

Review

Forty years in CATALYSIS: what have we learned?

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1. Introduction

The title implies that the author is mainly looking back and, on his work only. Nevertheless, also an incidental reader might be interested to learn how this particular research developed.

The years 1950–1960 were extremely important for ‘Catalysis as Science’ and ‘Keystone of Technology’. Due to the most influential papers by Dowden [1], Schwab [2], Eley [3], Roginsky [4], Boudart [5] and others, scientists turned from a purely empirical approach to catalysis, mostly based only on formal kinetics, to the search for the relation between catalytic activity and parameters characterizing the solid state of heterogeneous catalysts. Such a relation when established, should have had a predictive power and open the way to a scientific explanation of the catalytic activation of molecules. From studying the influence of the solid state parameters on catalysis, it was only a small step to the studies on the chemisorption bond and, on its role in catalysis.

Several papers published between 1950 and 1960, made clear (see, for review, Ref. [6]) that one single molecule (a potential reactant in a catalytic reaction) can exist on a surface in several forms, which have different properties and thus different roles in catalytic reactions: from active species to ‘spectators’ or ‘poisons’ of the catalytic overall reactions. The ingenious use of exchange (H...D) reactions [6–9] between hydrocarbons and deuterium revealed that on metals species coexist such as those shown for CH₄ in Fig. 1, in the upper part. Later, various spectroscopies (mainly, vibrational ones) confirmed this conclusion and added new species to the list and, some of them are shown for ethene in the lower part in Fig. 1.

Physical measurements (electric resistance of thin metal films, work function) revealed that even so simple adsorbed species as hydrogen atoms, can exist on metal surfaces in different forms, which distinguish themselves by different polarity of the metal–hydrogen bond and different participation in the bond of various metal orbitals (*ns*, (*n* – 1)*d*) [10–12]. There were also some indications that hydrogen adsorbed up to different surface coverages possesses different reactivity [13,14]. With this

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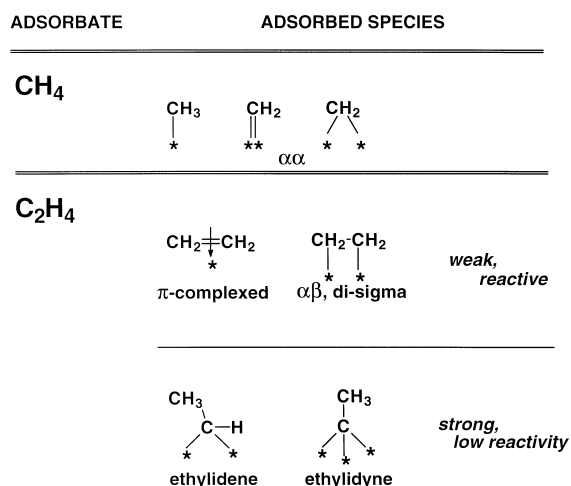


Fig. 1. Variety of species formed upon chemisorption of CH_4 and C_2H_4 on metals.

knowledge it seemed to be an attractive problem to investigate whether the varying reactivity of adsorbed hydrogen atoms can be also seen in a simple surface reaction of it with a (we thought foolishly-simple) molecule of cyclopropane. With my closest friends in Prague, we attempted to attack this problem. The original idea failed, but some other useful results were obtained. In any case we were set (1964) by them on the rails of the SELECTIVITY re-

search, which thereafter stayed to be ‘the author’s topic’ till nowadays.

Merta and Ponec [15] established a rule governing the selectivity in the cyclopropane reactions (1 to 3) shown in Fig. 2. Merta (1968) showed namely that the selectivity to the reactions 1 to 3, depends on the degree of dehydrogenation of the species formed by the chemisorption of cyclopropane. If the degree of the C–H bond dissociation (dehydrogenation) upon chemisorption is low, such as with Pt or Pd, the selectivity to propane is high. Vice versa, a ‘deep’ dehydrogenation induces hydrogenolysis. A correlation of a similar nature has been suggested during the same Congress in Moscow (1968) by Charles Kemball [16]. He pointed out that metals with a high hydrogenolytic activity show also a high propensity to form metal–carbon multiple bonds ($\text{M}=\text{C}$, $\text{M}\equiv\text{C}$), the latter being formed by dehydrogenation of the hydrocarbon. The mentioned correlation was later fully confirmed by van Broekhoven [17] and van Broekhoven and Ponec [18] who also established that small particles of a given metal are more reluctant to form the multiple bonds, than the large ones [18]. The studies concerning the relation between the chemisorption modes on a metal and the activity

