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# The universal character of the Mars and Van Krevelen mechanism

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Dedicated to Prof. H. Knozinger

## Abstract

This review deals with the mechanism that is arbitrarily called below the Mars and Van Krevelen (MvK) mechanism. The characteristic feature of this mechanism is that some products of the reaction leave the solid catalysts' surface with one or more constituents of the catalysts' lattice. First in this review, the position of this mechanism amongst other ways of catalytic activation will be defined. Then, the experimental evidence for this mechanism will be presented. Some less common reactions running with this mechanism will be discussed in more detail, among them the deoxygenation of nitrocompounds and carboxylic acids.

The participation of the lattice components (O, S, Cl, H) in the formation of products leads to a relation of the catalytic activity with the thermodynamic parameters characterizing the catalysts lattice. A proper use of such quantified relation will be also discussed. © 2000 Published by Elsevier Science B.V.

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## 1. The principles of catalytic activation

It was Berzelius [1] who first identified a group of reactions that had one feature in common: they took place in the presence of a compound that was not consumed by the reaction. Berzelius ascribed this phenomenon to “a new power to produce chemical activity belonging to both inorganic and organic nature which is surely more widespread than we hitherto believed and the nature of which is still concealed from us. When I call it a new power, I do not mean to imply that it is a capacity independent of

the electrochemical properties of the substance ... catalytic power actually means that substances are able to awaken affinities that are asleep at this temperature” [2]. Even today, we can still agree with this text; however, we would not agree with the sentence with which Berzelius continued: “the substances (catalysts) do it by their mere presence and not by their own affinities.” Berzelius actually assumed that the catalytic power somehow acts on a large distance. To our knowledge, there are very few examples for which this idea about the catalytic action would apply. One of them is probably the reversible conversion of *ortho* and *para* hydrogen, catalyzed by localized magnetic moments in the solids, for example, such as in rare earth oxides.

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At the same time as Berzelius formulated his ideas, Michael Faraday explained the catalytic effect of platinum as “the result of an attractive force exerted by the solid on the gases” [2]. In other words, the catalytic effect is according to Faraday induced by the adsorption of reaction components. This idea appeared to be very stimulating; nevertheless, up till now, discussion is going on regarding the problem as to how the adsorption affinities are related to the catalytic effect. A great deal of truth is probably expressed by the so-called Sabatier or Balandin principle [3]: the optimal adsorption bond is neither too weak nor too strong.

A mathematical form of Faraday’s idea appeared later. The “active mass” in the expression for the rate is related to the surface coverages that are calculated from the corresponding Langmuir isotherms (see [3–5] — in [4] is given the development of the theory summarized). This approach is usually called the Langmuir–Hinshelwood kinetics. Homogeneous enzymatic reactions were described in a formally similar way much earlier by Henri [6] and Michaelis and Menten [7].

With the adsorption mechanism, catalytic reactions occur as interactions among adsorbed molecules, adsorbed radicals or fragments of the reactant molecules. However, it has also been suggested (see e.g. [3]) that a reaction by collision of molecules from the gas with the adsorbed species is possible too. So far, this so-called Rideal mechanism has been only confirmed indirectly, from the reaction kinetics.

In the shadow of the development of the Langmuir–Hinshelwood kinetics, another idea on the catalytic activation was, but only very slowly, getting its shape — the idea that the catalysts’ lattice components appear in the reaction products. Pease and Taylor [8] studied the oxidation of hydrogen on copper and they conclude their paper with these words: “the results are believed to be satisfactorily explained by assuming that the combination takes place mainly as a result of the alternative oxidation and reduction of the catalyst.” Independently, a very similar conclusion on the mechanism appeared in other papers of that time [9,10]. An oxidation mechanism upon which lattice oxygen enters the desorbable products was later much more explicitly formulated by Kroeger [11]. However, the broad

catalytic public even then did not really acknowledge the importance of the new idea that oxygen is not simply added to the reductant but is first activated by transformation into a lattice oxygen. The steps of the lattice oxygen depletion and the subsequent replenishment can even be separated into two consecutive steps (swing reactor), with sometimes an appreciable technological advantage (e.g. to circumvent the explosion limits). The real breakthrough in the appreciation of the idea only took place after the publication of the paper by Mars and Van Krevelen, in 1954 [12] and after a series of papers with a successful application of the idea in the kinetics (see e.g. [12–14]).

It can be expected that sulfides, chlorides or hydrides also can sustain a similar mechanism like that observed with oxides. Here, we called it the Mars and Van Krevelen (MvK) mechanism, but one can find for it other names also in the literature: redox or regenerative mechanism. However, all oxidations are redox reactions, even when the prevailing mechanism can not be called an MvK mechanism.

To complete the list of various ways of catalytic activation we shall mention that with some reactions radicals are created on the surface which are then released into the gaseous phase where they react further (see e.g. [15–18]). The well-known examples of these reactions are the ammonia oxidation [19] at high temperatures and the oxidative coupling of methane [20,21]. Of course, there are also low temperature oxidations involving radicals [22], but these reactions involve adsorbed radicals and are thus of the Langmuir–Hinshelwood (L–H) type.

