MARCO PIUMETTI[1], NIK LYGEROS[2]
[1] Department of Applied Science and Technology, Politecnico di Torino, 10129, Torino, Italy.
[2] LGPC (UMR 5285), Université de Lyon, 69616, Villeurbanne, France.

Some new concepts on the complexity of catalytic systems

ABSTRACT: As a whole, a catalyst acts as a hyperoperator computing a non-linear combination of several complexity structures; then, the overall complexity can be described through a non-linear combination of chemical and structural complexity. The latter is characterized through the fractal dimension and depends on the geometric and electronic factors.
Therefore, it has been observed that catalytic processes can be either well or ill-conditioned systems, depending on the condition number (k). A system with a low k value is said to be well-conditioned, while a system with a high k appears ill-conditioned. Thus, structure-sensitive reactions can be classified as ill-conditioned systems, since small variations on the catalyst surface produce large effects on the catalytic activity. Finally, it has been proved that the overall complexity of a catalytic system is a state of function and there is an inverse correlation between entropy and complexity.

1. INTRODUCTION

The catalyst surface is structurally and compositionally complex, exposing adsorption/reaction centres that act either singularly (single sites) or in group (cluster of sites), in fact, it can also have a fractal texture. These catalytic active sites behave as dynamic entities in the space-time domain and then their physico-chemical properties strongly depend on the operating conditions [1-4]. During catalytic reaction, the solid surface typically receives a mixture of reactant molecules and often has to carry on intricate reaction networks with multiple steps and pathways in a general graph [5,6]. Therefore, the catalyst operates through complex self-organizing phenomena, in which both the geometric and electronic factors play a key role on the chemical kinetics [7,8]. Open systems, far from the equilibrium - reactions at steady-state flow conditions - can be described by a set of non-linear partial differential equations, combining the chemical kinetics with the diffusive phenomena of the adsorbed species, as follows:

$$\frac{\partial x_i}{\partial t} = F_i(x_j, p_k) + D_i \nabla^2 x_i$$

where x_i are the state variables (e.g. surface concentrations) of the reacting molecules, F_i are the non-linear operators expressing the chemical kinetics, D_i are the diffusion coefficients and p_k are a set of parameters [9].
These non-equilibrium systems have the capacity to be creative due to the chaos but also to their inner complexity, since new structures may appear with radically different behavior from the classical. Indeed, there is an unexpected relation between the chemical kinetics and the transport phenomena.
Non-equilibrium processes were first studied by I. Prigogine [10] who denoted them as "dissipative structures", latter incorporated in the framework of synergetics by H. Haken [11]. Moreover, they belong to the class of irreversible processes creating entropy but also structures and then can be described via the kinetic equations with broken time symmetry instead of the canonical equations [12]. This means that such systems cannot be described through classical dynamics or quantum mechanics with deterministic, time-reversible approaches, and this point explains also their high complexity.
As we introduced in our previous work [13], self-organizing phenomena at surface catalysts reflect the presence of i-complexity structures, defined as the structural relations among the n-elements (e.g. adsorption/reaction centres, reactants, products, etc.) with p-physico-chemical properties variable over the space-time domain. Complexity structures arise with multiple forms, including the self-repair of active centres, interactions among adjacent sites, dynamic networks of "sites-joined" and so on (Figure 1).
In agreement with the Theory of Hypergroups introduced by the mathematician F. Marty in 1934 [14], and more generally the Theory of Hyperstructures, the catalyst acts as a hyperoperator ($\circ$) computing a non-linear combination (multivalued operation) of complexity structures ($C_{s,i}$) and then the overall complexity of a catalytic reaction (λ) can be written as:

$$\lambda = C_{s,1} \circ C_{s,2} \circ C_{s,3} \dots \circ C_{s,i}$$

Since the catalytic behavior of catalysts typically results in a non-linear combination of i-complexity structures, then the performances of multicomponent systems (e.g. zeolites, metal oxides, etc.) and nanostructured materials appears different from a sum of different factors. Therefore, in the present work, we propose some novel concepts and theoretical descriptions for decoding the complexity of catalytic processes.