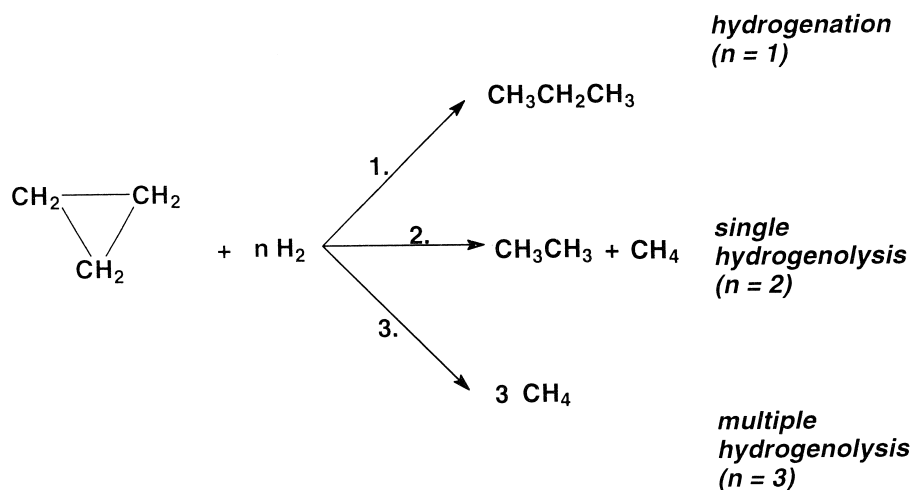


Fig. 2. Reactions with cyclopropane–hydrogen mixtures on metals.

or the selectivity of the same metal continued to appear in the literature, many of them originating from the Laboratory headed by Gabor Somorjai (see e.g., Ref. [19], Fig. 4 therein).

The 3rd International Congress on Catalysis took place in Amsterdam in 1964. According to the wish of the organisers a substantial part of this Congress should have been devoted to the problems of SELECTIVITY. However, to a great disappointment of the organisers only a few papers dealing explicitly with this problem were submitted. That was, for us in Prague, the main reason why we definitely focussed on the selectivity problems, after 1964. At the Congress in Moscow (1968), the first results (mentioned above) of this research could be presented.

2. Problems of catalytic selectivity: an introduction

The example of cyclopropane reactions (vide supra) shows that a catalyst can make a reaction possible, which is kinetically impossible. Addition of dihydrogen to unsaturated molecules (as $c\text{-C}_3\text{H}_6$ is) is, without a catalyst, actually impossible. Moreover, when several reactions are thermodynamically possible (such as the reactions 1 to 3 in Fig. 1), a catalyst can stimulate one reaction more than the other. For example, platinum or palladium stimulate reaction (1), from the reactions in Fig. 2, cobalt would stimulate the reactions (2) and (3), etc. The first phenomenon (the mere addition of H_2) is a typical example of catalytic activity, the second phenomenon (catalyst stimulates only one reaction of many) illustrates the selectivity of catalytically active materials.

As already mentioned the selectivity can be observed, when several reactions can occur simultaneously. A very simple scheme in Fig. 3 presents the three main types of simultaneous reactions [6].

The natural question is: which factors determine the catalytic selectivity in the three men-

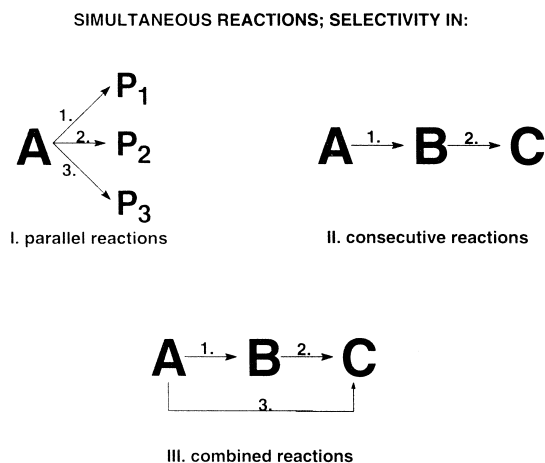


Fig. 3. Various types of simultaneous reactions.

tioned types of reaction, (1) to (3)? Reforming reactions of hydrocarbons on metals and alloys are at low temperatures an example of (1), similar to the synthesis gas (CO/H_2) reactions on metals or deoxygenation of carboxylic acids on oxides. Example (3) can be illustrated by hydrogenation reactions of ethyne or of unsaturated aldehydes on metals. All these reactions have been studied in Leiden (1970–1997) and will be mentioned below. However, first the definitions which will be needed in the discussion.