## 2. Early experimental evidence for the Mars and Van Krevelen mechanism

Roginsky summarized in 1953 [23] his earlier work [24] on the exchange of isotopically labeled atoms between gas molecules and solid catalysts and wrote: “substantial result of those papers (published in the thirties) was that a propensity has been clearly proven of various catalysts of halogenations (halogenides of Al, Fe, Sb) for fast isotopic exchange with organic halogenides and, there was also a certain parallelism found between the reactivity of halogenides in the exchange and in halogenation, as well as in isomerization of halogenated organic mo-

lecules.” However, in the same paper [23], Roginsky was much skeptical about an analogous behavior of oxides. He seemed to be supported by the early experiments with labeled oxygen [25]. It did not last long and several reports appeared with results strongly supporting the MvK mechanism in oxidations. A perfect analogy with halogenations was thus confirmed [26–30]. The oxidation mechanism has been revealed in further details. With Bi–Mo oxides, different metal–oxygen pairs appeared to be involved in either the dehydrogenation of propene and the insertion of oxygen steps. This implied a transport of oxygen ions through the lattice, a step that can in principle complicate the application of isotopes in the studies of mechanism [31,32].

The just mentioned isotopic experiments are the most reliable evidence for the MvK mechanism, if the side reaction like fast isotopic scrambling does not spoil the play. However, a rather strong support for this mechanism has been obtained from other experiments also.

Operation of the MvK mechanism can be detected in the ‘swing’ type experiments, with alternating oxidation and reduction steps, with pure reductant or oxidant in the feed. When the rates and selectivities of the swing and the continuous catalytic reactions are similar, this observation can be a good indication that the MvK mechanism operates [11–13]. When a valid kinetic equation can also be derived on the basis of the MvK mechanism, the support becomes still stronger [11–13].

When a reaction really runs with the MvK mechanism, one can reasonably expect that there is some relation between the rate of the catalytic reaction and the metal–oxygen, metal–halogen or the metal–sulfur bond strength. Such a correlation has been looked for and indeed found for the M–X (X = O, Cl, S) bond strength averaged over the lattice. The latter is conveniently defined as, for example, the heat of the highest oxide formation (of the element in question) normalized per one oxygen of the stoichiometric formula. One can not expect too much from these correlations; they are suitable to indicate the trend, and not to answer subtle questions. However, they can be useful [14,18,33–35]. Also, some other correlation has been suggested and rationalized, as for example, a correlation with the virtual pressure of oxygen or chlorine etc. [14,35].

Exchange of isotopes among dioxygen molecules catalyzed by oxides revealed some phenomena, which first surprised the experimentalists very much but later were perfectly explained just by the operation of the MvK mechanism. The surprising aspect was that the apparent equilibrium constant of the exchange dropped in the initial stages of the exchange reaction from its theoretical value of ca. 4 to ca. 2 and slowly returned to its theoretical value. The corresponding description of the reaction kinetics [36] assumed the existence of three ‘visible’ exchange modes characterized by three reaction rates  $R$ , having the following meaning:  $R^0$  — the exchange occurs without any participation of the lattice oxygen;  $R^1$  — upon each sojourn of a dioxygen molecule on the surface, one of the oxygen atoms is exchanged for lattice oxygens; and  $R^2$  — both atoms of gaseous dioxygen are exchanged upon a single sojourn on the catalyst. The last two exchange rates can be called single and multiple exchange, respectively. It appeared that the results on the oxygen exchange on oxides simply *can not* be explained without the assumption that the lattice oxygen participates in the exchange, i.e. without the assumption that the MvK mechanism operates [36–39]. It is interesting to notice that the kinetics derived by Klier et al. [36] has been with success applied also to the exchange of deuterium and hydrogen on hydrides [40] or to the same reaction on EDA-complexes (alkali metals on aromates), confirming that, with these systems too, the MvK mechanism operates [41].

### 3. Some recent results indicating the operation of the MvK mechanism

In the course of time, a large volume of experimental results had been obtained on the oxygen exchange reaction. Together with an elucidating discussion, results are summarized in several comprehensive reviews [36–40,42]. Notwithstanding all these efforts, a close look revealed that the information available was still insufficient to make a reliable conclusion on, for example, the similarity or difference in the variation of the  $R^1$  and  $R^2$  along the period of elements, on their possible relation with, respectively, the deep and the selective oxidation etc.

Some speculations therefore appeared to be doubtful [43]. One of the shortcomings of the early reports is that they often report on the total rate,  $R^0 + R^1 + R^2$ , and not on the individual rates. Therefore, the oxygen exchange experiments on various oxides have been repeated and the relevant results are presented in Fig. 1 [44,45].

From Fig. 1, interesting conclusions can be drawn immediately: (i) the two rates vary along the periods of elements, with  $Z$  being the atomic number, in a very similar way; (ii) variation in the reciprocal of the average bond strength shows the same periodicity which suggests that the three parameters are mutually related. Further, point (i) contradicts the speculations made in [43] with regard to the relation of the rates with the selectivity in oxidations.

Experiments in [44] have been performed as an attempt to gain more information on the problem as

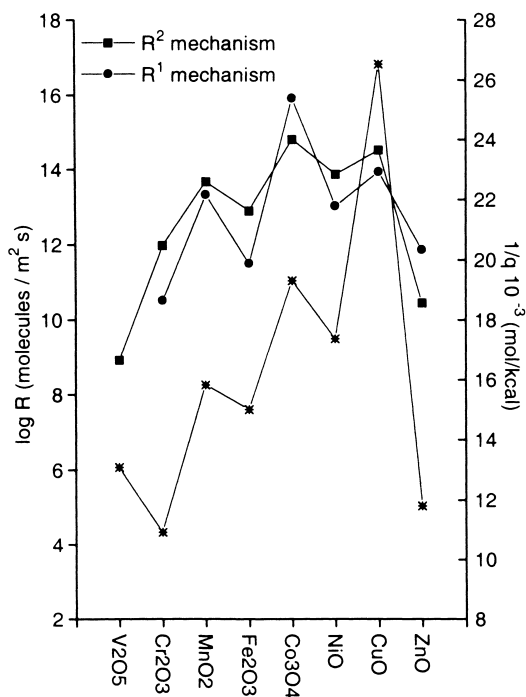


Fig. 1. Exchange reaction of dioxxygen ( $^{16}\text{O}_2 + ^{18}\text{O}_2$ ) over oxides; compared at  $T = 573\text{K}$ . The variation in rates of  $R^1$  (single-exchange mechanism) and  $R^2$  (multiple-exchange mechanism) are given as a function of atomic number (position in the first long period of the periodic table). On the right-hand side is given the reciprocal of the  $q(\text{M}-\text{O})$ , the average M-O bond strength in oxides [45].

