Marco Piumetti

Complexity structures of active sites in catalysis

MARCO PIUMETTI[1]*, NIKOS LYGEROS[2]

*Corresponding author

1. Department of Applied Science and Technology, Institute of Chemistry, Corso Duca degli Abruzzi 24, Politecnico di Torino, I-10129, Turin, Italy
2. LGPC (UMR 5285), Université de Lyon, 69616, Villeurbanne, France

ABSTRACT

Four types of solid catalysts, having different complexity structures, are considered in this mini-review to show the key role of self-organizing phenomena in catalysis: i) single-site heterogeneous catalysts; ii) supported metal nanoparticles; iii) zeolites and iv) transition metal oxides operating via redox cycles. These self-organizing phenomena are an intrinsic property of any catalyst and reflect different complexity structures, as the self-repair and reorganization of active sites, the mutual interactions between neighbouring sites, the mass transfer limitations (i.e. shape selective control), the dynamic networks of "sites-joined", etc. Consequently, the catalytic process typically results in a non-linear combination of various complexity structures and hence catalytic behaviours may appear. All these aspects are considered in the present paper to illustrate the nature of active sites and their complexity in catalysis.

48

INTRODUCTION

Many investigations have confirmed that active sites are dynamic entities that can continuously change their physico-chemical properties depending on the reaction conditions (1,2).

It has been demonstrated that active centres may include more than one single site to form "reactive groups" (3). For instance, in the case of dissociative hydrogen adsorption on Pd(111) surface, an aggregate of three or more vacant sites is needed to form an active centre for efficient H_2 dissociation, as revealed by dynamic STM analysis and DFT calculations (4, 5). Similarly, spectroscopic studies have shown that the activity of sulfonic acid resins for reactions taking place in a network of $–SO_3H$ groups (i.e. dehydration reactions of alcohols) is typically higher than that of resins with isolated $–SO_3H$, suggesting the important role of H-bonded active networks (5).

However, with the exception of the simplest gas-phase reactions, a detailed knowledge of reaction mechanisms (i.e. kinetic parameters for the individual steps) is often very difficult to achieve (6-10). During a reaction, indeed, the catalyst surface usually interacts with a mix of fluctuating molecules (i.e. reactants, products, pollutants, etc…). Therefore, many active centres (or regions) on the surface may interact with each other through mass transport phenomena and/or surface strain (2, 7). Typically, the more complex the reaction, the slower the turnover rate as the elementary reaction steps involve more complex molecular rearrangements (11).Moreover, the catalyst surface may regenerate itself through the products desorption, the self-repair and reorganization of active sites and their environment after each catalytic cycle. This means that catalysts may operate through sophisticated self-organizing phenomena taking place on the catalyst surface, in which both structural and chemical complexity play a role (6).

The concept of "self-organization" indicates the formation of order in both thermodynamically closed and open chemical systems (2). Closed systems tend to reach equilibrium by lowering their free energy, although kinetic constrains may limit the attainment of full equilibrium. On the other hand, open systems far from the equilibrium (i.e. reactions at steady-state flow conditions) exhibit the interplay between chemical reactions and transport phenomena. These systems belong to the category of irreversible processes creating entropy and may be described through kinetic equations with broken time symmetry instead of canonical equations (12). This leads to the formation of concentration patterns and structures on mesoscopic (i.e. > 1 µm) scale in the framework of non-linear dynamics (2).

These non-equilibrium systems were first investigated by I. Prigogine (Nobel Prize 1977) (13) who denoted them as "dissipative structures". Specifically, Prigogine showed the complexity of time in non-equilibrium systems, through the concepts of symmetry breaking, irreversibility and time's arrow. This means that catalytic reactions cannot be reduced to classical dynamics or quantum mechanics in deterministic, time-reversible descriptions (12). Therefore, the temporal behaviour of such systems can be described by a series of coupled non-linear differential equations for the individual concentration variables. However, it is not possible to know exactly the temporal and spatial self-organizing phenomena occurring in open systems far from equilibrium due to fundamental limitations originating in the mathematical structures (8). The causality of time-space seems inaccessible by strictly deterministic processes, and the complexity of time is still greater than one can imagine in a linear framework (14).

