Available online at www.sciencedirect.com
ScienceDirect
Catalysis Today 117 (2006) 69–74
CATALYSIS TODAY
www.elsevier.com/locate/cattod

The boiling pot at oxide surfaces

B. Delmon [*]

Catalyse et Chimie de Matériaux divisés, CABI, Université catholique de Louvain, Place Croix du Sud 2/17, B-1348 Louvain-la-Neuve, Belgium

Abstract

The contribution concerns the crucially important layer near the catalyst surface (here, called Z^* for convenience) that turns out to be often thicker than usually assumed. Special experiments [M. Alifanti, J. Kirchnerova, B. Delmon, D. Klvana, Appl. Catal. A 262 (2004) 167] indicate that Z^* could possess electrochemical features, more precisely promote polarization effects. Measurements of thermodynamical activity and introduction of foreign species in Z^* could lead to progress in fundamental interpretations. Examples are given and suggestions made, concerning the use of polarizable dopes in the gas phase or in the catalyst (possibly containing two or several phases), or the application of physical activation techniques. Some speculations are proposed concerning new advances.

Keywords: Catalyst surface composition; Adsorbate polarization; Dynamic processes in catalysis; Oxygen mobility

1. Introduction

Must we change our vision of the active sites in some catalytic oxidation processes? Can we discover new approaches to reaction mechanisms? Additional information on catalytic processes comes from adjacent fields of science. Can this suggest new ways to modify activity and selectivity? These are some of the questions this communication attempts to answer. It is becoming clear that the reacting zone in oxidation catalysis (and probably in other types of reactions) is much thicker and broader than the usual picture of adsorbed species on a perfectly located small spot, the active site. Reactants bind to catalysts and interact with each other in a relatively thick layer near the surface, that we shall indicate as Z^* for convenience (the ‘‘boiling pot’’). The objective of the communication is to propose a few lines for interpretation or investigation. What is the added value that the recent advances do bring? This is the additional question to examine.

The surface (more precisely the near-surface region) of oxide catalysts undergoes modifications, including amorphization (Table 1) [1–6]. This is logical, considering the laws of irreversible thermodynamics, because catalysis is a dissipative process, creating entropy, i.e. potentially destroying order. The continuous incorporation of oxygen or other species into Z^* and release in the form of reaction products necessarily leads also to changes in local structures. For example, in the oxidation of butane to MAA, how could seven oxygen atoms be removed to produce maleic anhydride and water, and subsequently be re-inserted, without a considerable modification of structure in and near the reaction site? Many data show that the oxygen atoms involved in the catalytic reactions may come from over 10 or 15 layers below the surface [2]. Incidentally, this last point was recognized very early. This was particularly emphasized by Haber. The frequent impossibility to distinguish between the roles of surface and bulk oxygen also implies the involvement of several layers (see Ref. [7] and references cited in that article). In addition, the elemental composition of the surface, as measured by XPS, is rarely identical to that of the bulk. The study of reaction mechanisms must therefore deal with the whole near-surface layers, namely Z^*, rather than just a molecularly thin surface.

The existence of the Z^* layer raises questions like the following ones:

- Thermodynamically, what is the situation of this amorphous or partially amorphous layer Z^*? In particular, what is the chemical activity (in the thermodynamic sense) of its constituents?
- To what extent can the species contained in Z^* be mobile? More specifically, what is the degree of mobility of the reactants, especially oxygen, and products?

---

[*] Tel.: +32 478 24 01 27; fax: +32 10 47 36 49.
E-mail address: delmon@cata.ucl.ac.be.

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.05.009

Table 1
Representative cases of catalytic reactions in which relatively thick near-surface regions are involved and/or reconstruction of the surface occurs

Reaction	Catalyst	Authors
Butane to maleic anhydride	VPO	Hutchings et al. [1,2]
Propane to propene	VMgO	Pantazidis et al. [3]
Propene to acrolein	$MoO_3 + Sb_2O_4$	Gaigneaux et al. [4]
Toluene ammoxidation	VPO	Brükner (and A. Martin, B. Lücke, etc.) [5]
Propane to acrylonitrile	AlV oxynitrides	Florea et al. [6]

- Does Z^* possess some organization, some structural features that explain catalytic activity and selectivity? More specifically, does it possess chemical and physical characteristics that permit the reaction? Does it promote co-ordination configurations favorable to supramolecular associations permitting selectivity?