to which factors determine the selectivities in the deep and selective oxidations, respectively. The literature already strongly indicated [46] that there is probably a relation between the parameter  $q(\text{M}-\text{O})$  and the rates of *deep* oxidations of hydrocarbons and those of the oxidation of hydrogen, but a similar reliable information on *selective* oxidations was missing.

Let us mention in this place another interesting and elucidating information [47]. The rate of oxidation of hydrocarbons can be correlated with the mean bond strength  $q(\text{C}-\text{H})$  in the hydrocarbon. On one and the same oxide, the higher the rate, the lower is the parameter  $q(\text{C}-\text{H})$ . An antipathic correlation is also found for one given reaction and the  $q(\text{M}-\text{O})$  parameter of oxides used as catalysts. In the just mentioned reactions, hydrocarbons act as reductants of the oxide and both the hydrogens and the carbons of the hydrocarbon transport oxygen of the oxide (MvK) in the gas phase.

Doornkamp also followed [44] the oxidation of allyl iodide by dioxygen, with oxides as catalysts. The reason for choosing this molecule was the following one. The selective oxidation of propene to acrolein is initiated by splitting off of the allylic hydrogen and formation of adsorbed allylic species. On many oxides, the splitting needs such a high temperature that the fragment then reacts immediately further, up to carbon oxides and water. However, the formation of adsorbed allyl from allyl iodide is easy and requires a much lower temperature, under which the intermediates and the products of selective oxidation can persist. Using allyl iodide, one can thus study a larger number of oxides in the selective oxidation reactions. Some results of this study are shown in Fig. 2. We can see there that the variation in the rates reminds one of that in Fig. 1.

Analyzing the data in more detail reveals the following: (1) the rate of the deep oxidation and the sum of the oxygen exchange rates all vary in phase, with  $Z$ ; (2) the selectivity in acrolein formation varies in antiphase, with regard to the two other parameters. We can see it in Fig. 3.

The message from Figs. 2 and 3 is as follows. The ratio of the two rates, that for deep oxidation to that for selective oxidation is high on those oxides which show a high rate of oxygen exchange and have a low bond strength  $q(\text{M}-\text{O})$ . Obviously, *the*

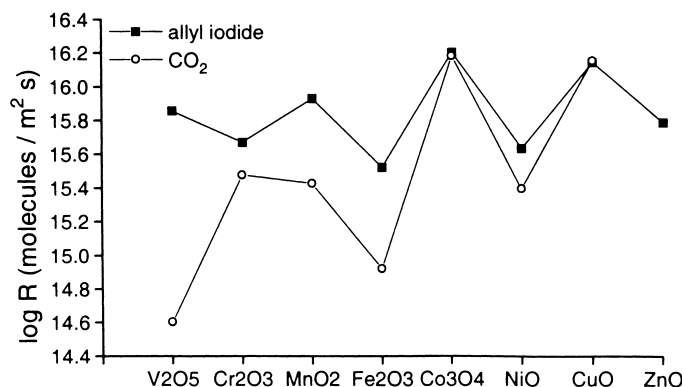


Fig. 2. Rate of the allyl iodide total consumption (oxidation) and that of CO<sub>2</sub> production at 523 K (a measure of deep oxidation), both as a function of atomic number, along the first long period of elements [44].

*non-selective oxides have a higher portion of active lattice oxygen for participation in the catalytic reactions.* Such a correlation has been predicted under the assumption of operation of the MvK mechanism already by Sachtler et al. in 1968 [48]. These authors also brought an experimental support for their assumption: when benzaldehyde was admitted into the catalyst at rather low temperatures, the infra-red absorption bands corresponding to benzoic acid appeared immediately.

Doornkamp et al. [44] studied the allyl iodide oxidation in the presence of isotopically labeled dioxygen <sup>18</sup>O. The oxide contained only <sup>16</sup>O. These experiments clearly confirmed the operation of the MvK mechanism, even on an oxide with a rather low activity — vanadium pentoxide. This can be seen in Fig. 4.

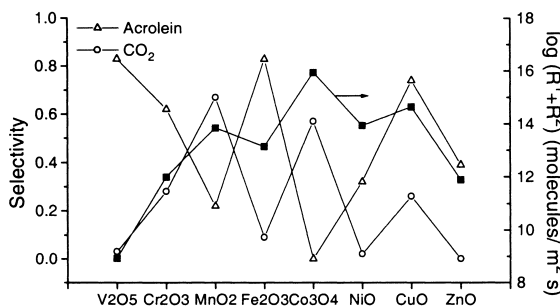


Fig. 3. Allyl iodide oxidation at 523 K; selectivity to acrolein ( $\Delta$ ) and CO<sub>2</sub> ( $\circ$ ) as a function of the atomic number. In the same graph is given the total exchange rate ( $R^1 + R^2$ ) of dioxygen at 573 K [44].

Notwithstanding the presence of labeled oxygen in the gas phase, the products of the initial stage of oxidation contain only the non-labeled oxygen from the oxide. This holds for both the deep and the selective oxidation, so that both of them evidently run with the MvK mechanism.