Such effects have been investigated for CO oxidation over Pt single crystal surfaces by G. Ertl (Nobel Prize 2007) (2, 8, 15). Ertl and co-workers, indeed, revealed that under certain external conditions (i.e. p_{CO} and temperature) the Pt surface can alternate between two states with high and low activities,

giving rise to regular oscillations in reaction rate. However, at high CO partial pressure (p_{CO} = 5.2 10^{-5} mbar) a new irregular dynamic behaviour takes place, reflecting the transition to chaotic phenomena (8). Such phenomena occur in different areas of the catalyst surface and require some forms of interaction between different sites (or regions) and spatial self-organization (8, 15).

In agreement with our previous study (16), the aim of this paper is to underline the complex nature of active sites, namely complexity structures, corresponding to different types of solid catalysts, with a focus on the self-organizing phenomena occurring in open systems. Indeed, these phenomena can be found in catalytic systems and may reflect various complexity structures, such as the self-repair and reorganization of active sites, the interactions between adjacent sites, the mass transfer limitations, the dynamic active networks of "sites-joined", and so on.

SINGLE-SITE HETEROGENEOUS CATALYSTS

These "dream catalysts" are highly desired in the field of heterogeneous catalysis, since they provide high selectivities in a wide variety of catalytic reactions (i.e. selective oxidations, selective hydrogenations, isomerizations, oligomerizations, etc.) (17-19). Indeed, a key factor in the design of highly selective heterogeneous catalysts is the isolation of active sites in which:
i) no complications (i.e. oscillatory or chaotic behaviour) arise as a consequence of interactions between neighbouring sites;
(ii) the chemical kinetics are similar to those observed for single-site homogeneous catalysis (20).
As a whole, one can refer to different types of SSHCs:
i) isolated active sites (i.e. ions, atoms, molecular complexes or bimetallic clusters) anchored to high-surface area solid supports (i.e. micro-/mesoporous silica); ii) immobilized asymmetric organometallic species at high-surface area mesoporous materials (pore diameters 15 to 50 nm); iii) "Ship-in-bottle" structures, in which isolated active sites are entrapped within zeolitic cages that are accessible to certain molecules;
iv) microporous materials with pore diameters in the range from ca. 3.5 Å to 10 Å in which the active sites are located at (or adjacent to) ions that have replaced framework ions of the parent structure (19). Here, we refer to transition metal ions (i.e. Ti, V, Fe, Cr etc.) grafted on to high surface area silicas, in which "no" electric fields and/or mutual interactions arise among different sites either in the framework or extra-framework. Moreover, we consider materials in which mass transfer limitations do not play a significant role on the catalytic behavior of SSHCs. On the contrary, these assumptions cannot be considered valid for multicomponent systems (i.e. zeolites) in which self-organizing phenomena take place on various forms. Typically, an important step of reactions at solid surfaces concerns the self-repair of the weakened (or disrupted) bonds once the catalytic cycle has been concluded. Indeed, to regenerate the active sites, the displaced atoms must return to their original positions. Self-repair processes are an intrinsic property of any effective catalyst and occur locally at each active site. They represent the lowest level of self-organization phenomena occurring at catalytic surfaces (10) and hence can be also expected in active and selective SSHCs.

An example that illustrates the importance of self-repair mechanisms in heterogeneous catalysis is found in the Ti-Silicalite (TS-1) catalyst, very effective for epoxidation of linear olefins with aqueous H_2O_2 as oxidant.

In this catalyst, titanium isomorphously replaces silicon in a tetrahedral site of MFI structure (10). It has been observed that in an active selective TS-1, titanium is present in tetrahedral coordination, preferentially as isolated Ti(IV) atoms. Moreover,

