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New possibilities and opportunities for basic and applied research on selective oxidation by solid catalysts: an overview

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Abstract

This introductory contribution to the issue 'New Concepts in Selective Oxidation over Heterogenous Catalysts' provides an overview of the specific contributions on different selected topics to put them in a more general and comprehensive perspective and, in particular, outlines the possible extensions and limitations of the new concepts discussed in this issue. Four main topics are discussed: (i) development of catalysts/technologies for selective oxidation at room temperature using dioxygen, (ii) new approaches to generate active oxygen species, (iii) the search for new types of oxidation catalysts and (iv) new opportunities for oxidation catalysts. A final short section is included to comment some new possible directions for future research in terms of new types of oxidation syntheses. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

About a quarter of the industrial production of monomers and chemical intermediates is made using selective oxidation processes on solid catalysts and there is thus wide basic and applied interest for this area of the research. Most of the catalysts used in these industrial processes are well established, but there is still need for further (minor) improvements based on both better engineering of the process (reactor design, in particular) and better tuning of catalyst reactivity and properties [1]. There are also some clear driving forces which stimulate new breakthroughs in this area and thus the development of new processes and catalysts: (i) the use of new, more economical, raw materials (alkanes, in particular, in substitution for the olefinic feedstocks; an example is the process of acrylonitrile synthesis from propane instead of that from propene [2]) and (ii) the ecological issue (for example, cyclohexanone ammoximation to the corresponding oxime and consecutive Beckman rearrangement made using metal-zeolites in order to avoid the large production of ammonium sulphate that occurs in the conventional process [3]).

An example of a recent breakthrough in the field of selective oxidation is the discovery of Ti-silicalite (TS-1) and its applications [4] which also stimulated a large and more general interest on the use of transition metal containing microporous materials for liquid phase heterogeneous conversion of hydrocarbons using either H_2O_2 or other peroxo compounds. The problems of (i) transition metal leaching and catalyst deactivation (apart from the

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specific case of TS-1) and (ii) the cost of these oxidation reagents (H_2O_2, organic peroxides, etc.), however, have considerably limited the possibility of industrial application of these reactions. Another area of considerable research interest originated from the discovery of the methane coupling reaction [6], although the difficulty in reaching acceptable yields in products has led to a decrease in the scientific interest in recent years.

Notwithstanding the problems in arriving at a practical application, the two above fields of activity are breakthroughs in the area, because they have extended the horizons of selective oxidation, introducing new concepts: (i) selective oxidation at isolated metal ions using H_2O_2, but in an hydrophobic local environment and with the metal ion anchored to a quasi-rigid solid matrix (both these factors are the key parameters which allow the stability, selectivity and nearly negligible activity in H_2O_2 decomposition of TS-1), and (ii) the selective behavior of gas phase radical reactions, which are initiated at the solid surface. The two above examples also illustrate that after the discovery of a new catalyst or reaction the subsequent research activity is initially driven mainly by the 'analogy factor', but then the identification of the key concept(s) is the necessary step to establish the basis for a more scientific approach and eventually to arrive at practical applications. The identification of new key concepts is thus a fundamental element of stimulus of innovation and at the same time an indicator of the dynamism of a scientific field.

The analysis of the field of selective oxidation at solid surfaces in terms of new concepts developed in recent years, however, reveals a general lack of elements of novelty with a consequent absence of main directions of research, and scientific activity mainly is confined to consolidating knowledge on existing catalysts and reactions, rather than being focused on exploration of new directions of research. There are, however, some side areas under initial development which can open 'fresh' new prospects and thus can act as a stimulus for innovative breakthroughs and the discovery of new applications.

The scope of this issue 'New Concepts in Selective Oxidation over Heterogenous Catalysts' is to highlight some of these new areas, the concepts underlying and the possible (sometimes only speculative) extensions of these concepts. Each of the selected authors was asked to outline a specific area of research centred around a specific new concept, using the concept-by-example approach. In this contribution, these various parts are discussed in a common fashion and put in a more general perspective as the introduction to the specific following examples.