An interesting point concerning the correlations of the rates with atomic number  $Z$  of the catalysts' cation is the shape of these correlations and the size of the ups and downs in fluctuations in the rate. From the literature and from our own data, we know that the dioxygen exchange reaction, the deep oxidation of saturated hydrocarbons, oxidations of olefins and acetylenes, as well as the deoxygenation (see below) of nitrobenzene (Ph-NO<sub>2</sub>) and of benzoic

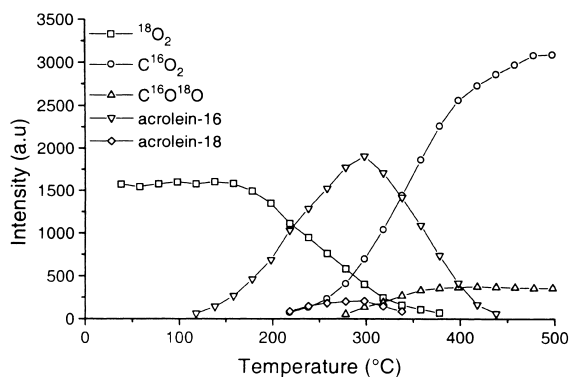


Fig. 4. Temperature-programmed oxidation of the allyl iodide on V<sub>2</sub><sup>16</sup>O<sub>5</sub>, in the presence of <sup>18</sup>O<sub>2</sub>. Concentration of various compounds in the gas phase. Notice the early production of <sup>16</sup>O-(ex oxide) — acrolein [44].

acid (Ph–COOH), they all show a similar saw-tooth like correlation with  $Z$ . The two initially mentioned reactions show, however, large differences between the minimum and maximum rates, up to seven orders of magnitudes. The rates of the last two mentioned reactions vary with  $Z$  within only one order of magnitude. This can be probably explained as follows. The rate of oxidation that comprises extraction of oxygen out of the lattice depends on the metal–oxygen bond strength. Oxidation of organics requires, however, also splitting of the carbon–hydrogen bond and the simultaneous association of both fragments with the pair M–O of the catalyst, which is again a kind of oxygen extraction step, the rate of which depends on the M–O bond strength. When the splitting of the C–H bond is difficult (also the splitting of the O=O bond upon the dioxygen exchange reaction is difficult), the dependence of the rate on the  $q(\text{M–O})$  is then more pronounced and the differences between the maxima and minima on the correlations with  $Z$  are particularly large. In contrast to it, the hydrogen of the ring in nitrobenzene and in benzoic acid is activated by the substituent, its splitting off is easy, and consequently, the fluctuations in rates as functions of  $Z$  are less pronounced. With allyl iodide, the formation of the reactive intermediate is easy, much easier than from propene. In this respect, the acetylenic hydrocarbons are near allyl iodide, while olefins represent an intermediate case.

#### 4. Deoxygenations by the Mars and Van Krevelen mechanism

In chemical technology, it is sometimes easier to produce, or to isolate from natural products, molecules that contain more oxygen than desired and to remove in a separate step one of the oxygens (selective deoxygenation). Examples of such reactions already studied are the above-mentioned conversion of nitro- into nitrosobenzene, or the production of aldehydes from carboxylic acids. These reactions are commercially quite interesting.

Reduction of nitrobenzene to aniline is used in the dye industry for a long time already. It is a straightforward addition of hydrogen catalyzed by metals, at moderate temperatures. On a less active metal like

copper, one can detect an intermediate of this reaction — phenyl hydroxylamine — in the solution above the catalyst. Reaction to nitrosobenzene is less easy. The classical technology is a two-step process: nitrobenzene is first converted into phenyl hydroxylamine by adding to it Zn and HCl, and subsequently, this intermediate is oxidized to nitrosobenzene by chromates. This batch-wise production does not require much investment, but it is environmentally very unfriendly. With each kilogram of nitrosobenzene, about 3 kg of inorganic waste are produced simultaneously. Therefore, there is a high demand for waste-free technology. This can already be provided now in the form of deoxygenation of nitrobenzene on oxides. The MvK mechanism plays a dominant role in it. Let us take a close look at the deoxygenation of nitrobenzene described in the patent literature; see e.g. [49,50].

When we start with manganese(IV) dioxide and pure nitrobenzene (no dihydrogen), the oxide is first reduced by the ring as reductant up to  $\text{Mn}_3\text{O}_4$ , producing only carbon oxides and water. Then, a rather selective formation of nitrosobenzene sets in. We can also prereducate the catalyst up to MnO by dihydrogen or CO, and then in the stream of nitrobenzene, the catalyst is first reoxidized into its steady state of  $\text{Mn}_3\text{O}_4$ , whereafter a steady production of nitrosobenzene takes place [51]. Such a behavior alone is already a strong indication that the MvK mechanism operates. This conclusion has been confirmed by experiments with labeled molecules. In the study [52], Mn oxide catalyst was labeled by  $^{18}\text{O}$  and nitrosobenzene was admitted at various temperatures (batch reaction). Both nitrobenzene and the products of deep oxidation initially contained oxygen from the catalyst. On oxides with a high M–O bond strength, like aluminum oxide, nitrosobenzene undergoes disproportionation, and in the gas phase, nitrobenzene appears with only light oxygen, from other nitrosobenzene molecules, most probably, according to the following reaction:



The adsorbed fragment most likely dimerizes.