two different types of Ti centres can be observed in TS-1 catalysts: the so-called perfect "closed" Ti(OSi)$_4$ tetrahedral site and the defective "open" structure, Ti(OSi)$_3$(OH). The latter can be considered as deriving from the "regular" closed site by hydrolysis of one Si-O-Ti bridge or deriving from incomplete reaction of Ti(IV) with the hydroxyls of a nest (21). When contacted with a single-site Ti(IV) site, the reaction takes place involving a peracid-like mechanism with an electrophilic cyclic structure as active centre (21, 22). A schematization of this reaction mechanism is illustrated in Figure 1. The marked ability of Ti sites inside the silicalite framework to self-repair in a reversible (or nearly reversible) way their local environment upon interaction with adsorbates is probably the key of the reactivity of this important material (23). This renders such material a powerful Lewis catalyst for a range of low-temperature oxidation reactions with H_2O_2, including the hydroxylation of benzene, the ammoximation of cyclohexanone, the epoxidation of olefins, the oxidation of hydrocarbons and alcohols, etc. (24, 25). Although weak electrostatic interactions occur between neighbouring Ti atoms, the support itself may play a key role during reaction, influencing not only the active phase dispersion and mass transfer phenomena, but also the reactivity of active centres and their coordination environments (26, 27). On the other hand, mass transfer limitations may be significantly reduced with Ti-containing mesoporous silicas (i.e. Ti-SBA-15, Ti-MCM-41, Ti-MCF, etc.), although the self-repair mechanism of active sites could be less effective in large pores of amorphous silica.

SMALL METAL PARTICLES

During the last few decades, nanoscale metal particles dispersed in micro- and mesoporous materials have attracted much attention due to their important applications in heterogeneous catalysis. It is well known that both the activity and selectivity of several nanostructured systems may be intimately related to the size and shape of the metal particles, as well as to the features of the support (28-31).

Physico-chemical properties of nano-sized metal particles mainly change as a function of their size. Typically, small metal particles are more reactive than larger ones due to the higher number of coordinatively unsaturated surface sites. For instance, the relative fractions of exposed corner and edge
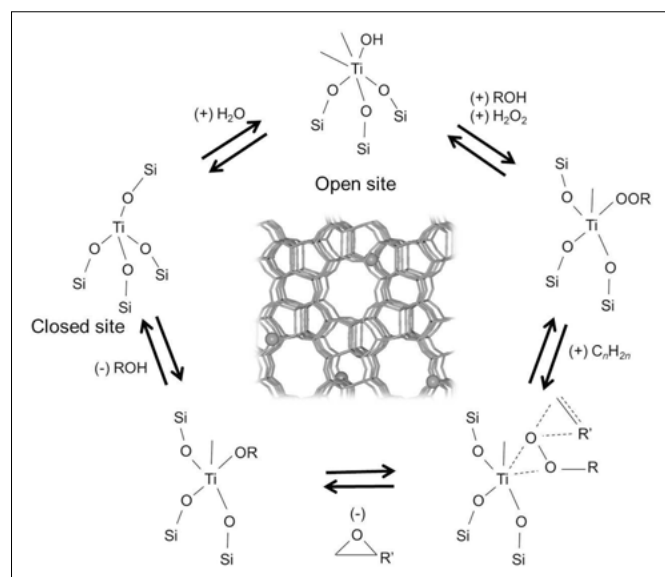

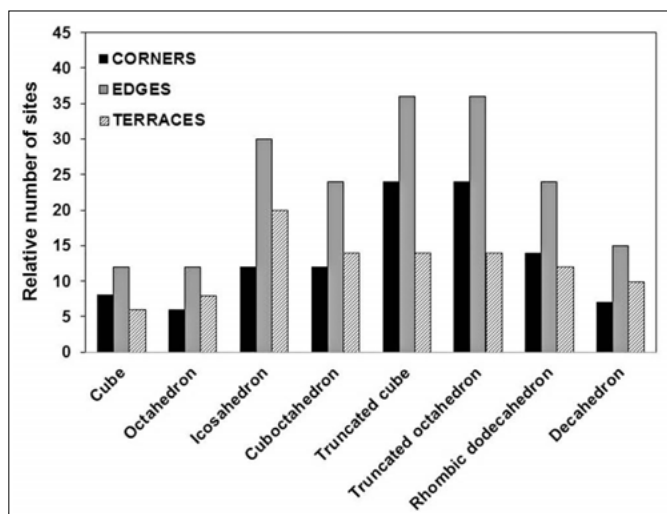*Figure 1. Epoxidation reaction cycle by Ti sites in TS-1. Adapted from (10, 22).*

49

Figure 2. Numbers of edges, corners and terraces of particles having various convex structures.

atoms for nanogold increase significantly as the particles' size is lower than 3-4 nm, as showed elsewhere (16). However, the relative amounts of these surface sites, and hence the catalytic activities, vary considerably with the particles' size, i.e. in the range from 1 to 10 nm.