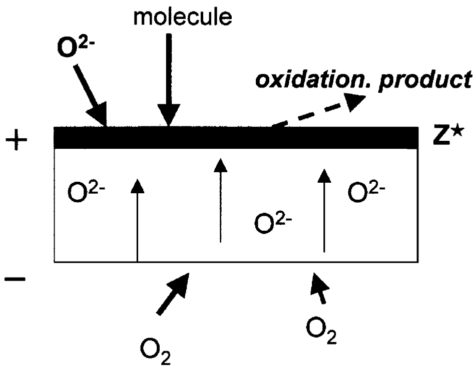
This constitutes the context for the present contribution.

2. Some background: selected experimental data from literature

This picture of a poorly structured or non-structured Z^* coincides with the views of Vayenas, when interpreting the striking effect of electrochemically “pumped” ions in Z^* on catalytic reactions [8–10] (Scheme 1). A group of investigators in Tsukuba [11] also investigated the phenomenon. Vayenas called this effect NEMCA (Non-faradaic Electrochemical Modification of Catalytic Activity). The injection of electrically pumped ions corresponded to considerable activity enhancement factors that have no equivalent in conventional oxidation catalysis.

The NEMCA effect is characterized by the following features:

- The catalysts were deposited on ion conductors (stabilized zirconia, β-alumina, TiO_2, Nafion, CaF_2).
- Various species (O^{2-}, Na^+, K^+) were injected to the surface thanks to an electric bias Δ.
- Different partial and complete oxidation reactions were investigated: oxidation to ethylene oxide, propylene oxide, formaldehyde, oxidative dehydrogenation to olefins, oxidative coupling of methane.
- The molecules reacting with oxygen were CO, CO_2, H_2, H_2S, hydrocarbons, methanol, etc.
- About 10 different catalysts were used (mainly metals).



Scheme 1. Schematic representation of the NEMCA effect.

It was shown that one single electrically injected ion could bring about a change in turnover and/or selectivity affecting hundreds or thousands of molecules [8]. The magnitude of this effect is reflected by an enhancement factor Λ, corresponding to the ratio of the additional number of molecules transformed by the NEMCA effect over the number of pumped ions.

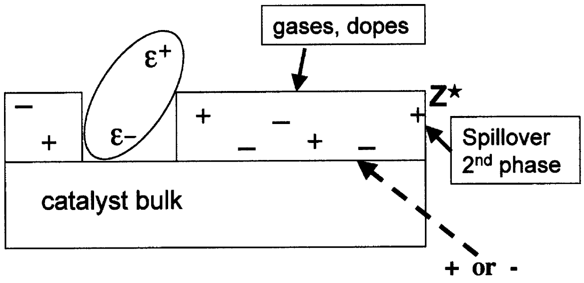
Inhibition of reactions as well as enhancement could be observed.

The theory, further developed independently by Metcalfe [12,13], rests on the existence of a sort of electrochemical layer, facilitating the activation of reactants in Z^* thanks to polarization (Scheme 2). Of particular interest for the present topic is the fact that the effects observed by Vayenas and co-workers may correspond to either increase of activity or inhibition (Λ higher or lower than 1), and the fact that Λ can vary when the applied potential Δ is modified. Maxima or minima can be observed. The theories developed by Vayenas and co-worker [9,10] and Metcalfe [12,13] explain all these effects.

This shows that polarization in or near the catalyst surface has a considerable influence on the catalytic process. Some of the species exerting this action (alkali ions) do not participate as reactants in the catalytic reaction.