2. Catalysts and technologies for selective oxidation at room temperature using O_2

The selective oxidation processes using gaseous oxygen as the oxidizing agent can be classified in (1) high temperature processes usually on mixed oxide catalysts (gas–solid reaction) and based mainly on a Mars–van Krevelen type mechanism (the active sites are lattice oxygens and gaseous dioxygen simply reforms the site to close the catalytic site) and (2) low temperature processes in the liquid phase, usually involving a radical type mechanism with the oxygen activated by a homogeneous catalyst such as Co^{2+} salts or through hydrocarbon auto-oxidation processes [7]. The latter, however, still require relatively high temperatures/pressures and cannot be applied to a very wide range of substrates and types of oxidation reactions.

A challenge in the field of selective oxidation is thus to understand how to oxidize selectively hydrocarbons or other organic molecules under very mild conditions (room temperature, atmospheric pressure) using gaseous oxygen. In this issue, two different approaches are described to address this problem: (i) a photochemical approach [24] and (ii) an electrochemical approach [25].

The first approach is different from the classical oxidation photoactive catalysts, where usually a charge separation is produced from ultraviolet light and then gaseous oxygen is activated at localized surface electrons. Besides the cost of the energy source (recent developments indicate, however, the possibility of using visible light, for example on TiO_2 modified by transition metals added by ion implantation [8]) and other technical problems, the main limitation in this approach is the difficulty of controlling the reaction and thus selectivity. Usually, in this kind of photochemical oxidation a wide range of products is obtained. The new approach presented by Frei et al. [24] is based on a completely different concept. The hydrocarbon and oxygen are confined in a restricted environment (zeolitic cavities) and in the presence of a strong electrostatic field due to Ba^{2+} ions, react with each other when irradiated by visible light, selectively (100% selectivity in some cases) forming oxidation products, for example, toluene and oxygen to give benzaldehyde. Even light alkanes are selectively oxidized under these conditions. The concept is the induction of a charge transfer from the hydrocarbon to oxygen molecule to form a radical cation and a superoxide species due to absorption of a photon (or even spontaneously thermically), but in the presence of (i) a large electrostatic field which stabilizes the highly polar charge-transfer states and (ii) diffusional constraints to avoid radical coupling reactions.

Although the details of the reaction mechanism should be better clarified [for example, the Ba^{2+} ions are only responsible for the electrostatic field, or also play a direct role in the mechanism? What is the mechanism of charge transfer and the influence of zeolite properties (pore structure characteristics, Si/Al ratio, zeolite structure)? etc.], and there are several critical questions to solve before arriving at practical applications of the concept [for example, (i) the effective productivity and selectivity, (ii) the possibility to transfer to a flow system, (iii) the possible effect of other gas phase components such as water, etc.]. However, this area of research opens new prospects in the field of selective oxidation. It should also be noted that in theory this interesting chemistry is not only restricted to hydrocarbon–O_2 systems, but may be extended to other cases such as hydrocarbon–CO_2 and hydrocarbon–N_2 systems with thus a very wide range of possibilities.

The electrochemical approach described by Otsuka and Yamanaka [25] has in common with that of Frei et al. [24] the formation of oxygen species active at room temperature and very selective in hydrocarbon oxidation, but generated at the surface of an electrochemical cell. Different options are possible: (i) the hydrocarbon is oxidized by water at the anode site and the electrons formed used at the cathode side to form water from oxygen (ethylene oxidation to acetaldehyde, for example), (ii) the in situ generation of hydrogen peroxide at the cathode (in a H_2–O_2 fuel cell) which in the presence of Fe^{2+} ions (also generated in situ from Fe^{3+} salt) gives rise to the Fenton reagent, able, for example, to hydroxylate benzene to phenol, or (iii) even dual oxidation at the cathode and the anode (for example, the simultaneous epoxidation of propylene to propylene oxide at the anode and the benzene hydroxylation to phenol at the cathode). Besides the advantages in terms of separation of hydrocarbon and oxygen, room temperature operations and in some cases also of cogeneration of electricity, the electrochemical approach also offers the advantage of fine tuning the reactivity and selectivity by controlling the applied voltage. For example, in Wacker type oxidation of propylene on a Pd-black anode, the change in applied voltage determines not only the rate of formation of the products (acrolein, acetone, CO_2), but also especially their selectivity. Although also in this case problems exist in transferring the concepts to a practically applicable level (in particular cost and productivity), it can be stated that this approach is also a good direction towards the challenge of synthesizing chemicals on an industrial scale via selective oxidation at room temperature.