As previously recognized by Langmuir (33) *"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"*. Consequently, inward relaxation and reconstruction of surfaces (self-repair phenomena) are much more marked at low coordination sites (i.e. steps and corners) which are more "flexible" and self-repair the surface at higher rates. Indeed, the faster the rate of restructuring, the higher the reaction turnover rate, although it has also been observed that rapid restructuring of surfaces may cause instability (34).

The equilibrium shape of a metal nanoparticle is determined by the Wulff rule (35), according to which the convex envelope of planes (perpendicular to the surface normal) minimize the surface energy for a given enclosed volume (36). Depending on the surface energy of the facets and on the adsorption bond strength of molecules from the surrounding gas-phase, metal nano-sized particles typically form convex polyhedral structures, having the Euler characteristic of the sphere ($\chi = 2$). These structures are dominated by various crystallographic faces which exhibit different surface atom densities, electronic structure, bonding, chemical reactivities and thermodynamic properties (37, 38). In addition, the relative ratios of edge, corner and terrace sites mainly depend on the particle's shape, as shown in Figure 2. Consequently, changes in the specific particle's shape and atomic structure lead to different reactivities of the corresponding surface sites, since their coordination numbers vary.

Many studies have investigated the equilibrium shapes of fcc metal nanoparticles (i.e. gold, platinum and palladium) showing several convex polyhedra structures, including icosahedron and truncated icosahedron, decahedron, truncated octahedron and cuboctahedron (or variants of these shapes), as well as singly or multiply twinned (fcc) structures (37-39). Non-convex structures ($\chi \neq 2$) like Kepler-Poinsot polyhedra may also form as a consequence of selective passivation and blocking of edge and corner sites during growth, coupled with anisotropic growth rates in different orientations (40).

Although many of the computational and theoretical studies agree on the energetic order of different particle's shapes, they do not necessary agree with experimental observations.

These discrepancies between experimental data and thermodynamic modelling of metal nanoparticles are often attributed to kinetic effects. Consequently, the competition (or cooperation) between kinetic and thermodynamic factors leads to non-linear self-organizing phenomena at solid surfaces. On the other hand, mutual interactions between neighbouring sites take place to form catalytically active regions (or sites) variable both in space and time, as a function of the external conditions. The presence of metal oxides, the electrostatic interactions between metal particles and support, the acid-base and redox properties of support further increase the complexity of these catalytic systems and hence non-linear dynamics are expected during reactions.

ZEOLITES

Zeolites are multicomponent materials made up of tiny crystals of specific morphologies, containing a number of defects of various origins and a certain nanoscopic (at unit cell level) and macroscopic (at crystal level) distribution of active centres, either acid, basic or redox, or a combination of them (41-43). These 3-D catalysts can act as reaction channels whose reactivity can be modified by introducing transition metals and many group elements, such as B, Ga, Fe, Cr, Ge, Ti, V, Mn, Co, etc. (41). Indeed, whereas pure silica frameworks are electrically neutral, the substitution of trivalent aluminum for tetravalent silicon imparts a negative charge to the material that has to be balanced by positively charged extra-framework cations. Consequently, the presence of strong electric fields and controllable adsorption features within the pores will produce a unique type of catalytic material (41).

Similar to enzymes, zeolites with their well-defined microporous non-convex structures 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 (42). As is known, different types of shape selectivity may occur within a given zeolitic structure: i) reactant selectivity; ii) product selectivity and iii) transition-state selectivity (43). 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. Therefore, the reaction pathway can be strongly influenced by the framework geometry in the neighborhood of the active site and hence the steric constraints assume a significant importance for driving the reaction towards the desired products (41). Typical examples of transition-state selectivity include the inhibition of coke formation within ZSM-5 crystals and the cracking of paraffins within the pores (45).

Zeolite catalysts 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. The polarity of a given zeolite can be modified by varying the Si/Al ratio during the direct synthesis (or post-synthesis treatments) and hence it is possible to prepare zeolites within a wide range of surface polarities (41). As a whole, when a guest molecule presents a polar character and/or the zeolitic framework is not purely siliceous, the electrostatic interactions cannot be neglected. Specifically, when a molecule is confined in the pores of a zeolite, the sorption energy depends on different energetic terms. Indeed, the electric field and its gradient play a significant role in the adsorption and reactivity of hydrocarbons within the pores of zeolites, as observed with the cracking of paraffins on several aluminosilicates. While the effect of field gradients, which weaken some hydrocarbon bonds, depends on the charge density (i.e. aluminum content), the temperature, the zeolitic structure and the polarizing effect of cations (44).