The activity of ions in Z^*, as defined by thermodynamics, must play a central role in the control of the catalytic reaction. Estenfelder and Lintz determined simultaneously both values [12,13]. This allowed them to get insights into the mechanism of aldehyde oxidation to a carboxylic acid, in particular into the synergy between the components of the catalyst. It is surprising that so few in situ (in operando) studies did include oxygen activity measurements until now.

Approaching catalytic oxidation (and ammoxidation) in a similar way, as suggested in Scheme 2, might be fruitful in many cases where the existence of a Z^* regions is suspected. A question is whether the controlled addition of polarizable species in small amounts could have such dramatic effects as those observed by Vayenas. Another one is whether corresponding experiments



Scheme 2. Polarization of the near-surface layer Z^* and schematic representation of possible actions on the composition of this layer.

could help understand catalytic oxidation. The frequently mentioned role of oxygen spillover probably constitutes a positive, but limited answer. It seems logical to suspect that the concept of a polarizable catalytic layer will suggest new kinds of measurements and experiments. New approaches, as the one mentioned above, could provide additional data.

3. The polarizable layer (thin or more or less ‘thick’, as Z^*): can it be modified?

The suggested nature of the layer implies some mobility of the reacting species. This comes in line with the conclusions of Misono who detected a liquid-like behavior of some heteropolyacid catalysts in selective oxidation on the basis of kinetic data. Many results, relatively old or recent, are more easily compatible with a liquid-like behavior of the catalyst than with the vision of a rigid surface. PO_4 ions are always in substantial stoichiometric excess to vanadium in alkane selective oxidation in spite of the fact that the corresponding crystallographic structures indicate stoichiometry (see, for example, Ref. [5]).

Ruiz and co-workers demonstrated the important effect of gases normally not involved in the catalytic reaction [15–17]. The case of CO_2 is illustrative. Assuming a Z^* structure, is it possible to attribute the modifications due to CO_2 exclusively to its oxidizing action? Actually, this could be an indirect consequence of carbonate formation and corresponding changes in the balance of ions in Z^* that would modify the reaction pathways. Surprisingly, the addition of such “spectator species” results in a change of the oxidation/reduction state of the catalytic surface [16,17]. Experiments using gases not involved in the reaction could perhaps be re-interpreted: N_2O, NO, NO_2, pyridine [5], NH_3 in small amounts, dimethyl ether, etc. Examples are presented at this congress. An explanation could be that the various equilibria taking place in zone Z^* are altered by the presence of components coming from the “spectator species”. This would modify the thermodynamic activity of reactive oxygen and lead to oxidation or reduction.

The presence of hydrogen brings about conspicuous changes in the selectivity of catalytic oxidation reactions, permitting the production of unexpected molecules. A possible hypothesis could be that it reacts to form hydroxyls, thus modifying the properties of Z^*. Adequate measurements upon introduction of such species or, for example, mobile doping agents or spillover species could offer new tools for understanding the mechanisms at the origin of activity and selectivity. The role of hydrogen in selective oxidations is attracting much attention, both for possible applications and in view of a better understanding of mechanisms. Does it act as H_2 or through in situ generated H_2O and possible formation of hydroxyls as mentioned above?

There are many possible explanations to the role of steam in catalytic oxidation. Particularly intriguing is the necessity to use a large amount of it in the selective oxidation of ethane to acetic acid: does it act as modifier of the number or nature of catalytic sites, or through polarization effects due to the high dielectric constant of adsorbed or condensed water molecules?

Quite surprising reaction conditions are used in certain selective oxidation reactions. A process of the Tosoh Corp. transforms benzene to phenol at 200 °C, in the presence of air and hydrogen using acetic acid as solvent. This takes place under pressure, thus possibly making thicker the Z^* layer. This remark triggers another question: besides acetic acid, could other solvents be used in order to obtain completely new Z^* layers. The polarizable or partially ionic structure of Z^* suggests ionic liquids as candidates. The number of oxidation reactions in ionic liquids may increase in the future.