The thermal programmed desorption from the layer of adsorbed nitrosobenzene on manganese oxide revealed how the temperature determines the

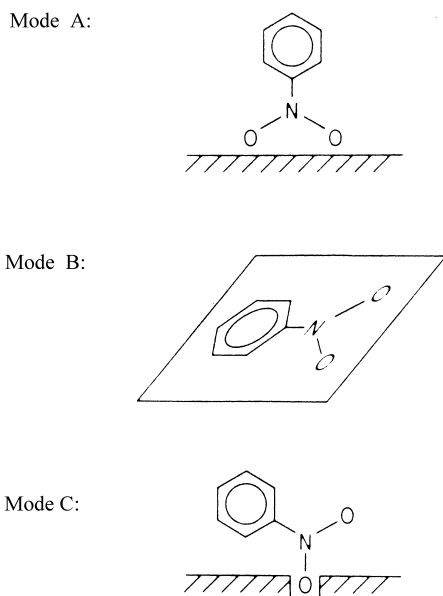


Fig. 5. Different adsorption modes of nitrobenzene on manganese oxides.

ratio of oxidations by either the lattice oxygen or by oxygen from other molecules. At 473 K and higher, oxidation by lattice oxygen prevails; at lower temperatures, the contribution by disproportionation increases. The relative contribution by any of the mechanisms is determined by the population of the relevant adsorption state. The most probable adsorption modes are depicted in Fig. 5.

The situation wherein a reaction by the MvK mechanism is accompanied by a Langmuir–Hinshelwood reaction occurs probably quite frequently. Both reactions can lead to the same or to different products. A higher steady-state concentration of oxygen vacancies under a running catalytic reaction would stimulate the MvK mechanism, by stimulating the adsorption in the relevant mode (see Fig. 5).

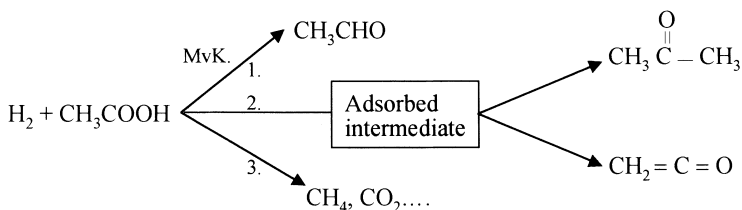


Fig. 6. A scheme of reactions occurring on oxides with acetic acid and dihydrogen mixture.

It is interesting to note that a vigorous prereduction of the catalyst shifts the selectivity from nitrosobenzene to aniline production. The use of a higher pressure of dihydrogen in the reaction mixture shifts the selectivity towards aniline too. It seems that the number of oxygen vacancies controls the selectivity.

Another example of practically important deoxygenations is the conversion of aliphatic or aromatic carboxylic acids into corresponding aldehydes. The classical two-step batch technology converts the acids first to chlorides that are in the second step reduced on a metal by dihydrogen. This technology causes serious environmental problems that can be avoided by using, for example, selective deoxygenation reaction on an oxide.

Most of the results shown below have been obtained with acetic acid, a model molecule, but they can be easily generalized. However, for the sake of comparison, we shall refer to the results on benzoic acid also.

Under wide experimental conditions, acetic acid reacts in several parallel reactions, shown in Fig. 6.

Research performed in Leiden revealed the following about the mechanism of this reaction [53–59]. After adsorption, the reaction can proceed by one of the pathways indicated in Fig. 6. When the adsorption occurs on a surface with a high number of oxygen vacancies, the deoxygenation and formation of aldehyde is stimulated. Other reaction conditions and the state of the surface might prefer dissociation of the C–H bond in the adsorbed species and the pressure of the reactants determines how the reaction proceeds further from this point on. For example, an unmodified metal surface and higher temperatures direct the reaction along path 3. However, with a metal like iron, it is sufficient to oxidize the metal surface by the acid in the feed to create islands of oxides with oxygen vacancies and, at lower tempera-

ture, MvK pathway 1 can prevail [59]. Vice versa, a preoxidized surface of an oxide with a high M–O bond strength would strongly stimulate the ketonization (Sabatier reaction). The C–H bond dissociation in step 2 is suppressed when the surface is covered by hydrogen. A lower M–O bond strength and a higher dihydrogen pressure are beneficial for it. Tertiary aliphatic acids and the benzoic acid have no alpha-hydrogen and this closes the way along path 2 [58]. Benzoic acid forms, however, other side products, which decrease the yield of aldehyde [60].

Let us now leave the description of individual reactions and turn our attention to various comparisons and generalizations. There are some similarities among the various deoxygenations, but let us start with the differences, for example, those between the aliphatic and aromatic acids on one side and the nitro compounds on the other side. The nitro substituent activates the rest of the molecule, the benzene ring, so strongly that the reaction can proceed well without external reductant, as autoreduction. With acids, no deoxygenation by autoreduction is possible.

Nitroalkanes show still another interesting reaction, which, however, prevents their heterogeneous deoxygenation to nitroso compounds on reducible oxides. Upon adsorption on oxides, the alpha-hydrogen, when present in the compound, is split off and an adsorbed nitronate ion with a very reactive bond C=N is formed. This bond induces a destructive oxidation of the adsorbed nitronate ion by lattice oxygen and no nitroso compound is formed. The carboxylic acids show a certain analogy to this by their reactions to ketenes, but ketenes are less susceptible to subsequent oxidations.

The two groups of acids differ markedly in their reactions on metal-containing catalysts. With aliphatic acids, the performance of e.g. titanium dioxide is improved, and its activity and selectivity to aldehydes enhanced, when a metal is added to the oxide. Obviously, because a higher concentration of hydrogen on the surface leads to a higher concentration of oxygen vacancies and simultaneously reaction, step 2 of Fig. 6 is suppressed. However, the presence of a metal is detrimental for the selectivity to benzaldehyde in the deoxygenation of the benzoic acid. The ring is activated by adsorption on the metal and hydrogenated subsequently. The situation is quite different with aliphatic acids. The hydrogenation of

the aromatic ring is obviously not blocked by the adsorption of acid on the metal. With the aliphatic acids, hydrogen too is present on the metal, next to the adsorbed acid, but the competing reaction is not hydrogenation now but hydrogenolysis which requires a higher temperature than deoxygenation on the oxidic component of the catalyst.

