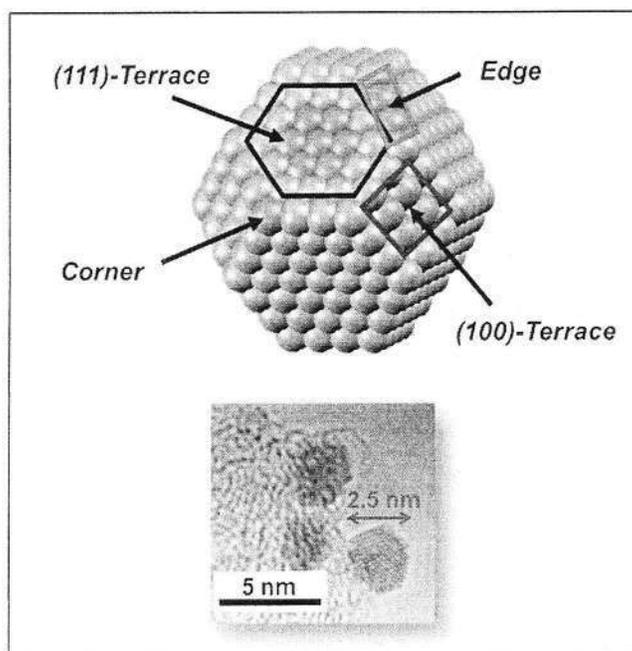


Fig. 2: Schematization of an ideal Pt-nanoparticle (~ 2.5 nm) with a truncated octahedron structure (above) . HRTEM micrograph of the Pt20C nanoparticles exhibiting truncated octahedron shapes (below).

Although many computational and theoretical studies agree on the energetic order of distinct particle shapes, they do not necessary agree with experimental observations. Such discrepancies between experimental data and thermodynamic modelling of small metal particles are often attributed to kinetic effects. In fact, the cooperation (or competition) between kinetic

and thermodynamic factors may lead to non-linear dynamics at solid surfaces. For instance, combined techniques revealed that icosahedral Au particles, thermodynamically more stable in small clusters, are also observed in larger nanoparticles, as a consequence of kinetic effects [31-34]. Moreover, non-convex shapes ($X \neq 2$), as Kepler-Poinsot polyhedra, may also form during reactions as a consequence of selective passivation and blocking of edge and corner sites during growth, coupled with anisotropic growth rates in different orientations [35].

All these convex and non-convex solids belong to the class of polytopes, geometrical structures with any general number of dimensions. Indeed, the term of n-polytope is used to refer to a n-dimensional structure.

The polytopes are fine as a model to describe the complexity of the geometrical structures. For instance, a polygon is a 2-polytope, a polyhedron is a 3-polytope, a polychoron is a 4-polytope and so on. In addition, the elements of a 3-polytope are its vertices (0-dimensional face), edges (1-dimensional face) and terraces (2-dimensional face).

Since metal clusters and nanoparticles are formed through the assemblage of atoms in three dimensions, they can be considered 3-polytopes. However, these clusters/nanoparticles are not static but change over time, i.e. depending on the external conditions, and hence they can be denoted as polychorons, four dimensional polytopes. Similarly, self-repairing mechanisms, occurring locally on vertices, edges and terraces during catalytic reaction, can be included in the class of polytopes variable over the time, having 1, 2 and 3-dimensional structures, respectively. As a result, the polytopes can be considered the initial set of the action of hyperstructures.

3 Multicomponent systems: zeolites

Although the first description of zeolites dates back to 250 years ago, over the last five decades there has been a growing interest in zeolite research activities. At present, almost 200 different structural types of zeolites have been recognized, differing in the size, shape and connectivity of their channels [36,37]. These materials are much more than just an ideal 3-D regular arrangement of TO_4 tetrahedral having channels and voids that hold appropriate active sites. They are multicomponent systems made up of tiny crystals of definite morphologies, containing defects of various origins and a certain nanoscopic (at unit cell level) and macroscopic (at crystal level)