4. Nature and properties of oxygen in the Z^* layer

The re-oxidation step in the Mars van Krevelen mechanism (MvK) is often too slow, with the consequence that catalysts get reduced in the corresponding reduction–reoxidation cycle. Remembering the fact that the reactivity of oxygen, and especially its ability to permit selective oxidations (for example, as ‘nucleophilic’ species), strongly depend on its electronic structure, its seems legitimate to examine whether the polarization of Z^* could allow the production of the most adequate species. In principle, small ionic or polarizable species could modify the number of favorable oxygen activation regions, and correctly ‘tune’ the electron donating or accepting properties of oxygen. A puzzling observation often mentioned has been that the same doping species, in particular alkali and alkaline-earth elements can, according to cases and concentrations, enhance or diminish selectivity. This may be a replica, in classical catalysis, of the maxima or minima observed by Vayenas that were mentioned above. If this is the case, the picture of a ‘double layer’ might guide investigations.

Estenfelder and Lintz used an experimental set-up that constitutes a sort of mirror image of that used by Vayenas (Fig. 1).

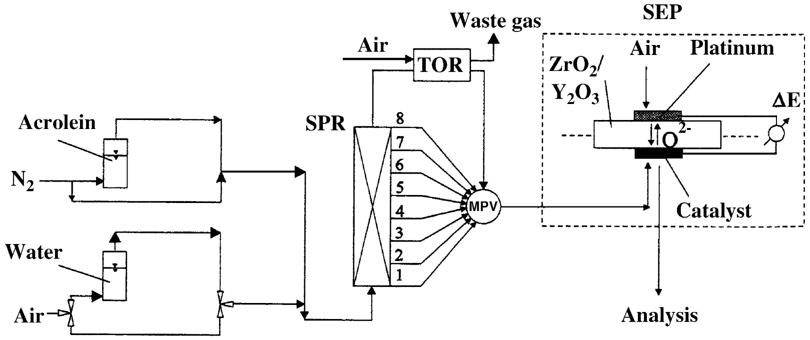


Fig. 1. Experimental set-up for the simultaneous measurement of catalytic activity and oxygen thermodynamic activity [14].

They demonstrated that during catalysis the oxygen activity was identical on both phases of a catalyst when synergy operated [14]. This can obviously be taken as a proof that oxygen spillover takes place in the oxidation of acrolein to acetic acid. Phase co-operation seems to be accepted now as the reason for the better performances in many complex catalysts. In the corresponding 'job separation', one of the phases involved, a sort of 'Dope' D, is usually not catalytically active when alone. The identical thermodynamic activity on both surfaces could mean that the favorable modification of activity of the other one, the Active one, be due to the fact that D produces 'good' oxygen species. These 'good' species would adjust the Z^* layer to a better polarizing structure. With respect to the mechanism of its action, spillover oxygen would act exactly the same way as the 'NEMCA' oxygen. This interpretation would obviously be welcome for the tenants of the Remote Control concept.

5. Insight into the other species present in the Z^* layer

In the paragraphs above, only one part of the components of Z^* has been considered, namely oxygen. It seems possible to examine additional aspects by following the series of speculations triggered by the existence of the Z^* layer and the partial knowledge we have of it. Recent results [5] and some contributions in the present congress are raising the question of whether the PO_4 ions, often in excess to stoichiometry in catalysts able to activate alkanes, are really attached to vanadium or act essentially to modify the whole of Z^*. Alkali ions and other elements are often used to modify selectivity. When selecting these additives, a guiding line is often to modify acidity. Results frequently justify the approach, but sometimes do not correspond to expectation. The modification of acid–basic properties may be only one aspect of the action of doping agents. Some of them are probably highly mobile in Z^* and their charge modifies the balance between the other ions. Making explicit a remark already made, the expectation could therefore be that they could have opposite effects on the two sides of a critical concentration, similarly to observations of Vayenas [10]. Could the experimental approach of Estenfelder and Lintz help understand the effects?