2. CHEMICAL AND STRUCTURAL COMPLEXITY

The complexity of a catalytic reaction depends on the chemistry of the process (e.g. reaction steps, pathways, etc.) and on the nature of catalyst (e.g. surface reactivity, morphology, textural properties, etc.). The latter, also defined as structural complexity, may affect the reaction chemistry and then the chemical complexity of the process.
Therefore, the overall complexity of the catalytic reaction would be described through a non-linear combination (hyperoperation) of chemical complexity ($C_{chem.}$) and structural complexity ($C_{struct.}$), as follows:

$$\lambda = C_{chem.} \circ C_{struct.}$$

This means that λ exists in the hyperplane *Hp* defined in the space-time domain (Figure 2). As we have introduced in our previous work [15], the chemical complexity of a catalytic process can be described in terms of cooperative hyperstructures (CH), synergistic hyperstructures (SH) and strong synergistic hyperstructures (SSH). The latter classification, however, has to be considered in the frame of the Theory of Posets which generalizes the Theory of Lattices [16], since there are reactions (e.g. Belousov-Zhabotinsky reactions, Pt-catalyzed oxidation of CO by O_2) whose their chaotic or oscillating behavior make them appropriate as case studies in complexity [17]. On the other hand, the structural complexity of a solid catalyst can be characterized through the fractal dimension. Indeed, real (defective) surfaces can be reflected by n-polytopes, geometrical structures with n-dimensions (Figure 3). For instance, metal clusters are formed through a 3-D assemblage of atoms/ions, and then they can be reflected by 3-polytopes. Since these particles act in the space-time (four dimensions), then they are geometrically described by polychorons (4-polytopes). Similarly, self-organizing phenomena occurring at solid surfaces can be described by means of 3-polytopes acting in four dimensions. It must be pointed out, however that a fractal approach with $(3 + e)$ dimensions, where *e* represents the dimension of the boundary, is much more appropriate to describe the dynamic behavior of a solid surface [18,19].

Since the physico-chemical properties of a solid catalyst depend on the geometric ($F_{geom.}$) and electronic ($F_{electr.}$) factors then the following equation can be written:

$$C_{struct.} = F_{geom.} \circ F_{electr.}$$

Both the geometric and electronic factors result from a non-linear combination of complexity structures of active sites; the latter factors, indeed, are able to influence with each other. This suggests that the structural complexity of a solid catalyst can be approximately described as follows:

$$C_{struct.} \simeq F_{geom.} \simeq F_{electr.}$$

Considering the general equation:

$$\lambda = C_{s,1} \circ C_{s,2} \circ C_{s,3} \ldots \circ C_{s,i} = F_{geom.} \circ F_{electr.} \circ C_{chem.}$$

Then, the overall complexity of the catalytic reaction can be estimated as:

$$\lambda \simeq F_{geom.} \circ C_{chem.} \simeq F_{electr.} \circ C_{chem.}$$

This approximation would appear better for structure-sensitive reactions and for reactions over nanocatalysts.

3. WELL AND ILL-CONDITIONED CATALYTIC SYSTEMS

Stability is a fundamental property of dynamical systems which means that the qualitative behavior of the trajectories is unaffected by small perturbations.

Then, an equilibrium solution f_e to a system of first order differential equations is stable if for every (small) $\epsilon > 0$ there exists a $\delta > 0$ such that for every solution $f(t)$ having initial conditions within distance δ

$$\|f(t_0) - f_e\| < \delta$$

the equilibrium remains within distance ϵ

$$\|f(t) - f_e\| < \epsilon$$

for all $t \geq t_0$.

In this scenario, the condition number k of a function with respect to an argument x measures how much the output value of the function modifies for a small change in the input argument. Then, a catalytic system with a low-condition number is said to be well-conditioned, while a system with a high k value is said to be ill-conditioned. It must be pointed out that the condition number is an intrinsic property of the catalytic system, despite the operating conditions play a key role on the catalytic behavior of the reaction over time. Thus, given a small change Δx in x variable, the relative change in x is

$$\frac{\Delta x}{x}$$

while the relative change in $f(x)$ is

$$\frac{[f(x + \Delta x) - f(x)]}{f(x)}$$

Comparing the ratios of the norms $\|\cdot\|$ for the domain/codomain of $f(x)$ and assuming an infinitesimal change δx, the following relation appears:

$$\frac{\|f(x + \delta x) - f(x)\|}{\|f(x)\|} \leq k \frac{\|\delta x\|}{\|x\|}$$