Two other contributions in this issue address the general question of developing new approaches to room temperature selective oxidation, but from a different perspectively, namely the biomimetic approach, ie. bioxidation reactions mimicking biological oxidative processes [26,27]. Enzymes which activate dioxygen to oxidize organic substrates can be classified in two types: dioxygenase incorporates two oxygen atoms into the substrate and monooxygenase transfers only one oxygen atom, but requires a cofactor [NAD(P)H]. Cytochrome P-450 is the better known example of the second and more interesting class of oxidation enzymes. The active species for the reaction is a high valent iron oxo species (Fe^{IV}=O) (oxene like) which forms by heterolytic O–O bond cleavage of the (Fe^{III})–O_2H^- species in the presence of H^+ ions. The latter species forms by dioxygen activation on Fe^{2+} ions (produced by an electron addition to the (Fe^{III})–P-450 enzyme) and requires a further electron and a proton addition to generate the precursor of the active iron oxo species. The role of NADPH is to mediate this electron and proton transfer, avoiding substrate degradation. The active iron oxo species may form in anaerobic conditions by reaction with peroxo species (‘shunt path’). A wide range of catalytic systems mimick this ‘shunt path’ concept of cytochrome P-450. Among the most effective are

Ti-silicalite (TS-1) and heteropoly compounds that in the presence of H_2O_2 are very selective in a range of mono-oxygen transfer reactions, such as olefin epoxidation, and aromatic and alkane hydroxylation. The obvious drawback is the quantitative consumption of expensive oxidants which limits the application to high value products. In the Section 3, this problem will be discussed in more detail.

The mimiking of the full concept of monooxygenase (formation of oxene-like active species with the assistance of protons and electrons from the strong reducing agent, NAD(P)H) may be expected to establish new effective oxidation systems with molecular oxygen, but a sacrifical reducing agent is required. A challenge in this area is to use H_2 as the reducing agent especially in terms of eco-compatibility (generation of H_2O) of the process, apart from the technical problems in its use due to the (i) low solubility in solution and (ii) large explosion limit region, which may be solved at least in part using new reactor engineering solutions (catalytic membrane diffusors for hydrogen). New developments in this area are the liquid phase selective hydroxylation of benzene to phenol on Pt–V_2O_5/SiO_2 catalysts [9] and propylene epoxidation on Au/TiO_2 catalysts [10] both using a O_2/H_2 feed. Both reactions occur under mild conditions (around 60°C) and are very selective, but in both cases a point of weakness is the waste of hydrogen and thus low selectivity when based on O_2. For the synthesis of fine chemicals, however, the use of different, but more reactive reductants are preferable. In this case aldehydes and oxygen can generate peracid that reacts for example with low valent ruthenium complexes [27] to form $Ru^{IV}{=}O$ complexes biomimetic of the P-450 enzyme. These complexes are active in a variety of reactions of interest for fine chemicals production such as oxidation of β-lactams, alcohols, alkanes and ketones. The reductive activation of oxygen is thus a new interesting direction for the development of new industrial oxidations.

3. New approaches to generate active oxygen species

In the Section 2, possibilities of generating active oxygen species at room temperature from gaseous O_2 in order to realize selective oxidation processes under very mild conditions were discussed, but also some of their drawbacks and limitations were shown. On the contrary, a huge amount of data exist in the literature about selective oxidations using mono-oxygen donors such as peroxide species, mainly using homogeneous complexes, but recently also using solid catalysts [5]. Hydrogen peroxide is the preferred agent in terms of cleanliness of its use, producing only water as the byproduct, but limitations for its application in the production of several chemicals (propylene oxide, for example) are (i) the cost of H_2O_2 production and (ii) the necessity of a dedicated plant for H_2O_2 production which is very capital intensive. A challenge in this area is thus to develop catalysts and technologies for the in situ generation of the H_2O_2 used for the oxidation of the organic substrate. This is the central topic of the contribution of Clerici and Ingallina (chap. 6).