The presence of platinum on titanium dioxide is beneficial for the deoxygenation of acetic acid and it improved the performance of the catalyst so dramatically that it became desirable to investigate the specific roles of the individual catalysts' components [56,57]. In this study, a given amount of Pt/titanium oxide was taken and a varying amount of additional TiO<sub>2</sub> added to it. Addition of titanium dioxide did not change the apparent activation energy but clearly increased the rate, obviously by increasing the number of active sites. The deoxygenating sites are thus on the oxide. This result is illustrated by Fig. 7 [56,57].

When a pure titanium dioxide is severely pre-reduced, aldehyde formation is stimulated. This observation too indicates the role of oxygen vacancies in the activity and selectivity of an oxide. Moessbauer spectra supplied another argument for the idea that the oxygen vacancies induce the MvK deoxygena-

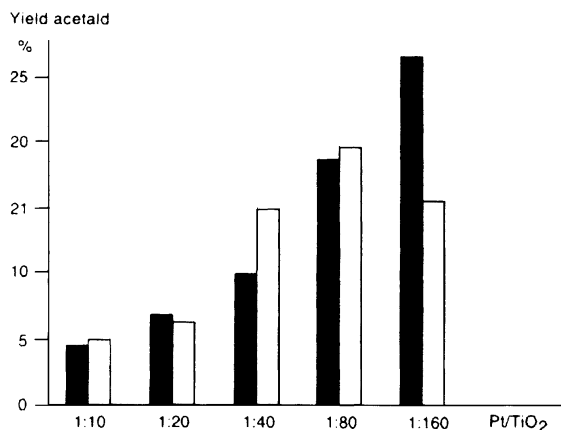


Fig. 7. Reaction of acetic acid on Pt/TiO<sub>2</sub> catalysts at 673 K. A yield of acetylaldehyde as a function of the catalyst composition is given. Black bars: a constant amount of Pt/TiO<sub>2</sub> is diluted by the TiO<sub>2</sub> added. The total amount of Pt in the reactor is constant, but the amount of TiO<sub>2</sub> increases from the left to the right. Empty bars: the total amount of TiO<sub>2</sub> is kept constant, and the amount of Pt in the reactor varies — it increases when going from right to the left.



tion of acids. An iron catalyst strongly prerduced showed the deoxygenation activity only after detectable amounts of an oxide had formed on its surface by reaction with the acid in the feed [59].

The above-described role of oxygen vacancies is itself an indication that the deoxygenation reaction is an MvK reaction. Oxidation of benzaldehyde, the reversed reaction, can run with only the oxide lattice oxygen, as has been seen in IR spectra [48,61]. The IR spectra of adsorbed acetic acid were studied and they provided an indication that acetic acid interacts with oxygen vacancies upon formation of an asymmetric bidentate adsorption complex [62]. With regard to the mechanism of benzoic acid deoxygenation, the following is of importance. The selectivity to benzaldehyde depends very much on the reaction conditions and the catalyst used. This dependence can be understood on basis of the MvK mechanism and the assumed role of oxygen vacancies in it. At higher pressures of hydrogen, higher temperatures and with oxides of lower M–O bond strength, the steady-state concentration of oxygen vacancies is too high, and consequently, the selectivity shifts from benzaldehyde to toluene. With an oxide of a higher M–O, this shift occurs at higher temperatures. Formation of toluene can also be suppressed by using higher pressures of benzoic acid or by adding water vapor to the feed [57,60,63]. In full analogy with benzoic acid, too high a concentration of oxygen vacancies (caused by too high a pressure of hydrogen in the reaction mixture or too severe a prerduction of the oxide) shifts the selectivity in the deoxygenation of nitrobenzene, from nitrosobenzene to aniline.

The acids play a role in the feedback control of the state of the catalysts' surface, either, as mentioned above, by annihilating some oxygen vacancies or, when a metal is present in the catalyst, by blocking most of the other reactions on the metal but allowing hydrogen adsorption to occur [64]. With benzoic acid, however, the last mentioned effect is insufficient to secure a high selectivity to benzaldehyde.

The message of what is said above is clear. The information on the solid-state reactions of oxides and, on their redox properties in relation to their composition, can be used for future improvements of deoxygenation catalysts. These reactions and their

MvK mechanism would certainly also deserve more attention of quantum chemists.

## 5. Hydrodesulfurization (HDS) reactions

Hydrotreatment of crude oil, comprising the desulfurization step, is one of the most important processes in the petrochemical industry. Thanks to the ever-improving technology of oil and coal desulfurization, the disastrous deterioration of woods in middle and west Europe has been stopped. In the same period of time, the fundamental knowledge on desulfurization has increased amazingly. An interested reader can admire the progress made in one of the excellent reviews on this subject now available [33,65]. The volume of the literature on the subject is enormous; one [33] of the reviews gives 1514 quotations. However there are still some unsolved problems!

The exact nature of the adsorption site for sulfur-containing molecules is still being discussed (is there always only one type of adsorption site?) so that it does not surprise that we do not know enough about the adsorption modes most important in dehydrosulfurization. A collection of possible modes can be found in the reviews; the most important of them remind of those of Fig. 5. Essentially, a sulfur-containing molecule can stay perpendicularly to the surface, with its sulfur atom in a sulfur vacancy or, less probably, through a sulfur–sulfur bond. It can also be oriented parallel to the surface, being held through its pi-system. Impression from the literature is that the first mode is most important with small and with aliphatic molecules.