There are several possibilities how to characterize selectivity (s_i) to the product i . A very convenient way is to use a normalized ratio of rates of the particular reactions,

$$S_i = \frac{r_i}{\sum_i r_i} \quad (1)$$

If the reaction is followed at a (nearly) steady state, in a continuous flow mode of measurements, the net rate is at low conversions α , related to the concentration of the compound i in the gas effluent from the reactor. Then the parameter:

$$S_i = \frac{C_i}{\sum C_i} \quad (2)$$

is also very informative. When the catalyst is being studied under such experimental conditions that the conversion is high and the product i arises from the network of reactions, the ratio (2) is no more simply related to (1), but it is still useful. We met this situation in e.g., naphtha reforming at high temperatures, or with the n -butene isomerisation to isobutene.

The rate r_i of a heterogeneously catalyzed reaction can be described, in the framework of the activated complex theory [20], by expressions such as:

$$r_i = \kappa N_i \frac{kT}{h} \exp\left[\frac{\Delta S^*}{R}\right] \exp\left[-\frac{E_{\text{act}}}{RT}\right] \times f(C_A C_B K_i \dots) \quad (3)$$

where κ is the transition coefficient, N_i the number of active sites, available for the formation of activated complex(es), k the Boltzmann constant, h the Planck constant, ΔS^* the standard entropy of the activated complex formation, E_{act} the activation energy, and f is the function expressing the dependence of the rate on the surface concentrations. The last term shows a weak temperature dependence through the adsorption equilibrium constants K_i . The overall temperature effect is mainly determined by the ‘Arrhenius factor’, involving activation energy E_{act} .

In principle any of the terms of Eq. (3) can be decisive for the selectivity of the catalyst, but most authors focus on the Arrhenius factor, on E_{act} . So it is also with the first and, up to now still the single existing general theory of catalytic selectivity, formulated by Balandin [21] 70 years ago. However, as we shall see below this restriction to E_{act} is by no means justified; for the reaction discussed below, the terms N_i are equally or even more important. The factor N_i can be varied by the choice of the catalytic material (e.g., a metal vs. an alloy), by the choice of a certain crystallographic structure of the well defined single crystal metal surfaces,

by the introduction of promoters (an additive not active itself, but influencing the activity or the selectivity) or by interaction of the catalyst with the reaction mixture (induced reconstruction of metal surfaces, gas induced segregation of alloys, reduction of oxide surfaces, etc.) [19,22,23].¹

3. Principles of catalytic activation of molecules

There are attempts in the literature to formulate rules which apply indiscriminately to all reactions or to large groups of reactions and predict the activity/selectivity of the catalysts (see e.g., Ref. [27]). However, it can be doubted whether this is a universal and always fruitful approach. Probably, it is better to define first different categories of catalytic reactions, according to the way of catalytic (heterogeneous) activation and, to discuss these categories separately. Further it is necessary to distinguish first, what is the catalyst, co-catalyst, promoter, support, diluent, etc.

In this line of thinking, we can divide all reactions into four categories, (i) to (iv), according to the mechanism of activation.

3.1. (i) Berzelius mechanism: an action on distance

This is a very rare type of interaction, although Berzelius considered it as the main (or the single) type [28,29]. An example of it is the ortho–para-hydrogen conversion, occurring by a non-dissociative mechanism, in which the spin-flip is induced by magnetic moments of the surface atoms (e.g., of rare-earths oxides). Another examples are perhaps, the cases in which a catalyst plays a role of a ‘third body’, absorbing the energy released by vigorous interactions.

¹ Creation of active sites by the reaction mixture can always be suspected to occur, when the reaction shows an induction period on stream, see examples in Refs. [24–26].