distribution of active sites, either acid, basic or redox, or a combination of them [38]. The diversity of morphologies is also increased by the presence of elements other than Al for Si in the framework, which may be either aliovalent (2+ or 3+) or isovalent (4+), and the search for new materials is encouraged by the knowledge of hypothetical geometries that have been shown to be energetically possible [37]. The faujasitic zeolites X and Y provide excellent examples of many of the important types of zeolite structural chemistry. In Al-containing X and Y systems, the siting of extra-framework cations introduced either during the synthesis or subsequently by cation exchange is very important in the determination of their physico-chemical properties. Fig. 3 shows some possible extra-framework sites in zeolite Y with associated cages and channels. Cations can be located at different sites, depending on the particular zeolite framework, cation size, dehydration state and nature of adsorbed molecules. Moreover, whereas pure silica frameworks are electrically neutral, the substitution of trivalent Al for tetravalent Si ($\text{Al}^{3+} \leftrightarrow \text{Si}^{4+}$) induces a negative charge to the material that has to be balanced by positively charged extra-framework cations within the pore space. Thus, the presence of strong electric fields and controllable adsorption features within the pores will produce a unique type of material [36].

As a whole, when a guest molecule presents a polar character and/or the zeolitic framework is not purely siliceous, the electrostatic interactions among atoms and/or molecules cannot be neglected. Specifically, when a molecule is confined in the channels of a zeolite, the sorption energy depends on different energetic factors. Among these, there are the van der Waals interactions (i.e. attractive and repulsive forces), polar, field-dipolar and field gradient-quadrupole forces, sorbate-sorbate intermolecular interactions and the acid-base chemical interactions [36].

The interaction in the confined space of the pores is characterized by the geometry of the environment of the active center (i.e. van der Waals interactions) and by the chemical composition of the environment (i.e. polar and field-dipole terms). When the size of a guest molecule approaches the sizes of the zeolitic channels, it is also necessary to consider the electronic confinement, which can affect the energetic state of reactants, modifying their reactivities [36]. Moreover, the effect of field gradients, which weaken