The following is a much discussed problem: which is the exact sequence of elementary steps? Is it the sulfur extraction first, followed by hydro/dehydrogenation steps or is dehydrosulfurization initiated by hydrogenolysis/hydrogenation steps? Probably [33,65], the small molecules strongly prefer the first alternative, while for the large aromatics, the opposite is true.

Dehydrosulfurization rate of dibenzothiophene (DBT) shows a significant correlation with the metal–sulfur bond strength in the catalysts used. However, it does not mean that sulfur extraction is the rate-determining step. Hydrogenation steps re-

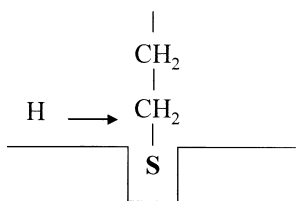


Fig. 8. Scheme of adsorption of a sulfur-containing molecule.

quire adsorbed hydrogen atoms and, through the process of chemisorption, the bond strength too can play its role.

Recently, a new mechanism has been suggested [34] — a hydrogen-assisted sulfur extraction from the molecules. In this process, molecules are anchored in a sulfur vacancy, as indicated in a scheme in Fig. 8.

This mechanism has been derived from the results of advanced quantum chemical calculations and it seems to be in compliance with many pieces of information in the literature [33,65–68]. The role of sulfur vacancies and that of the MvK mechanism in dehydrosulfurization is perhaps not really universal but it is most probably important enough to be always considered.

## 6. General conclusions with regard to the mechanism and the activity correlations

It seems almost self-evident that, in the catalytic reactions that involve a transfer of an atom between the solid and gaseous phases, the M–X bond strength (X = O, S, H, Cl) should play some role. However, how does it work when we look more closely?

The M–X bond strength shows as a function of  $Z$  characteristic variation, as we can see for oxides in Fig. 1. One can reasonably expect that the variations of the rates of the MvK reactions would all show a similar pattern, and this is for some oxidations true indeed. Instead of looking for just similarities, one can also eliminate  $Z$  from the above-mentioned correlations and plot the catalytic rates directly as functions of the bond strength  $q(\text{M–X})$ . Below, we shall discuss these correlations for oxidations and deoxygenations on oxides and for dehydrosulfurization on sulfides.

Fig. 9 shows the dehydrosulfurization rate of DBT, as a function of  $Z$  [33,69].

The lowest correlation differs from the analogous correlation in Fig. 1, but on the other hand, it looks like the correlations for metals, for example for the sublimation energies. Also, some reaction rates on metals vary with  $Z$  in a similar way (see for example cases in [70]). The data in Fig. 9 can be alternatively plotted in one unifying graph when using the average metal–sulfur bond strength as the parameter of the correlation. The bond strength is here [33] calculated from the heats of formation of sulfides. Upon such calculations, the data are normalized either per cation or per X atom. Each choice has quite a different justification, but for the quality of correlation, it does not matter too much [71–73]. Fig. 10 shows the data for DBT dehydrosulfurization, after normalization per cation, Fig. 11 presents the data for nitrobenzene deoxygenation, after normalization per anion of the stoichiometric formula.

Figs. 10 and 11 could be a nice illustration of the Sabatier–Balandin principle [3]: the optimal strength

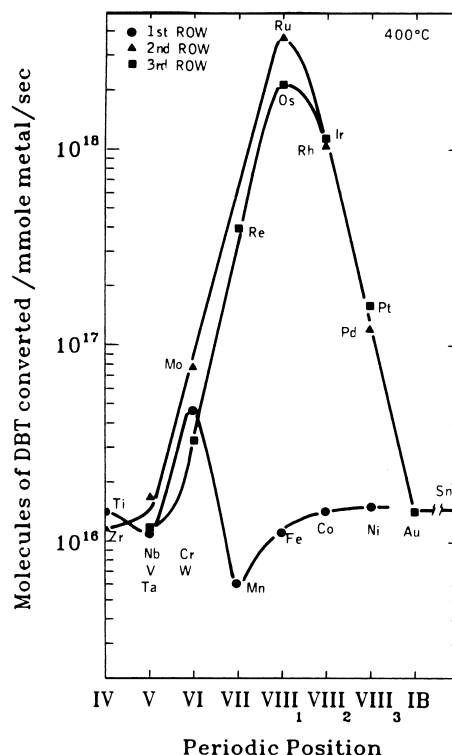


Fig. 9. Variation in the rate of DBT conversion by dehydrosulfurization, as a function of the atomic number of the cation in the sulfide used. The rate is normalized per millimole of catalyst [33,69].

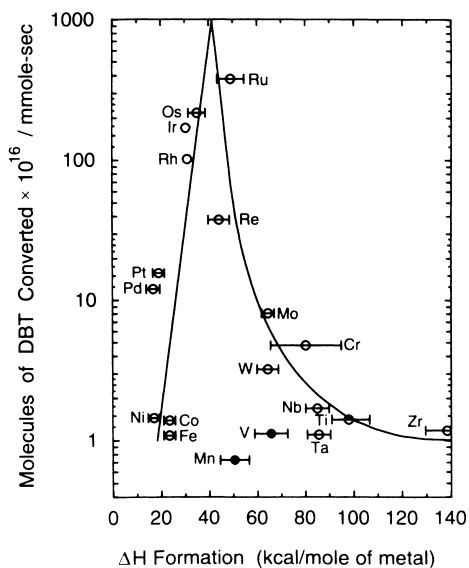


Fig. 10. HDS rate as a function of M–S bond strength, the latter being characterized by the corresponding heat of sulfide formation, normalized per mole of metallic component [33].

is neither too strong nor too weak. However, before we get too enthusiastic about the correlations and about the principle, let us consider the following. In

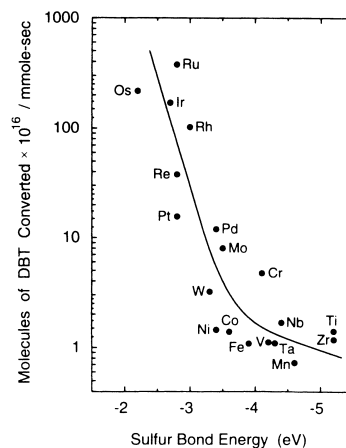


Fig. 12. The HDS rates for DBT, as a function of the M–S bond strength, calculated theoretically [33].