3.2. (ii) Langmuir–Hinshelwood reactions: interactions in the adsorbed layer

Catalysts of these reactions have often (metals) something like free-valencies on their surface. Examples of these reactions are plentiful—addition of dihydrogen to unsaturated compounds (C=C, C=O, C=N, etc. on metals), oxidation of ethene to oxirane (ethylene oxide) on Ag, or synthesis gas reactions on metals. Through their ‘free valencies’ metal atoms enter the activated (transition) complex of the rate determining step (or one of the steady state steps) of the reaction.

A large group of these reactions, many of them being most important for the industry, is characterized by the fact that the reaction is induced by hydrogen atoms (protons) bound to the catalysts instead of by free valencies of atoms. These H’s return to the surface after the catalytic cycle on the surface has been closed.

Hydrogenation on oxides, whereby the oxide switches between ‘O’ and ‘OH’ (see e.g., Ref. [30]), can be either seen as a ‘Langmuir–Hinshelwood’ reaction or, as a simple case of the following (iii) type of activation.

3.3. (iii) Mars and van Krevelen mechanism

It was probably Kröger [31] who first formulated the idea, but Mars and van Krevelen [32] brought a lot of evidence for it and formulated the first applicable kinetic equations on basis of this mechanism [32,24]. Kröger, Mars and van Krevelen indicated a possible relation of the activity to such parameters as metal–oxygen bond strength, etc. Such relations have been later studied by many authors (see e.g., a review in Ref. [33]). Upon a reaction running by this mechanism, a component of the solid catalyst (oxygen in oxides, sulfur in sulfides, chlorine in chlorides) is being transferred between the catalyst and the reactants, this lattice component appears in the products of reaction.

3.4. (iv) High temperature reactions involving free radicals (mechanism Semenov–Roginsky [34])

Examples are the oxidation of NH_3 to nitrogen oxides (production of nitric acid), high temperature combustion of hydrogen or hydrocarbons, or—the recently much studied—oxidative coupling of methane to ethene and ethane. With this mechanism, radicals are released from the surface into the gas phase and react there further.

All reactions which have been studied in Leiden belong to either group (ii) or group (iii).

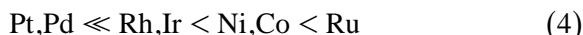
4. Selectivity in hydrocarbon reactions

4.1. Reactions of hydrocarbons on metals

As already mentioned, Merta and Ponec [15] has distinguished two groups of metals, with regard to cyclopropane reactions (hydrogenation/hydrogenolysis) on metals. Group (I), with Pt and Pd (1.7) and group (II), with Mo (1.6), Ni (1.5), Rh (1.4). The values in parentheses show the H/C ratio of the adsorbed layer, at 273 K and standard conditions upon adsorption of cyclopropane. The two groups differed substantially in the contribution of hydrogenolysis: with Pt and Pd (which form C_3H_5 (allyl?) upon adsorption) this was zero, with other metals (dehydrogenating cyclopropane more, in the adsorbed state) fraction of carbon atoms in hydrogenolytic products was 8–27%, under standard condition reaction. Hydrogenolysis is stimulated by dehydrogenation upon chemisorption. There is now much more information in this direction. Davis et al. [35] determined the H/C ratio in the chemisorbed layer of ethene on Pt and obtained a curve schematically shown in Fig. 4. Similar exact information on the ‘hydrogenolytic’ metals (such as Ni, Co, Ru...) is not known, but according to the indirect information in the literature, we can expect for these metals a similar curve, but shifted to the left

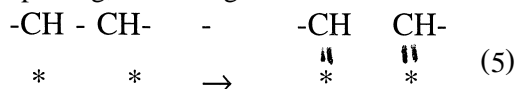
(see Fig. 4). Upon dehydrogenation, i.e., upon decreasing H/C ratio of the adsorbed layer, multiple bonds are formed with the surface (e.g., ethynidyne from ethene, etc.).

Van Broekhoven and Ponec [36] monitored the exchange reaction in cyclopentane/D₂ mixtures and, established that the propensity to form multiple bonds between the metal atoms and carbon atoms in hydrocarbons, follows the order:



With these metals, the propensity to form multiple bonds (a parameter characterizing this propensity is on the y-axis) is a function of the average particle size d (x-axis), as can be seen for methane in Fig. 5. Obviously, small particles are more reluctant to form M–C multiple bonds.