There are various possible routes for the in situ generation of H_2O_2, but the two main routes of interest are the antraquinone route (analogous to the commercial route of hydrogen peroxide production) and the catalytic hydrogenation of oxygen, carried out on Pd-based heterogeneous catalysts in solution (an aqueous/organic solvent mixture) and in the presence of strong mineral acids and halide ions. The critical problem in developing an in situ H_2O_2 generation system is the compatibility of the reaction conditions (temperature, pressure, solvent, pH, etc.) with those of the consecutive step in which the H_2O_2 produced is used for the selective oxidation step. A number of problems are discussed in the contribution of Clerici and Ingallina (chap. 6) which, however, makes clear that in some cases (synthesis of propylene oxide, in particular) this technology can be very promising. It is also shown in this contribution that while recent progress in situ oxidations has been made possible by the discovery of effective oxidation catalysts (for example, Pt/V_2O_5–SiO_2 catalysts for the hydroxylation of benzene with a H_2/O_2 mixture, or transition metal complexes in the oxidation with aldehyde/oxygen mixtures), the methods for in situ generation of H_2O_2 or organic peroxides are substantially unchanged from previous known ex situ routes. Specific effort in this direction is thus necessary especially to minimize the mismatch between the optimal conditions required by the generation of the mono-oxygen donor (H_2O_2, organic peroxides, etc.) and the consecutive step of consumption of the mono-oxygen donor. In this connection, more efficient and economical ex situ production of H_2O_2 is still an important target of future research.

The contribution of Clerici and Ingallina [28] is centred on the generation and use of H_2O_2 in solution, but the same concept may be extended also to gas phase reactions. The propylene epoxidation on Au/TiO_2 using a H_2/O_2 feed [10] (see also Section 2) is an example of this concept applied to a gas phase situation. A main reason why gold is used in this case instead of palladium (Pd/C is the preferable catalyst for H_2O_2 synthesis from H_2/O_2 in solution) is that palladium is active for the reaction only when it is in the reduced form. Differently from the liquid phase, in the presence of gaseous O_2 oxidation of the Pd surface is fast, whereas gold is not oxidized. This example evidences that notwithstanding the apparent analogy between liquid–solid and gas–solid generation of H_2O_2, the catalyst must possess different key properties and thus care must be taken in simply transferring by analogy one example to a different situation without having analyzed the problem in detail.

The concept of generation of H_2O_2 at a gas–solid interface may be applied not only to the formation of mono-oxygen donor species which are then the active element for selective oxidation (in the case of Au/TiO_2 probably a Ti–OOH surface species is responsible for propylene epoxidation), but also to other cases which can widen the field of application of this concept. For example, it is possible to generate singlet oxygen by reaction of H_2O_2 with some catalysts [(MoO_4^{2-}, $Ca(OH)_2$] [11] and the reactivity of this singlet oxygen is certainly different from that typical of mono-oxygen donor species. It can thus be expected that using this approach (generation of H_2O_2 at gas–solid interfaces from H_2/O_2 mixtures and simultaneous use of H_2O_2 to generate singlet oxygen) it will be possible to develop different kinds of selective oxidation reactions.

New types of active oxygen species can also be generated at a gas–solid interface from ozone. Total oxidation of organics in solution by ozone is well known, but limited data exist on its use as a selective oxidant in the gas phase [12]. At low temperature, ozone generates reactive peroxide species at the surface of the solid catalyst [12] and these active oxygen species can be used for new low temperature oxidation reactions especially in the field of the synthesis of fine chemicals.

N_2O is another powerful precursor of active oxygen species already known from several years (for example, its use for the selective dehydrogenation of alkanes [13,14]), but which has recently received new attention due to the discovery of the possibility to generate α type oxygen species by interaction with Fe/ZSM5 and the use of these species for the selective synthesis of phenol from benzene or methanol from methane [15]. This is the topic of the contribution of Panov et al. [29] which also points out the peculiarities of this form of adsorbed active oxygen (O_α) with respect to other known adsorbed oxygen species such as O_2^- and O^-. The discovery of the remarkable behavior of this O_α species has led in this case to the development of a novel technology for phenol synthesis directly from benzene [15]. The key aspect of the technology is that N_2O, formed in large amounts as a by-product in adipic acid manufacture, can be used to produce phenol from benzene using a Fe/ZSM5 catalyst. Phenol can then be hydrogenated to cyclohexanone which is an intermediate for adipic acid. However, economic estimations have shown that the production of phenol may be competitive to the commercial process (taking into consideration the worldwide surplus of the acetone coproduced in the classical cumene process of phenol synthesis), even when N_2O is synthesized on purpose, and is not available as a cheap byproduct. In fact, in adipic acid manufacture the N_2O which forms must be catalytically converted to N_2, if not used, and thus a process for its use for phenol synthesis has the additional economic advantage of avoiding the expenses for an end of pipe technology for the N_2O catalytic decomposition. However, the maximum possible worldwide production of phenol via this route is minimal. An economical process for phenol synthesis using N_2O produced on purpose can thus have a greater impact. Similarly to that discussed for in situ generation of H_2O_2, a key of success also in this case can be the direct in situ generation of the oxidizing intermediate which reduces the costs for two separate processes. However, it is necessary to develop selective and efficient catalysts for the in situ synthesis of N_2O from ammonia. The use of two ammonia molecules to generate one mono-oxygen donor molecule makes the synthesis of N_2O relatively expensive and thus this new oxidation chemistry should be preferably used for the synthesis of high value products (for example, hydroxylated substituted aromatics) more than bulk products (methanol from methane, for example) for which it cannot compete with the conventional processes.