This means that a catalytic system is well-conditioned for $k \approx 1$. The same approach can be used for *n*-variables $(x_1, x_2, \ldots, x_n \neq 0)$, where

$$f(x + \delta x) = f(x) + \delta x_1 \frac{\partial f(x)}{x_1} + \delta x_2 \frac{\partial f(x)}{x_2} + \cdots + \delta x_n \frac{\partial f(x)}{x_n} + O\| \delta x\|^2$$

then it can be obtained:

$$\frac{f(x + \delta x) - f(x)}{f(x)} = \frac{\delta x_1}{f(x)} \frac{\partial f(x)}{\partial x_1} + \frac{\delta x_2}{f(x)} \frac{\partial f(x)}{\partial x_2} + \cdots + \frac{\delta x_n}{f(x)} \frac{\partial f(x)}{\partial x_n} + O \frac{\| \delta x\|^2}{f(x)} \leq$$

$$\left| \frac{\delta x_1}{x_1} \right| \left| \frac{x_1}{f(x)} \right| \left| \frac{\partial f(x)}{\partial x_1} \right| + \left| \frac{\delta x_2}{x_2} \right| \left| \frac{x_2}{f(x)} \right| \left| \frac{\partial f(x)}{\partial x_2} \right| + \cdots + \left| \frac{\delta x_n}{x_n} \right| \left| \frac{x_n}{f(x)} \right| \left| \frac{\partial f(x)}{\partial x_n} \right| \qquad =$$

$$\left| \frac{\delta x_1}{x_1} \right| k_1 + \left| \frac{\delta x_2}{x_2} \right| k_2 + \cdots + \left| \frac{\delta x_n}{x_n} \right| k_n$$

The latter relation shows that greater k_n values occur when the first derivate of the function $f(x)$ increases, that is when $f(x)$ exhibits a strong dependence on a specific variable, namely

$$\frac{\partial f(x)}{\partial x_i} \gg 1.$$

Conversely, a complex catalytic system is usually one whose evolution is highly sensitive to initial conditions, or to small perturbations, and then it appears as an ill-conditioned system ($k \gg 1$). For instance, CO oxidation over ceria-based nanocatalysts is highly sensitive to the geometric structure of the catalyst and small variations in the catalyst surface produce large effects on the oxidation activity [20,21]. CO oxidation over ceria nanocatalysts, indeed, strongly depends on the presence of highly reactive low-index planes. In other words, structure-sensitive reactions can be classified as ill-conditioned systems ($k_i \gg 1$) since small variations on the surface properties produce large effects on the catalytic performances.

4. THERMODYNAMIC CONSIDERATIONS

In Thermodynamics, a state function is defined for a system relating state variables, or state quantities, that depends only on the current equilibrium state of the system. State functions such as the internal energy, Gibbs free energy, enthalpy and entropy do not depend on the path by which the system arrives at its present state. On the other hand, mechanical work and heat are path functions, because their values depend on the path between two equilibrium states.
Then, there is a fundamental difference between dynamical and thermodynamical states of a system. To define the dynamical state, indeed, it is necessary to have an exact knowledge of the position (and motion) of all molecules that compose the system. The thermodynamical state, on the other hand, is defined by giving only few parameters (e.g. temperature, pressure, etc.). Therefore, to the same thermodynamical state there correspond many dynamical states.
In statistical mechanics, criteria are given for assigning to a given thermodynamical state the number π of corresponding dynamical states. This number π is usually called the probability of the given thermodynamical state, despite it is only proportional to the probability in the traditional sense. The latter can be obtained dividing π by the total number of possible dynamical states. Then, there is a relationship between the properties of the probability π and the entropy S,

$$S = f(\pi)$$

as formulated by Boltzmann:

$$S = k_B \log \pi$$

where k_B is the Boltzmann constant and is equal to the ratio between the gas constant and the Avogadro's number [22]. Then, for a given set of macroscopic variables, the entropy measures the degree to which the probability of the system is spread out over possible microstates. In other words, entropy is a measure of the number of ways in which a system may be arranged, often taken to be a measure of "disorder".
Therefore, if we consider two dynamical states :

$$S_1 = f(\pi_1); \ S_2 = f(\pi_2)$$

The entropy of the system is the sum of the two entropies:

$$S = S_1 + S_2$$

and the probability of the whole system is the product of the two probabilities:

$$\pi = \pi_1 \pi_2$$

then:

$$f(\pi_1 \pi_2) = f(\pi_1) + f(\pi_2)$$

Assuming the complexity λ of the system as a function of dynamical states, then we have a relationship between entropy S and complexity λ

$$\lambda = g(S).$$

It follows that complexity is a state of function.