Finally, the following conclusions were drawn from the results: (i) A certain electronic structure is favouring the multiple bond formation. Most likely, multiple bonds facilitate the C–C bond splitting, according to:



One can state that the Pt- and the Pd-orbitals of the surface atoms are less suitable to form M=C bonds, than the orbitals of ‘hydrogenolytic’

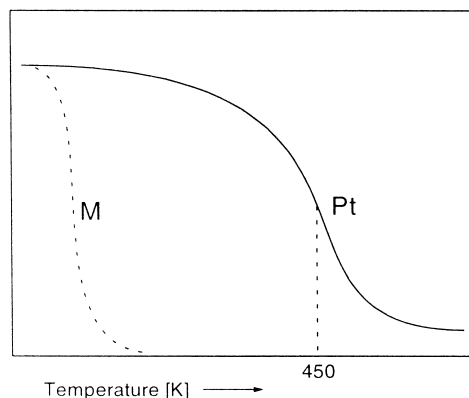


Fig. 4. Dehydrogenation of adsorbed species (schematically) of ethene. M = metals most active in hydrogenolysis; H/C ratio as function of T .

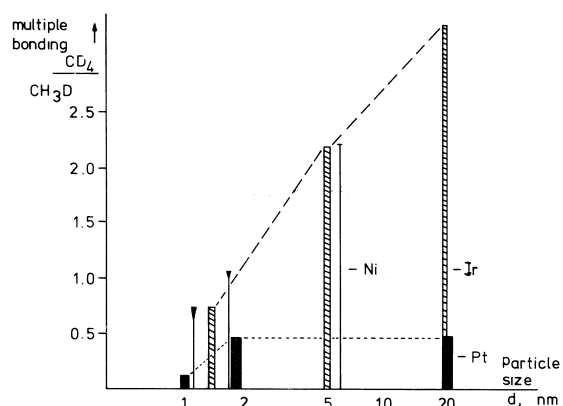


Fig. 5. Propensity of metals (characterized by the CD₄/CH₃D ratio measured at standard conditions) to form metal-to-carbon multiple bonds, as a function of particle size for platinum, iridium and nickel.

metals such as Ru, Co, Ni... (ii) The site, schematically indicated by an asterisk, can actually be an ensemble of atoms. The results in Fig. 5 show that it is probably more difficult to find the required ensembles, with a certain number of atoms and geometry, on smaller particles than on the large ones. Small particles have a surface more irregular than the large ones and, the atoms in their surfaces vibrate with a larger amplitude, what influences more the reactions requiring large ensembles (see detailed discussion in Chap. 5 of Ref. [37]) than those which can also run on one single metal atom.

4.2. Reactions of hydrocarbons on alloys

4.2.1. Alkanes

The idea that an ensemble of a certain number of atoms is necessary for a certain reaction to occur, has been postulated first by Balandin [38,39] and Kobozev [40].² The recent experimental test of this idea was a result of studies on alloys in Leiden and elsewhere. The essence of this approach can be formulated as follows.

Consider a hydrocarbon reaction on an alloy formed by an active (in the given reaction)

² For review, see Ref. [21].

metal (M_A) and an inactive one (M_B). Plot the rate of this reaction per unit of the total surface area (areal rate), divided by the areal rate of the pure metal M_A , as a function of the surface atomic ratio $x_s(M_A)$. The activity of a catalyst can be most conveniently defined as the areal rate under standard conditions. For this test, alloys with a known surface ($x_s(M_A)$) vs. bulk ($x_b(M_A)$) composition have to be used and further, one has to be sure that alloying with M_B did not cause any substantial change in the electronic structure of atoms M_A . Only then one can analyse the results obtained in terms of varying average ensemble size. Alloying M_A with M_B eliminates namely the larger ensembles more than the small ones. Note, that an alloy couple fulfilling these conditions, appeared to be the nickel–copper system. The result of such a test is (schematically) one of the two functions shown in Fig. 6. When each single atom M_A can catalyse the reaction—curve (I) results, when ensembles of M_A are required—the curve such as (II) is observed. The reactions can thus be divided into two groups [41]:

- (I) Reactions insensitive to the ensemble size.
- (II) Reactions sensitive to the size of the available ensembles.