The complexity of zeolites is still greater if one considers them as acid catalysts. The latter usually contain Brønsted acid OH groups, SiO(H)Al(OSi)$_3$, which represent the active sites and are capable of activating chemical bonds (41, 45). Thus, the total number of Brønsted sites in protonated zeolites (i.e. H-faujasite, H-ZSM-5, H-chabazite, etc.) is, in principle, directly related to the total number of framework T^{III} atoms present (41). The acid strength of sites can be also modified by isomorphic substitution of Si for trivalent atoms other than Al, such as Ga- and B-substituted zeolites showing stronger and weaker Brønsted sites, respectively (41). The framework types and the crystallographic positions of sites play an important role on the acidity of zeolites (45). The control of zeolite acidity is of paramount importance 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 the feedstocks and the reaction pathways network, the number of products is very huge. Therefore, these systems 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.

METAL OXIDE CATALYSTS OPERATING THROUGH REDOX CYCLES

Many catalytic oxidation reactions promoted by transition metal oxides take place via a Mars-van Krevelen mechanism (MvK) (46), whereby the active sites are not isolated species, but ensembles of atoms (ions) and electrons mutually interacting in a catalytically active network (47, 48). Consequently, these catalytic systems exhibit a high self-organization level since a dynamic network of "sites-joined" may promote both selective and total oxidation reactions (17, 47-49).

As a whole, two redox processes take place during catalytic reaction, one consisting in the injection of electrons into the catalyst, the other extracting electrons them from the oxide. This redox-cycle mechanism occurs quite frequently in selective oxidation reactions over vanadium oxide catalysts as originally described by P. Mars and D. van Krevelen (46). There is evidence, however, that also other metal oxides, such as those of Mo, Cr, and Fe can operate via redox cycles (10, 47-49). The basic requirement for the MvK mechanism seems to be the presence of i) a facile redox behaviour of the supported metal (i.e. V, Cr, Mo, etc...) and ii) a good mobility of both electrons and lattice oxygen anions within the framework (47,48). Other factors comprise the facile activation of reactant molecules, the presence of surface defects, the surface acid-base properties, and the reaction temperature (47-49). Surface reactivity also depends on the nature of the oxygen species. The different oxygen species on the surface have different stabilities and may react differently, *i.e.* via electrophilic or nucleophilic attack. Lattice O^{-2} ions at the surface are nucleophilic reagents and are usually responsible for selective oxidation, whereas electrophilic oxygen species (i.e. O$_2^-$, O$_2^{-2}$ and O$^-$) are highly reactive and eventually results in total oxidation. Moreover, the metal-oxygen interactions, as well as the properties of oxygen, are strongly affected by the electronegativity of the element present in the support (i.e. Al, Ti, Si) (10, 47-49). As a consequence, the effectiveness of active species may be largely conditioned by the support material.

The complexity of these catalysts, working in a dynamic active network, is further conditioned by the fact that acid-base and redox properties may be closely related to each other. For instance, it has been recently observed that the Oxidative DeHydrogenation (ODH) of propane over VO$_x$-SiO$_2$

catalysts also depends on the Brønsted acidity of V species, as measured by IR spectroscopy (50-52). The best catalysts (in terms of selectivity to propene) were characterized by the presence of weaker Brønsted acid sites. On the other hand, the oxidation state of surface V species seems to play a role in catalyst selectivity (53).

Therefore, many variables influence the performance of these redox catalysts, having ensembles of atoms (ions) and electrons mutually interacting in a catalytically active network. This further suggests that such systems are very sensitive to the operative conditions. Indeed, F. Cavani and co-workers (54) showed that the active layer in vanadium/phosphorus mixed oxide catalyst (VPO), effective for n-butane oxidation to maleic anhydride, depends not only on the VPO features (i.e. P/V ratio and oxidation degree), but also on the reaction conditions, including the temperature and the hydrolysis of the active surface. Similarly, previous studies revealed that surface redox-cycles on transition metal oxides typically occur at moderate temperatures (i.e. in the range from 300 to 500 °C) being replaced at higher temperature by radical processes in the gas-phase. However, below 100 °C oxidation reactions may occur through peroxidic mechanisms, in which adsorbed radicals are directly involved. A "transitional region" in the temperature range from 100 to 300 °C has been proposed in with complex surface re-oxidation mechanisms take place, and the latter should be responsible for the formation of total oxidation products (55). This means that both structural and chemical complexity are closely related to each other in transition metal oxide catalysts operating through a Mvk mechanism.