4. Toward new types of oxidation catalysts

The development of new type of oxidation catalysts is clearly one of the main directions for innovation in this field, but is also an area which is very difficult to review and discuss in terms of new concepts which can be extended to other cases. In this issue this topic was thus restricted to only two contributions, one for solid catalysts in the liquid phase [30] and one for solid catalysts in the gas phase [31]. Both contributions deal with the development of catalysts based on transition metals inside microporous materials, although they address mainly different questions and concepts: (i) how to stabilize an isolated metal ion or complex inside the internal pore structure of a microporous matrix in order to easily recover it from a solution and obtain a solid recyclable catalyst [the catalytic behavior (turnover number, selectivity) of this catalyst, however, is usually at best analogous to that of homogenous complexes], and (ii) how to prepare oxide nanoparticles inside a host microporous matrix with reactivity, however, different from that of the bulk oxide. In the first case, thus, the attention is mainly given to the problem of obtaining a catalyst which behaves in terms of reactivity as a homogeneous catalyst, but as an heterogeneous solid catalyst in terms of ease of recovery and recycle. In the second case, instead, the solid microporous matrix is used to stabilize oxide nanoparticles with different characteristics from those of the bulk and this is thus a methodology to create new catalytic materials.

The contribution of Sheldon et al. [30] analyzes the concept of confinement of redox active metal centres in molecular sieves with some extension to related materials (redox pillared clays, clay intercalated with metal complexes, redox aerogels and metal complexes incorporated in aerogels) for the liquid phase oxidation with O_2, H_2O_2 and RO_2H. Three main approaches for the confinement are discussed: (i) substitution of T elements (Si, Al, P) in the framework of the microporous materials, (ii) encapsulation of metal complexes in the intrazeolite spaces and (iii) grafting or tethering of metal complexes to the internal surface of the microporous material. Apart from Ti-silicalite (TS-1), the critical problem in all these catalysts is the stability, both as regards leaching of the metal and oxidative destruction of the ligand (in the case of encapsulated or tethered complexes). Another problem is the diffusion of reagents/products in the case of encapsulated complexes which, on the other hand, appear as the more stable catalysts up to now. The development of solid catalysts for liquid phase oxidation is thus an emerging area of research especially for the development of cleaner processes with respect to the commercial homogeneous syntheses, but much effort is still required to develop better and more stable catalysts. Two other observations are necessary: (1) most of the catalysts developed have been studied only for relatively simple reactions like epoxidation, etc., whereas much less attention has been given to analysis of how to develop catalysts for more difficult reactions, such as the side chain oxidation of alkylaromatics or of complex functionalized molecules, and (2) too little attention has been given to developing catalysts active with gaseous oxygen instead of H_2O_2 and RO_2H. It is thus necessary not only to focus attention on the development of new kinds of catalysts based on the concept of metal ions or complexes inside microporous materials, but also to go further towards more practical problems. This will be the real challenge for this area of research.

Some other observations should be mentioned regarding the behavior of metal ions and complexes inside microporous materials for liquid phase oxidation. In the case of transition metal ions in T positions in zeolites, the zeolite matrix behaves as a quasi-rigid ligand and the catalytic behavior of a transition metal ion is very dependent on the nature of the ligand as is well known in homogeneous chemistry. Up to now research activity in this field has been mainly focused on analysis of the behavior of transition metal ions in substitutional positions or anchored at defect sites of mainly silica type microporous materials and a few other cases (MeAPO type mainly) which have an insulating character. It is possible to synthesize some microporous materials with semiconducting or even conducting properties which can thus influence in a different way the reactivity of the transition metal ion from that of silica type materials as well as influence the electrostatic field inside the microporous structure. Therefore, this new direction of research would open new frontiers for the control of reactivity.