Open systems kept far from equilibrium exhibit spontaneous self-organization phenomena (order-formation) by dissipating energy toward the environment to compensate the entropy decreases. Some examples of self-organizing phenomena occurring in chemical systems are shown in Figure 4.

As a whole, the energy for pattern formation is minimized and self-organization (SO) is the inverse of entropy production. In agreement with the Shannon's formula [23] a possibile relationship between self-organization and entropy is

$$SO = 1 - \frac{S}{S_{max}}$$

where S/S_{max} is the ratio of the entropy to its maximum value S (Figure 5). Thus, if the system appears in a state of maximum disorder ($S \approx S_{max}$), then SO is close to zero and there is no order. If, however, ever, the elements in the system are ordered in a such a way that "given one element, the position of all other elements are well-determined" (= well-defined structural relation among the elements) then the system's entropy S vanishes to zero. Thus, self-organizing system is one whose "internal order" increases over time, and SO becomes unity, indicating a complex system with perfect order (= pattern formation). As a result, an inverse correlation between entropy and complexity of the system exists.

4. CONCLUSIONS

In the present work, some new concepts and theoretical descriptions have been introduced for decoding the complexity of catalytic reactions. Specifically, the following considerations have been proposed:

- The catalyst acts as a hyperoperator computing a non-linear combination of complexity structures; then, the overall complexity of a catalytic reaction appears different from a sum of different factors.
- The complexity of a catalytic reaction can be described through a non-linear combination of chemical complexity and structural complexity. The latter is characterized through the fractal dimension.
- The physico-chemical properties of a solid catalyst depend on the geometric and electronic factors and they are able to influence with each other. The structural complexity of solid catalysts, and hence their catalytic behavior, can be approximately described by considering one of these two factors.
- Catalytic processes can be either well or ill-conditioned systems, depending on the condition number (k). A catalytic system with a low k value is said to be well-conditioned, while a system with a high k is ill-conditioned.
- Structure-sensitive reactions can be classified as ill-conditioned systems, since small variations on the surface properties produce large effects on the catalytic activity.
- The overall complexity of a catalytic system is a state of function.
- There is an inverse correlation between entropy and complexity.

It must be pointed out, however, that the proposed concepts have to be experimentally confirmed. Then, new investigations are required for decoding the complex behavior of catalytic reactions.

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FIGURE CAPTIONS

Figure 1. Examples of complexity structures in heterogeneous catalysis. Adapted from [15].

Figure 2. Hyperplane in the space-time domain.

Figure 3. Geometric descriptions of real surfaces.

Figure 4. Examples of self-organizing phenomena occurring in chemical systems.
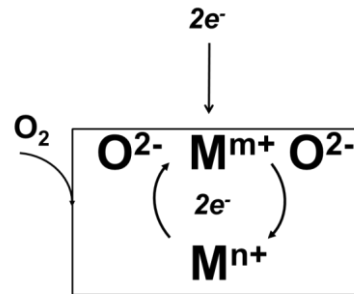
Figure 4. Relationship between self-organization and entropy.
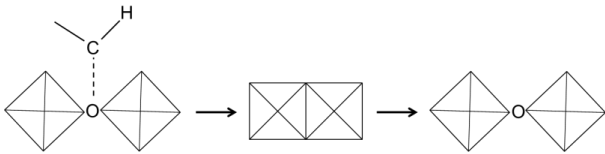
TRANSPORT PHENOMENA IN THE CATALYST

DYNAMIC BEHAVIOUR
Ensembles of sites and electrons interacting in a dynamic network.