Fig. 12, the DBT dehydrodesulfurization activities are plotted as a function of the M–S bond strength, but this strength is now theoretically calculated and not derived from the heats of formation. There is now no maximum, antipathic correlation results and it reminds one of the correlations found often for oxidations. The reason for the difference caused by the use of different bond strengths is not known.

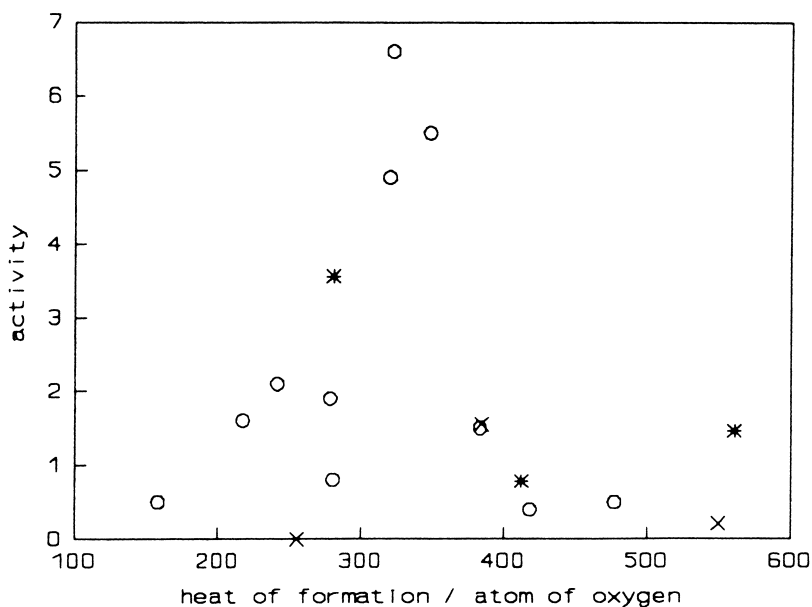


Fig. 11. The catalytic activity in nitrobenzene deoxygenation of the 3d (○) 4d (×) and 5d (\*) transition metal oxides as a function of the heat of oxide formation (kJ/mol), normalized per one oxygen atom of the stoichiometric oxide formula [74].

Evidence for the MvK mechanism operating widely is strong and the mere existence of such a mechanism indicates that there should be some relation between the catalytic rates and the thermodynamic parameters of the solid catalyst. However, how to understand and use the correlations properly?

We can learn from the literature that the exact value of the M–X bond strength is difficult to assess and one has to use one or another substitute. Thus, the first difficulty is how good is this choice and in which detail one can then trust the correlation obtained? Let us assume that the choice is a good one; what can we expect then from the correlation?

Since the 17th century, scientists know that a valid theory should lead to verifiable and valuable predictions. When the correlations between the catalytic rates and thermodynamic parameters of solid catalysts became a part of the theory of catalysis, scientists began to speak so often about using these correlations for finding still better catalysts that an impression was created as if it were better to define ever better parameters and to look for ever better ways to assess them, than to perform catalytic experiments directly (which are often easier to perform than to establish some of the parameters). This was not correct and it only brought the use of correlations in discredit. We can not ignore the following. The parameters averaged over the whole lattice mask the large differences between individual bonds, but the molecules interact with individual bonds that are, for example, crystal face specific. Using the plot activity versus  $q(\text{M–O})$  instead of plots with  $Z$  as the parameter, we can mask meaningful differences among the periods of the periodic table. It should be expected that a simple correlation with a single averaged bond strength can not answer such a subtle question like whether, for the hydrogenation of some new organic compound, iridium is a better catalyst than, for example, palladium. An analogous problem would be a question — is a manganese or a cobalt oxide better as a catalyst for the deoxygenation of some new, substituted nitrobenzene? However, for some other problems, it might be useful to consider such a correlation. The following example can perhaps illustrate this point.

A recent paper [60] reported on regularities in the behavior of oxides in reactions of benzoic acid. Oxides with a lower M–O bond strength showed

some activity already at lower temperatures. However, when the temperature was increased, they lost their selectivity to benzaldehyde easier than the oxides with a higher M–O bond strength, like dioxides of Ti, Zr and Hf. Therefore, the highest possible yield of benzaldehyde was obtained just with the last mentioned group of oxides. Namely, when the bond strength is too low, then the steady-state concentration of oxygen vacancies is too high and this induces too high a production of toluene and other side reactions. Within the group of Ti, Zr and Hf oxides, the antipathic correlation between the activity in the deoxygenation of the acid and the bond strength is exactly valid, in a way similar to the sympathetic correlation between the selectivity and the bond strength. Here, the reference to the correlation helps us to understand and to order the empirical knowledge, notwithstanding all the correct criticism in the literature on the parameter used and the correlation obtained with it. We express in conclusion the hope that a proper way of considering the above-mentioned correlations and the regularities in catalytic activities already established can perhaps lead to a design of new catalysts in a faster procedure than a combinatorial search.

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