In group (I) one meets e.g., hydrogenations of various isolated unsaturated bonds ($C=C$, $C\equiv C$, $C\equiv N$, $C=O$). Also the hydrocarbon–deuterium exchange is rather insensitive by its total activity, but some shifts in product distribution can be seen with alloys [37]. Group (II) is formed by reactions such as hydrogenolysis of hydrocarbons, some mechanisms of isomerisation, Fischer–Tropsch synthesis of hydrocarbons, ether formation and, perhaps some others [37]. In all cases a situation is met as in scheme/Eq. (5).

Alloying of an active with an inactive metal (Ni–Cu) can lead to appreciable SELECTIVITY EFFECTS, as can be seen in Fig. 7. In a similar way, dilution of Ni by Cu suppresses the hydrogenolysis (reaction 2) of cyclopropane and by that enhances the selectivity to hydrogenation of this molecule [37].

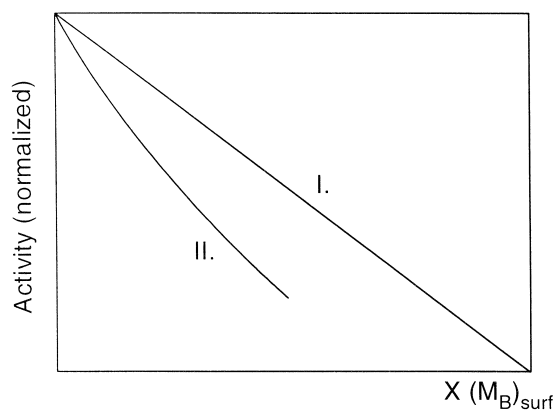


Fig. 6. Ensemble-size sensitivity of reactions on metals (curve II).

Obviously, the selectivity in the Langmuir–Hinshelwood type reactions on metals can be manipulated by alloying, if one of the reactions requires a large ensemble, while the other(s) do(es) not [37].

Reactions requiring large ensembles can also be influenced by e.g., carbonaceous deposits (formed from hydrocarbons used as reactants), or by various poisons and modifiers, such as sulfur. These observations have been made also by other authors [37]. In its turn, deposition of carbonaceous layers is a ‘large ensemble’ reaction. It was, for example, interesting to see that small particles were less self-poisoned by the carbonaceous deposits, than the large particles, most likely because the deposit formation itself requires an extended dehydrogenation of adsorbed species and thus, a larger ensemble of metal atoms on an exact distance from each other [42,43].

Let us turn back to the sequence of metals represented by Eq. (4), above. The metals Pt and Pd are very inactive in hydrogenolysis, but at high temperatures, at which skeletal reactions take place, they are—as compared with the active hydrogenolytic metals—most covered by the least reactive (graphitized) deposits [44,45], while other metals, such as Ni, Co, Ru and Ir show, in the presence of hydrogen, much more resistance to self-poisoning. From their surfaces ‘carbon’ is released into the gas phase as CH_4 . Alloying changes the process of deposition as