$$2e^-$$

$$O_2 \quad O^{2-} \; M^{m+} \; O^{2-}$$

$$2e^-$$

$$M^{n+}$$

SELF-REPAIRING
Self-repair mechanisms of the active sites

SYNERGY EFFECTS
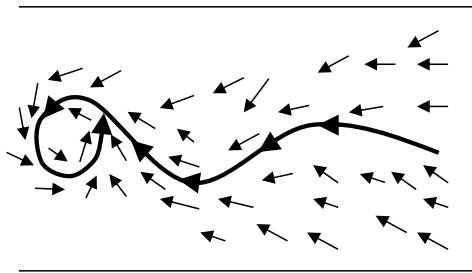Active sites on the surface mutually interacting each other.
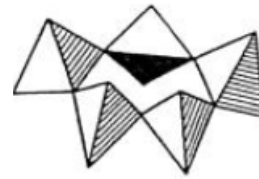
FIGURE 1
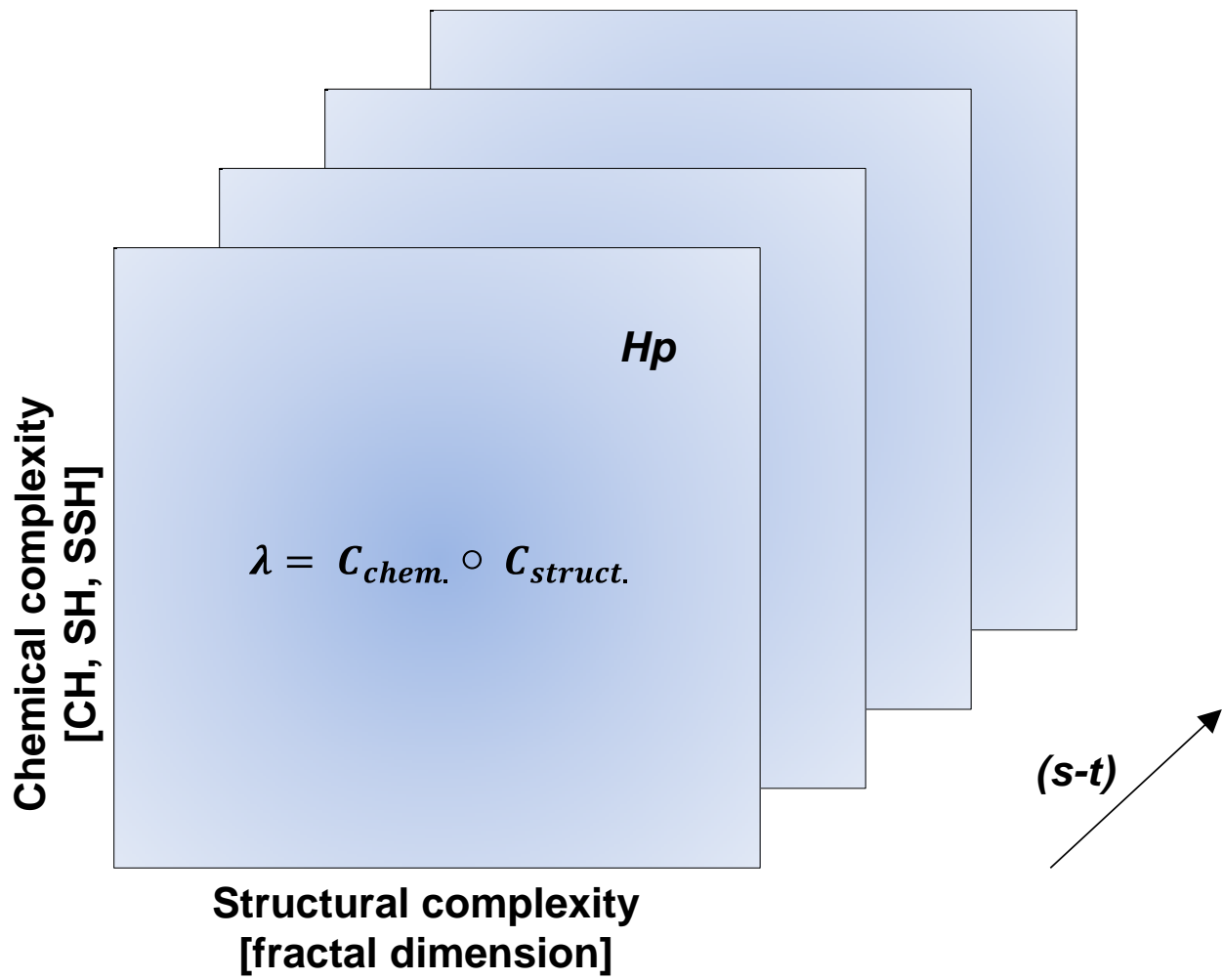
FIGURE 2
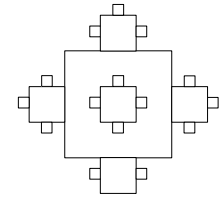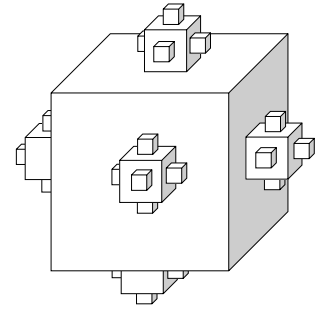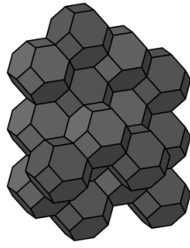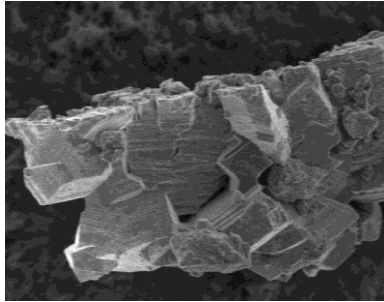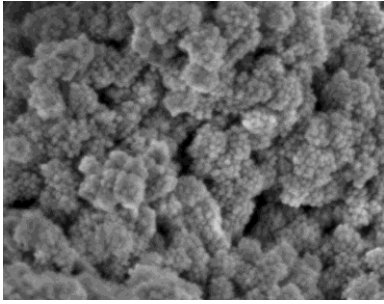
Cubic composition
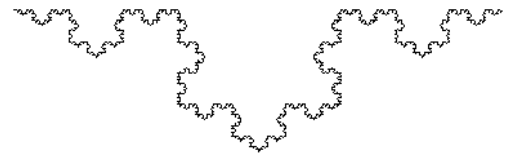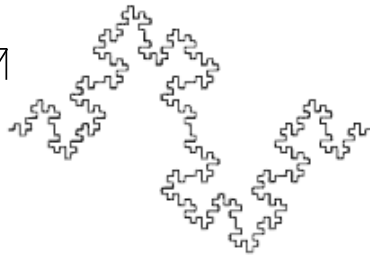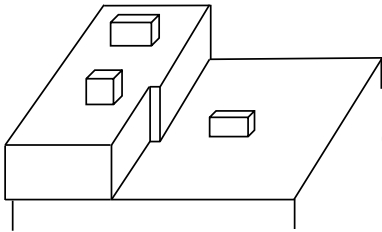
FIGURE 3