The case of the species that activate hydrocarbons also deserves attention. A tendency in recent literature is to consider smaller and less structured entities than previously, for example, isolated vanadate moities rather than polyvanadates [2,5]. The "liquid-like" behavior of heteropoly species mentioned by Misono possibly reflects this fact. Schlögl and co-workers investigated molybdenum-heteropoly compounds in conditions approaching those prevailing during catalysis [18]. They reached similar conclusions. 'In operando' investigations actually detect such clusters, for example, involving V and Sb [19], whose small size certainly facilitates the redox cycle.

Although the work initiated by Grange and co-workers on aluminium–vanadium oxynitrides [6,20–23] could not go to completion and does not yet permit definitive conclusions, the phenomena observed in the ammoxidation of propane leads to very similar speculations. This rests on (i) the solid-state mechanism controlling the nitridation of vanadium aluminate leading to 'AlVON' in different stoichiometries, and (ii) the reactivity of the oxynitrides. Data suggest that the nitrogen species inserted in the hydrocarbon are contained, together with vanadium, in a sort of 'reservoir' constituted of an alumina open framework. The picture is similar to that of Z^* in the sense that the content of the 'reservoir' also has a very flexible stoichiometry and no crystallographic structure. Special arrangements close to the alumina framework may exist, conceptually similar to those observed between the catalytically active molecular assemblies detected in magnesium vanadate in the oxydehydrogenation of propane to propene [3].

6. Perspectives

A preliminary remark is that the conjunction of results concerning the existence and chemical composition of the Z^* layer provides some approaches for 'bridging the gap' between heterogeneous and homogeneous catalysis.

The present section will be more focussed. It will present some speculations concerning future developments in oxidation catalysis.

6.1. Role of oxygen in multicomponent catalysts

The present document suggests at the same time new types of experiments and a background for interpretation that could be used in complement to those presented in recent literature. For example, results published in 1987 by a group working in Tsukuba [11] deserve attention. The authors injected oxygen electrochemically in the same way as Vayenas did. They found a NEMCA effect when passing a mixture of propene and oxygen over the catalyst. They produced acrolein, sometimes with considerable enhancement factors. The other point is that a different part of the work suggests the possibility to get deeper insights into the role of the various components of a complex catalyst. Actually, when passing propene alone, without oxygen, over the catalyst, the formation of acrolein was also observed if the catalyst was MoO_3 or bismuth molybdates. When more oxygen was pumped through the ion-conducting support, acrolein production was increased. No oxygen was produced. This shows that pure MoO_3 can use electrochemically pumped oxygen for selective oxidation. Bi_2O_3 alone released oxygen and CO_2 in the gas phase, but no acrolein. This result and the whole work suggest additional experiments using a physical mixture of MoO_3 and Bi_2O_3, rather than bismuth molybdates. In the absence of oxygen in the reacting mixture, would the system produce acrolein from exclusively electrochemically pumped oxygen? In the NEMCA experiments as well as in the interpretations of co-operative effects according to the Remote Control concept, the oxygen responsible for increased activity of the Mo-containing phases is distinct from that inserting into the oxidation products (acrolein and CO_2). Charging Bi_2O_3 with a considerable amount of an oxygen isotope, would it be possible to detect the difference of origin of oxygen and thus distinguish the oxygen acting as reagent from 'polarizing oxygen'? The conclusion is that the approach exemplified by the discovery of the NEMCA effect could help elucidate fundamental aspects of the mechanisms operating in 'normal' catalysis by mixed catalysts.

6.2. Correlations

Oxidation catalysis has led to innumerable attempts for correlating activity to catalyst composition. In the last years, characteristics linked to ionization potential or acid–base properties, like the ionic covalent parameter, 'optical basicity' (corresponding to Lewis basicity), and a partial ionic charge model [24] have been proposed and sometimes compared [25]. Except in the case of the Remote Control concept, major problem arose when catalysts contained several phases. A question is whether considering smaller species in the Z^* layer would lead to more fruitful developments and a more powerful potential for predictions.