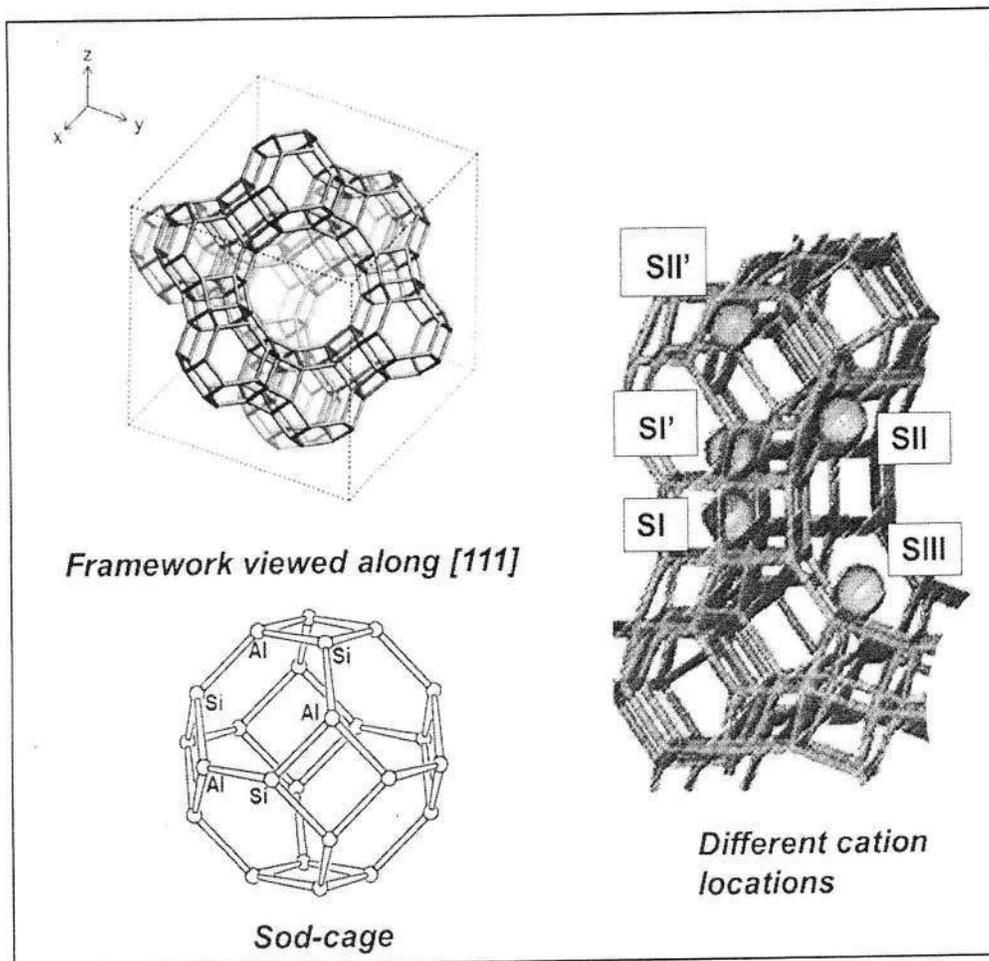


Fig. 3: Framework type of zeolite Y (left); Structures taken from C. Baerlocher W. M. Meier, D.H. Olson (ed) (2001), Atlas of zeolite framework types, 5th edn, Elsevier, Amsterdam. Extra-framework cation sites (SI, SI', SII, SII' and SIII) observed in the same material (right).

some hydrocarbon bonds, depends on the charge density (i.e. Al content), the temperature, the zeolitic structure and the polarizing effect of cations [40]. Although pure silica zeolites are highly hydrophobic, the isomorphous substitution of silicon with aluminum, and the subsequent neutralization of the framework with cations make the structure hydrophilic [37].

Indeed, zeolites containing charges are typically hydrophilic materials that, depending on the amount of extra-framework species and on the framework Si/Al ratio, can be more or less selective adsorbents for polar or non-polar compounds [36].

Zeolites are able to discriminate both reactant and product molecules by size and shape, when they have significant differences in terms of diffusivity through a given pore channel system. In addition, the relative orientation of the channels and cavities in respect to the crystal shape may affect the diffusion path of molecules through the crystals [38]. Thus, different types of shape selectivity may occur within a given zeolitic structure, namely reactant selectivity, product selectivity and transition-state selectivity [39]. The latter, in particular, takes place when the specific configuration around a transition state located in crystalline volume is such that only certain configurations are possible.

Moreover, the reaction pathway, and hence the chemical complexity, can be strongly affected by the framework geometry in the neighborhood of the active site. Thus, the steric constraints assume a significant importance for driving the reaction towards the desired products [36]. Typical examples of transition-state selectivity include the inhibition of coke formation within ZSM-5 crystals and the cracking of paraffins within the pores [40,41].

The complexity of zeolites is still greater if one considers them as solid acid catalysts. Indeed, these materials typically contain Brønsted acid OH groups (i.e. SiOHAl), which are responsible for the catalytic activity of reactions catalyzed by acids, such as cracking or isomerization of hydrocarbons [38,41]. For H-forms of zeolites (i.e. H-faujasite, H-ZSM-5, H-chabazite, etc.), the cracking rates of hydrocarbons were often found to increase linearly with the framework aluminum, which corresponds to the density of Brønsted acid sites [37]. For instance, a linear increase of the activity towards the *n*-hexane cracking rate with the Al content in the framework was observed, as long as the sites could be considered as non-interacting. The acid strength of sites can be also altered by isomorphic substitution of Si for trivalent atoms other than Al. Similarly, the Si-O-T bond angle, which depends on the zeolite structure type, affects the partial charge and the acid strength of the hydroxyl protons.

In addition to the local effects, the overall composition of the zeolite framework influences the acid strength of bridging OH groups, through the

mean Sanderson electronegativity (S^m). Typically, the acid strength of Brønsted sites increases with increasing S^m of the zeolite framework, that is, with decreasing of aluminum content [37].