Dynamic flow of molecules
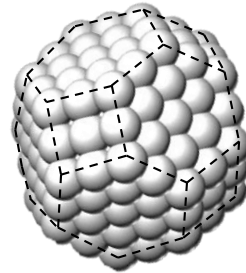
Cluster of metal atoms

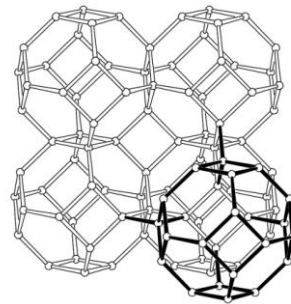**(111)**   **(100)**   **(110)**
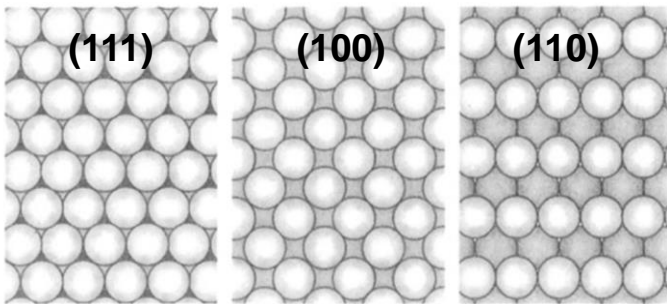
Ideal surfaces of a FCC crystal

Assembly of supertetrahedra in a zeolite

FIGURE 4

FIGURE 5