6.3. Insight into the fundaments of catalysis kinetics

In addition to conventional electrochemical theory, Metcalfe [13] resorted to Statistical Mechanics and the Transition-State concepts. His work opens new possibilities for mechanistic interpretations, and provides help in constructing reaction mechanisms. This suggests new access routes for applying theoretical chemistry, and developing microkinetics on the basis of first principles. Specialists could explore possible developments. It can just be noticed that polarizability and polarization of different parts of a molecular species, presumably controlling selectivity, can be estimated or calculated. The degree of polarization can be modified in different ways, including the use of purely physical methods.

6.4. Modification of catalytic processes by physical means

One feature of this contribution being to emphasize the role of polarization phenomena in oxidation catalysis and similar processes like ammoxidation, the contribution of physical techniques for modifying selectivity should be examined. In the development of chemistry, and catalysis in particular, all sorts of physical techniques have been used to promote reactivity. Those involving high energies (for example, radiochemistry) are breaking all sorts of chemical bonds, and cannot lead to selective reactions in principle. In photochemistry and photocatalysis, energies are of a few eV. They modify the state of valence electrons and can promote very selective processes. Looking at the other end of the energy range, molecular rotation or processes involving lower energies cannot be expected to have significant effects directly. But it is certainly worth considering the case of vibration energies. Kinetic theories, explicitly or implicitly, attribute reactions to a small fraction of reacting species or intermediates carrying a sufficient amount of energy. This fraction gets higher when bonds get more polarized. It is technically possible to produce electromagnetic waves of almost any possible energy. Microwaves are used, but they work in a range corresponding to molecular rotation or Brownian motion, namely heat (roughly speaking: 10^{-4} to 5×10^{-2} eV). According to the Transition State Theory, this is not too low for selectively activating chemical bonds. The use of microwaves for promoting catalytic reactions has been explored (see a recent review paper [26]). They have beneficial actions. Many effects are merely due to simple heating of the whole volume of the reactor. Other ones are attributed to specific heating of the catalytic part of a catalyst, in particular metal particles, due to heating. In addition, more detailed analysis shows that an acceleration or even an increase of selectivity can be observed without measurable heating of the reacting medium (so-called 'thermal effects'). It seems that the polarizing influence of microwaves might increase the probability to reach a transition state or one of the possible transition states. This seems well documented for reactions in general [27], and the review paper cited above examines this point [26]. This last article cites 20 catalytic reactions, mainly corresponding to fine chemistry, where favorable effects have been detected, but it seems that further investigations are necessary before deciding of whether precisely selected frequencies could not be more efficient, for example, by activating specific bonds, including those involved in chemisorption.

The results of Inoue and co-workers in Nagaoka showed that electromagnetic waves can increase the production of acetaldehyde from ethanol catalyzed by palladium [28]. The result is due to thickness-extensional mode resonance oscillations of the ferroelectric crystals serving as support for palladium. The electromagnetic waves covered the range between 1 and 50 MHz. This corresponds to very low 'quantum energies' of about 10^{-8} to 10^{-10} eV, namely lower then the energy of microwaves. The influence on the catalytic process is thus probably indirect and difficult to analyze.

On the basis of this example and that of microwaves, can we speculate that, in addition to physical means of action using relatively strong energies, other ones could be useful? Some of them, in particular microwaves, could allow in-depth interpretations or even modeling. They could create links with different fields of physical chemistry and perhaps explain published correlations. This would justify Loupy, editor of a book on microwaves [27], who examined specific effects of microwaves, and proposed in a lecture interpretations very similar or identical to those described by Matcalfe with respect to polarization in the electrochemical layer [13].

As a conclusion, one may speculate that, in addition to fundamental insights, practical improvements in activity or selectivity could be obtained. The use of very finely tuned physical techniques, like microwaves of specific wavelengths, is perhaps also feasible technically and economically, and with respect to regulations.

7. Conclusion

In this contribution, an attempt has been made to present a conjunction of results that permits a broader and deeper vision of processes operating in oxidation catalysis. Elaborate physicochemical techniques are beginning to elucidate molecular mechanisms. Broadening the perspective can allow a better understanding of the kinetic aspects of oxidation catalysis.