As it is known, the surface acidity of zeolites plays a key role in many catalytic reactions. For instance, catalytic cracking of alkanes and alkenes is a high-temperature reaction network that is acid-catalyzed and proceeds through the formation of carbocation transition states [5]. Because of the complexity of feedstocks and reaction pathways, the variety of products that can be obtained is huge.

This suggests that zeolites may display sensitivity to tiny changes in their states, and hence a small alteration in their condition at one instant may give rise to great differences in terms of reaction products.

Consequently, during a reaction various self-organizing phenomena may occur in multicomponent systems and their geometrical complexity can be described with polytopes acting in a discrete 3-D space. For instance, self-repair and reorganization of active sites on corners reflect 2-polytopes, as well as the electrostatic interactions between cations in zeolite framework and guest molecules may be described through polychorons. Similarly, mass transfer limitations (i.e. shape selective control) occur in 3-D frameworks containing well-defined pores and cavities of molecular dimensions. This means that self-organizing phenomena due to shape selective control give rise to geometrical structures consistent with polychorons.

Since self-organizing phenomena in catalysis may reflect complexity structures [18] their non-linear combination results in a hyperoperation (\circ), namely multivalued operation. Indeed, the catalyst may act like a hyperoperator in the sense of the theory of hypestructures [19,20]. This hyperoperator maps two reactants (x,y) of the catalytic process (H_v -structures) into the class of polytopes (a subset $x \circ y$ of H_v). Moreover, the hyperoperation is weak associative because two sets, i.e. $(xy)z$ and $x(yz)$, have at least one common element for all x,y,z in H_v . The weak associativity can be seen easily because different complexity structures (sets) contain n -polytopes as common elements in every catalytic reaction [19].

As a result, the complexity of heterogeneous catalysis can be fairly well described through the H_v -structures.

4 Dynamic active networks: transition metal oxides acting via redox MvK-type mechanism

Typically, oxidation reactions catalyzed by mixed oxides occur via a Mars-van Krevelen mechanism (MvK) [42] whereby the active centres are not isolated sites but ensembles of ions and electrons mutually interacting in an active network [43,44]. These catalytic systems exhibit sophisticated self-organization structures, in which dynamic networks of “sites-joined” may promote either selective or total oxidation reactions [17,45]. Indeed, the MvK-type mechanism requires that a hydrocarbon molecule (R-H) extracts lattice oxygen from the surface of the oxide catalyst ($\text{R-H} + \text{O}^{2-} \rightarrow \text{R-O} + \text{H}^+ + 2\text{e}^-$), so generating oxidized products and a reduced catalyst surface. Then, lattice oxygen is replenished by the reduction of gaseous oxygen ($\frac{1}{2} \text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$) [10]. In other words, two redox steps take place during catalytic reaction, one consisting of the injection of electrons into the catalyst, the other extracting them from the oxide.

This mechanism occurs quite frequently in selective oxidation reactions over vanadium oxides, as originally proposed by P. Mars and D. van Krevelen [41]. There is, however, evidence that also other metal oxides, such as those of Mo, Cr, and Fe operate via redox cycles [10,46].

Requirements for the MvK mechanism to take place comprise the facile redox behaviour of cations (i.e. V, Cr, Mo, etc.) and the good mobility of both electrons and lattice oxygens within the solid [43,44]. Other factors comprise the facile activation of reactants, the presence of surface defects (i.e. corners edges and terraces), the surface acid-base properties, and the temperature [43,44,46-48].

Catalytic performances of redox catalysts are also influenced by the nature of lattice oxygens. Indeed, the latter have diverse stabilities and may react differently, *i.e.* via electrophilic or nucleophilic attack. For instance, lattice O^{2-} (nucleophilic species) are usually responsible for selective oxidations, whereas electrophilic species (i.e. O_2^- , O_2^{2-} and O^-) are highly reactive and result in total oxidations [5,49,50]. Nevertheless, their properties are strongly influenced by the electronegativity of the element present in the support material (i.e. Al, Ti, Si, etc.) [51-53].

Noteworthy, the complexity of metal oxides acting via redox cycles further depends on the fact that acid-base and redox properties can be closely related to each other. For instance, it has been recently observed that the