Another necessary observation is that too little scientific attention has been given to understand the mechanism of leaching of transition metal ions from metal containing zeolites. There are several parameters which contribute to the stability of a transition metal ion (for example, Ti ions in substitutional position in zeolite) and can explain why Ti-silicalite (TS-1) is stable in the oxidation of organics with H_2O_2, but not Ti-β or Ti–MS (mesoporous) materials: (i) the hydrophobic character of zeolite with respect to the accessibility of H_2O_2 and water to the Ti center, (ii) the rate of change from tetrahedral to octahedral coordination (active form after formation of Ti peroxo species) and back after catalytic reaction with respect to the rate of hydrolysis of Ti–O–Si bonds especially when in octahedral coordination, (iii) the rigidity of the zeolitic matrix, etc. A more systematic study in this direction is the necessary step to develop more stable catalysts and thus to extend the concept developed initially with TS-1 catalysts.

The contribution of Yoo (chap. 9) is centred on the development of oxide nanoparticles inside microporous materials for selective gas-phase oxidations and specifically to the problems related to the synthesis and catalytic behavior of Fe–Mo-oxide nanoparticles in pentasyl type zeolites. It is known that oxide nanocrystals often possess quite different and peculiar reactivity properties in comparison with the corresponding bulk oxide, because changes are found in the crystalline habits, morphology, bulk oxygen transport properties, electronic properties, etc. Although various methodologies have been developed to synthesize these oxide nanocrystals [16], it is usually very difficult to control the characteristics of the nanocrystals obtained and especially to avoid recrystallization during catalytic runs. Both these problems can be overcome in principle when these oxide crystals are stabilized inside an ordered solid matrix such as zeolites which control both the growth and crystalline habit of the guest nanoxide. Furthermore, the presence of a strong electrostatic field inside the zeolitic channels, the possibility of synergetic cooperation between isolated transition metal ions and oxide nanoparticles and the possible presence of shape selectivity effects are further reasons indicating that the catalytic behavior of oxide nanoparticles within the cavities of host microporous materials can be significantly different from those of the same oxide, either in the form of bulk materials or conventional supported oxide materials. The inclusion (encapsulation) of oxide nanoparticles inside microporous matrices thus can be a very powerful direction of research to prepare catalysts with tuned properties and must not be viewed as simply the possibility to control the reactivity/selectivity by shape selective effects. Indeed, in the contribution of Yoo [31], it is demonstrated that Fe-Mo-oxide nanoparticles inside pentasyl type zeolite possess different properties from bulk iron-molybdate with a comparable Fe/Mo ratio.

In the synthesis of catalytically active oxides within ordered matrices the preparation is very critical. Some of the problems encountered in the preparation are to (i) avoid deposition outside the crystalline pore structure of the zeolitic matrix, (ii) avoid deposition of the oxide in such a way as to inhibit or limit diffusion of reactants or products of reaction, (iii) avoid an unselective catalytic role of the active sites already present in the zeolitic matrix (especially acid sites), (iv) control the effective local structure and composition of nanoxide particles within the zeolite, especially in the case of mixed oxides, and (v) deposit a sufficient amount of active components inside the zeolitic pores to have reasonably high reaction rates, etc. The preparation of oxide nanoparticles inside microporous materials thus requires a detailed study of the preparation methodology, the influence of parameters such as zeolite structure and defects, etc. The successful control of preparation variables to tailor the properties of guest oxide nanoparticles inside a host microporous matrix is the first necessary step for the development of a new family of oxidation catalysts and thus open new prospects in this field to control reactivity.