CONCLUDING REMARKS

In this paper four types of catalysts, having different complexity structures, have been briefly reviewed. It has been showed that self-organizing phenomena on the catalyst may occur in different ways, including the self-repair and reorganization of active sites, the mutual interactions between neighbouring sites, the presence of dynamic active networks and the mass transfer limitations (i.e. shape selective control). This means that self-organizing phenomena reflect different complexity structures of active sites, as schematized in Figure 3. The latter figure shows a possible classification of various complexity structures observed in different solid catalysts, namely single-site heterogeneous catalysts, supported metal nanoparticles,
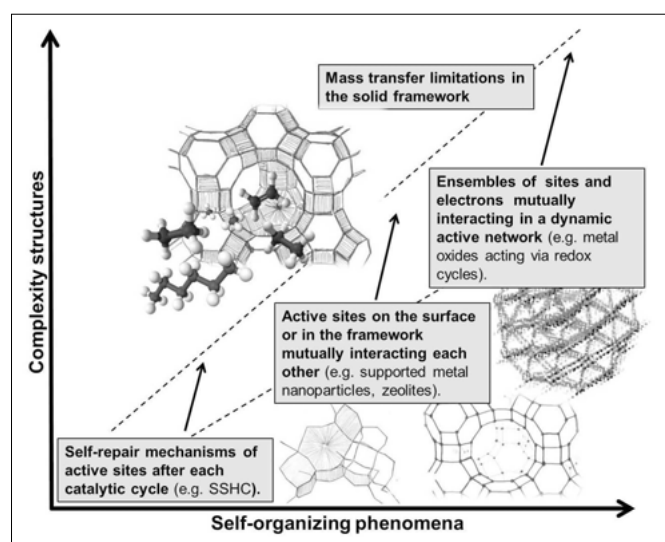
Figure 3. Complexity structures corresponding to self-organizing phenomena observed in different solid catalysts.

zeolites and transition metal oxides acting via redox cycles. On the other hand, mass transfer phenomena further increase their complexity depending on the type of catalyst structure, as well. Consequently, the catalytic process typically results in a non-linear combination of complexity structures and hence catalytic behaviours may appear. This suggests the possibility of having non-reproducible reactions, both in terms of reaction pathways and products, especially with multicomponent catalysts.

All these topics are under investigation and the algebraic hyperstructures (56, 57) will be considered in the next studies as model to describe the complexity of catalysis.