References

[1] G.J. Hutchings, A. Desmartin-Chomel, R. Olier, J.-C. Volta, Nature 368 (1994) 41.

[2] K.C. Waugh, Y.-H. Taufiq-Yap, Catal. Today 81 (2003) 215.

[3] A. Pantazidis, A. Burrows, J.J. Kiely, C. Mirodatos, J. Catal. 177 (1998) 325.

[4] E.G. Gaigneaux, P. Ruiz, E.E. Wolf, B. Delmon, Appl. Surf. Sci. 121/122 (1997) 552.

[5] A. Brükner, Catal. Rev. 45 (2003) 97.

[6] M. Florea, R. Prada-Silvy, P. Grange, Appl. Catal. A 255 (2003) 289.

[7] M. Alifanti, J. Kirchnerova, B. Delmon, D. Klvana, Appl. Catal. A 262 (2004) 167.

[8] C.G. Vayenas, S. Brosda, Stud. Surf. Sci. Catal. 138 (2001) 197.

[9] S. Brosda, C.G. Vayenas, J. Catal. 208 (2002) 38.

[10] C.G. Vayenas, S. Brosda, J. Catal. 216 (2003) 487.

[11] T. Hayakawa, T. Tsunoda, H. Orita, T. Kameyama, H. Takahashi, K. Fukuda, K. Takahira, J. Chem. Soc., Chem. Commun. (1987) 780.

[12] I.S. Metcalfe, J. Catal. 199 (2001) 247.

[13] I.S. Metcalfe, J. Catal. 199 (2001) 259.

[14] M. Estenfelder, H.-G. Lintz, J. Catal. 209 (2002) 177.

[15] F. Dury, M.A. Centeno, E.M. Gaigneaux, P. Ruiz, Catal. Today 81 (2003) 95.

[16] O. Demoulin, F. Dury, M. Navez, E.M. Gaigneaux, P. Ruiz, Catal. Today 91/92 (2004) 27.

[17] O. Demoulin, I. Seunier, F. Dury, M. Navez, R. Rachwalik, B. Sulikowski, S.R. Gonzalez-Carrazan, E.M. Gaigneaux, P. Ruiz, Catal. Today 99 (2005) 217.

[18] F.C. Jentoft, S. Klokishner, J. Kröhnert, J. Melsheimer, T. Ressler, O. Timpe, J. Weinhold, R. Schlögl, Appl. Catal. A 256 (2003) 291.

[19] M.O. Guerrero-Perez, M.A. Bañares, Catal. Today 96 (2004) 265.

[20] R. Prada-Silvy, M. Florea, P. Grange, Patent International Publication No.: WO 03/053913 A1 (July 3, 2003).

[21] N. Blangenois, M. Florea, P. Grange, R. Prada-Silvy, S.P. Chenakin, J.-M. Bastin, N. Kruse, B.P. Barbero, L. Cadús, Appl. Catal. A 263 (2004) 163.

[22] H. Wiame, PhD Thesis, Université catholique de Louvain, 2003

[23] M. Olea, M. Florea, I. Sack, R. Prada-Silvy, E.M. Gaigneaux, G.B. Marin, J. Catal. 232 (2005) 152.

[24] L. Moens, P. Ruiz, B. Delmon, M. Devillers, Appl. Catal. A 249 (2003) 365.

[25] F. De Smet, P. Ruiz, B. Delmon, M. Devillers, J. Phys. Chem. B 105 (2001) 12555.

[26] B. Toukoniitty, J.-P. Mikkola, D.Yu. Murzin, T. Salmi, Appl. Catal. A 279 (2005) 1.

[27] A. Loupy, Microwaves in Organic Synthesis, Wiley–VCH, Weinheim, 2002.

[28] H. Nishiyama, K. Izumi, N. Saito, Y. Inoue, Extended Abstract of IV World Congress on Oxidation Catalysis, Berlin/Postdam, September 16–21, DECHEMA Publication, 2001, p. 59.