5. New opportunities for oxidation catalysts

Selective oxidation reactions have usually been classified in liquid and gas phase processes, with the former subdivided into purely homogeneous reactions or occurring at a liquid–solid interface. While liquid phase reactions are usually characterized from a very high selectivity, the second type offer several advantages in terms of easiness of products separation, productivity, eco-compatibility, etc. Several attempts were made in the past to combine the two characteristics and heterogenize homogeneous catalysts, but normally with limited success. A new possibility is to develop supported liquid-phase catalysts, i.e. homogenous catalysts working in a thin liquid film supported over a solid material which can be inert or participate to the reaction mechanism. This is the topic of the contribution of Reilly and Lerou [32]. Two specific examples are discussed: (i) heterogeneous Wacker-type catalysts for ethylene to acetaldehyde and 1-butene to 2-butanone oxidation and (ii) Pd/Au based supported catalysts for ethylene acetoxylation. In the first case, the reaction is made at temperatures around 100°C over supported Pd catalysts, in which the support for palladium (V_2O_5/Al_2O_3, for example) plays the role of mediate reoxidation of reduced Pd by gaseous oxygen, similar to the role of copper in liquid phase Wacker catalyst. Water is an essential reagent for the reaction, but the large amounts required to maximize selectivity, its effect on the transient behavior, the negative effect of an increase in the reaction temperature, etc. indicate that it is needed not only as a reactant, but also that it plays a more complex role [17]. Estimations indicate, in fact, that a thin film of water forms over the surface of the catalyst during the catalytic reaction. The thin film serve as the solvent, dissolving the anchored complex, which thus works as in liquid phase, but with the advantage to be heterogenized and that gas phase reactants (hydrocarbon, oxygen) diffuse easily through the thin film. A different possibility is offered by the formation of a molten salt as the solvent for the supported liquid-phase. For example, in ethylene oxidation to acetaldehyde it is possible to create a molten salt with a KCl/CuCl mixture which acts as the solvent for the $PdCl_2/CuCl_2$ Wacker catalyst [18]. An intermediate situation is shown from heterogeneous Pd/Au based catalysts for ethylene acetoxylation. In this case, the presence of potassium acetate is essential for the reaction and at the typical reaction temperatures (around 150°C) and in the presence of acetic acid, potassium acetate forms a dimeric species present probably as a molten salt. Capillary condensation of acetic acid also occurs. The role of the supported liquid-phase is probably not only to dissolve the palladium complex, but also to provide a protective coating on the surface which impedes ethylene combustion and probably regulate access of reactants to the active centres avoiding side reactions.

The critical problem in the above studies is to really demonstrate the active state of the surface during the catalytic reaction and thus the exact role of the postulated supported thin liquid phase. Nevertheless, the extension of this direction of research can be a good possibility to heterogenize homogeneous oxidation catalysts. It should be also mentioned that the classical catalyst for SO_2 oxidation to SO_3 (a $K_2S_2O_7$–V_2O_5 molten salt supported on silica) and supported Pd/Cu catalyst for benzene oxidation to phenol (Pd and Cu salts in a thin phosphoric acid film over silica [19]) probably operates in the form of a supported thin liquid film. Therefore, this concept is more general and a new possibility to develop new kind of selective oxidation catalysts.

The contribution of Fornasari and Trifirò [33] deals with a different problem from that discussed above, but has in common the characteristic of a non typical surface chemistry of selective oxidation under mild conditions. The topic discussed in this paper is the reactivity in the selective oxidation of non redox oxides, and specifically the behavior of silica in the ammoximation of cyclohexanone to cyclohexanone oxime. There are two key points on this contribution: (i) the role of surface sites or impurities in generating radical type oxygen species active in low temperature oxidation and (ii) the role of surface carbonaceous species formed during the catalytic reaction in catalyzing the reaction itself. The role of the latter species, directly responsible for the catalytic behavior or acting as a cocatalytic factor, is often not considered in oxidation reactions, although in some cases it plays a critical role in determining the catalytic behavior. Clear evidences in this direction, for example, exists for the oxidative dehydrogenation of ethylbenzene to styrene as well as for the synthesis of cyclohexanone oxime on silica catalyst cited above [33]. Also, the first point evidenced in the contribution of Fornasari and Trifirò [33] is quite important, because it emphasizes the role of the radical type chemistry in the low temperature selective oxidation of hydrocarbons, a more general problems not restricted to this example. A better understanding of this oxidation chemistry at non-redox surfaces can be quite useful to discover new type of oxidation reactions.