ACKNOWLEDGEMENTS

REFERENCES AND NOTES

1. Che M., Védrine J.C., *Characterization of Solid Materials and Heterogeneous Catalysts*, Chapter I, Ed. Wiley-VCH, Weinheim (2012).
2. Ertl G., *Reactions at Solid Surfaces,* Ed. Wiley-VCH, Hoboken (2009).
3. Deutschman O., Knözinger H., Kochloefl K., Turek T., *Ullman's Encyclopedia of Industrial Chemistry*, Chapter XVII, Ed. Wiley-VCH, Weinheim (2012).
4. Mitsui T., Rose M.K., et al., *Nature,* **422**, 705-707 (2003).
5. Ertl G., Knözinger H. et al., *Handbook of Heterogeneous Catalysis*, 2nd ed., Chapter I, Ed. Wiley-VCH, Weinheim (2008).
6. Libuda J., Schauermann S., et al., *Monatshefte fur Chemie,* **136**, 59-75 (2005).
7. Libuda J., Schalow T., et al., *Microchimic Acta,* **156**, 9-20 (2007).
8. Ertl G., *Angew. Chem. Int. Ed. Engl.*, **29 (11)**, 1219-1227 (1990).
9. Libuda J., Freund H.J., *J. Phys. Chem. B,* **106**, 4901-4915 (2002).
10. Van Santen R.A., Neurock M., *Molecular Heterogeneous Catalysis*, Ed. Wiley-VCH, Weinheim (2006).
11. Samorjai G.A., Contreras A.M., et al., *PNAS,* **103**, 10577-10583 (2006).
12. Prigogine I., *Ann. N.Y. Acad. Sci.,* **988**, 128-132 (2003).
13. Nicolis G., Prigogine I., *Self-Organization in Non-Equilibrium Systems*, Ed. Wiley-VCH, New York (1977).
14. Hawking S., Penrose R., *The Nature of Space and Time*, Ed. Princeton University Press, Princeton (1996).
15. Ertl G., *Angew. Chem. Int. Ed.,* **47**, 3524-3535 (2008).
16. Piumetti M., Freyria F.S., Bonelli B., *Chem. Today,* **31(4)**, 55-58 (2013).
17. Thomas J.M., *Top. Catal.,* **50**, 98-105 (2008).
18. Thomas J.M., *Proc. R. Soc. A,* **468**, 1884-1903 (2012).
19. Thomas J.M., Raja R, et al., Angew. Chem. Int. Ed., **44(40)**, 6456-6682 (2005).
20. Psaro R., Lecture, School of Catalysis GIC-2008, Certosa di Pontignano - Italy (2008).
21. Damin A., Bonino F., et al., *J. Phys. Chem. B,* **106**, 7524-7526 (2002).
22. Beller M., Renken A., et al., *Catalysis,* Ed. Wiley-VCH, Weinheim (2012).
23. Lamberti C., Bordiga S., et al., *J. Phys. Chem B,* **102**, 6382-6390 (1998).
24. Aloise A., Bonelli B., et al., *Nuovo Cimento B,* **123 (11-12)**, 1425-1433 (2008).
25. Barbera D., Cavani F., et al., *J. Catal.,* **275**, 158-169 (2010).
26. Piumetti M., Armandi M., et al., *Microporous Mesoporous Mater.* **164**, 111-119 (2012).
27. Piumetti M., Garrone E., et al., *Chem. Today* **30 (3)**, 29-32 (2012).
28. Mager-Maury C., Chizallet C., et al. *ACS Catal.*, **2**, 1346-1357 (2012).
29. Barnard A.S., Chen Y., *J. Mater. Chem.*, **21**, 12239-12245 (2011).
30. Somorjai G.A., Park J.Y., *Catal. Letters*, **115**, 87-98 (2007).
31. Hu C.H., Chizallet C., et al., *J. Catal.,* **274**, 99-110 (2010).
32. Thomas J.M., Raja R., *Top. Catal.,* **53**, 848-858 (2010).
33. Langmuir I., *J. Am. Chem. Soc.*, **38**, 2221-2295 (1916).
34. Somorjai G.A., *Langmuir*, **7**, 3176-3182 (1991).
35. Wulff G.Z., *Kristallogr. Mineral.*, **34**, 449-530 (1901).
36. Barnard A.S., *J. Phys. Chem. B*, **110**, 24498-24504 (2006).
37. Barnard A.S., *Accounts Chem. Res.*, **45**, 1688-1697 (2012).
38. Barnard A.S., Curtiss L.S., *ChemPhysChem*, **7**, 1544-1553 (2006).
39. Mager-Maury C., Bonnard G., et al., *ChemCatChem*, **3**, 200-207 (2011).
40. Barnard A.S., Personal Communication (2013).

52

inform[Ex]

Celebrating our 30th Edition
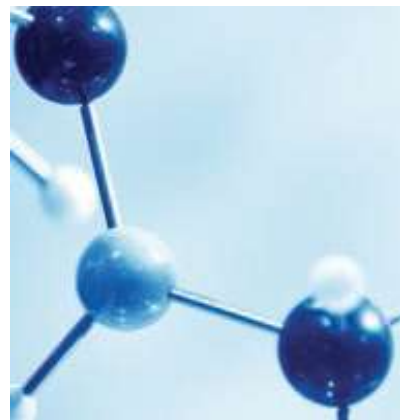
January 21–24
2014
Miami Beach, Florida

REGISTER NOW!

Where R&D, Procurement, and Custom Manufacturing Connect.

Find Us: www.informex.com

in t f

#myinformex

In Partnership with:

SOCMA
Society of Chemical Manufacturers & Affiliates

UBM