The last contribution of the issue [23] deals in general terms with the problem of the reaction mechanism in selective oxidation, but is specifically focused on the problem of the role of co-adsorbed species in determining the surface reactivity. Although specific studies on this topic are lacking, the roles of coadsorbed species to (i) mediate the oxidation reactions, (ii) enhance the rate of hydrocarbon activation, (iii) form more reactive surface sites and (iv) block surface sites responsible of side reactions are shown. In several cases, it was observed that the intrinsic surface properties of oxides are significantly altered by the presence of these coadsorbed species and that the catalytic behavior cannot be rationalized without taking into account of these effects. In some cases, the understanding of the role of coadsorbed species may allow to optimize the catalytic behavior (for example, in the ammoxidation of propane over vanadyl pyrophosphate - chap. 12) or to significantly promote the selectivity. An example of this effect is discussed in the contribution of Yoo (chap. 9) besides that in chap. 12 and refers to the remarkable effect of CO_2 in promoting the selectivity in *p*-xylene oxidation on Fe–Mo/zeolite catalysts. A correct understanding of the role of co-adsorbed species and more generally of the real nature of the working surface during the catalytic reactions is thus the necessary effort not only for a better understanding of the surface catalytic chemistry in selective oxidation reactions, but also for the more practical problem of a better control of the catalytic behavior.

6. Conclusions

The concepts briefly discussed above and better presented in the specific sections evidence that new opportunities are offered to the research in the field of selective oxidation, but it is necessary to go in different directions than to continue to consolidate knowledges on existing catalysts and reactions only. Some possibilities are presented in this issue which, however, does not cover systematically all new ideas in this area, but can be a stimulus for the future research. The examples discussed show that the innovation in the field of selective oxidation is driven from the identification of concepts and mechanisms underlying each working catalyst, the basis to identify how to apply the models and hypotheses to different catalysts, substrates, etc.

It is also necessary to pay a special attention on how to activate oxygen especially at low temperature, both as such or through the formation of an intermediate eco-compatible reactive oxygen carrier (H_2O_2 and N_2O). Although the elimination of this intermediate step is economically preferable, the cost of generation of these reactive oxygen carriers may be counterbalanced from the possibility to maximize selectivity or operate under mild conditions. The data reported for phenol synthesis by benzene oxidation with N_2O on Fe/ZSM5 (chap. 7) indicate that the process can be economic even in the case of on purpose generation of N_2O, because (i) eliminate a co-product (acetone) produced worldwide in a too large amount and (ii) process technology is simplified.

Selectivity, the elimination of waste or by-products, the technological simplification of processes will be the key words for future advances in the field of selective oxidation, besides the possible advances given from the use of less costly raw materials. In this respect, the functionalization of alkanes to chemicals by selective oxidation will be a challenge for the future. To date, too limited research attention was given to this topic, apart from the *n*-butane oxidation to maleic anhydride which, however, is already a commercial process [7]. There are several other reactions of alkane functionalization of possible industrial interest. Propane ammoxidation to acrylonitrile is already on a quasi commercial scale [2], whereas acrylic acid synthesis directly from propane still remain a challenge. Similarly, acetic acid directly from ethane is another interesting reaction of industrial interest which is still a challenge, whereas the selective synthesis of acetonitrile from ethane is possible [20]. The two nitriles can be hydrolized to the corresponding acid and ammonium salt and thus a two step synthetic process of the acrylic or acetic acid is possible, although no clear economical data in favour or against this are available. The key point, however, is to understand the reasons why the selective synthesis of nitriles from C2 to C3 alkanes is possible, but not that of the corresponding acids or aldehydes. This is only in part due to the different reactivities of the products (nitrile or acids, for example), because a key role is played from the modification on the surface reactivity induced by the ammonia reactant itself as discussed in chap. 12 and more in detail in a recent review [21]. This modification of the surface reactivity can also be induced from some other cofed components, added in small amounts to dope selectively the surface properties. This evidences a direct link between understanding of the surface reactivity and dynamics of catalytic reactions, and opportunities for the development of new oxidation reactions and processes.

Here, it may be worthwhile to point out the importance of the design of solid catalysts for practical applications at molecular atomic levels in selective oxidation. The necessity of being able to fine tune catalysts is already evident from the above discussion. The design in this direction may be possible by utilizing zeolite materials. Another promising material is heteropolyacids (or polyoxometallates). By taking advantage of their molecular nature, the catalyst design is very probably. This subject is not included in this issue, but has treated in the literature [22].

In conclusion, the field of selective oxidation is by no means a mature area of research, but there are several new idea and possibilities, the development of which will be the challenge for future research.

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