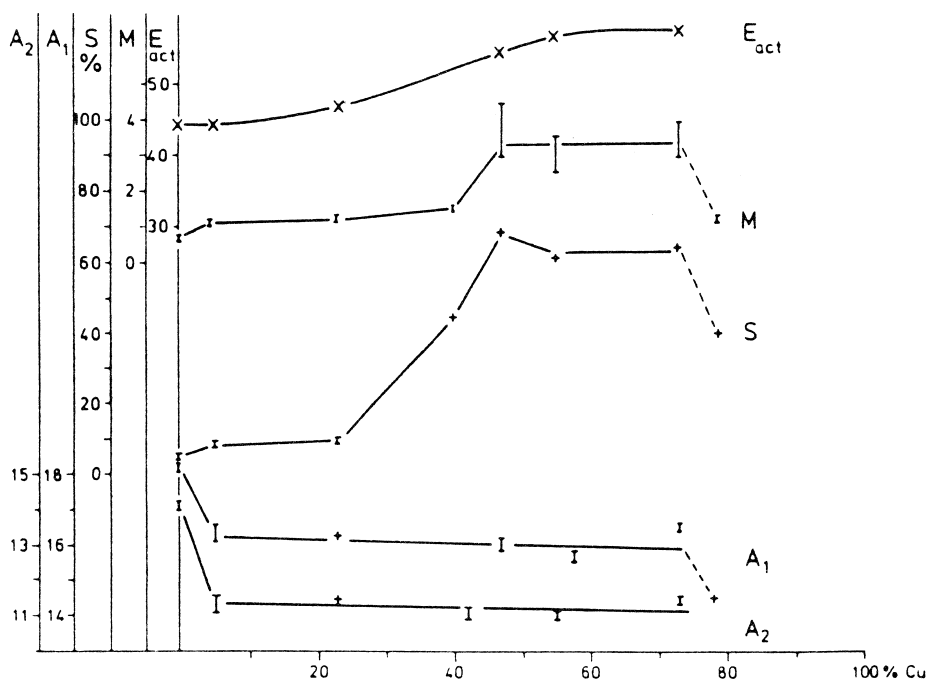


Fig. 7. Reaction parameters of *n*-hexane conversion by nickel and nickel–copper alloys. r_w : Rate per g catalyst, r_s : rate per cm² surface; $A_1 = \log r_w$ at 603 K, $A_2 = \log r_s$ at 603 K, activation energy of the overall reaction E_{act} , fission parameter M , (showing that Ni–Cu alloys behave more like Pt than like Ni), selectivity parameter S ; characterizing the extent of non-destructive reactions (mainly isomerization); all as a function of alloy bulk composition (in at.% copper). Support-free powder alloys used as catalysts.

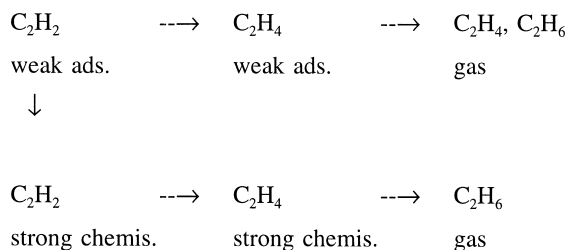
well and simultaneously, deposits induce the surface segregation [45]. Since blocking by carbonaceous deposits should have (in many cases we know, it has) a similar effect such as alloying of the active metal M_A with an inactive one, M_B , a question arose, how much of the phenomena such as the sequence expressed under Eq. (4), or of the effects of alloying, is actually due to carbonaceous deposits and how much it is the property of the metal alone. To answer this question van Wijk et al. [46] made experiments in small pulses of hydrocarbons and established that the selectivity of Pt can be to some extent modified by carbonaceous deposits, but the main features of Pt, i.e., a low hydrogenolysis and (in a certain temperature region) high isomerisation selectivity, are intrinsic properties of platinum.

When two active metals such as Pt–Ru on Pt–Rh form mixed ensembles in the alloy surface, the alloy can show a higher activity (or a certain higher selectivity), than any of the alloy

components alone. This is often called ‘a synergy effect’. The authors of Ref. [47] speculated on this effect on basis of their results with Pt–Cu, but much more indications for the synergy due to mixed ensembles have been obtained, mainly by Leclercq et al. [48] (for review see Ref. [37]).

4.2.2. Ethyne

With all available spectroscopic and kinetic data in mind we can postulate two parallel pathways from ethyne to ethene or ethane:



With palladium (and, to some extent is this also true with Pt), the lower pathway makes a negligible contribution. As a consequence, selectivity to ethene is high so long, as there is some ethyne in the gas phase. Ethyne displaces the weakly bound ethene and keeps the selectivity to ethene high (this is called a thermodynamic selectivity [6,37]). However, a metal such as iridium shows a low selectivity to ethene from the very beginning of the reaction (from lowest conversions). Probably, because the lower pathway in the scheme above makes a much larger contribution (this is called a mechanistically or kinetically determined selectivity [6,37]). Alloying of Pd or Ni with Au or Cu, respectively, showed some advantages in ethyne or dienes hydrogenations (e.g., keeping heat production under control, keeping the overall rate under the limiting rate of the mass transport of ethyne), but the effects are not very pronounced. Much more visible effects could be expected from alloying of iridium (in case of Cu and Au, modification of iridium is practically limited only to the surface) and this expectation was confirmed, as can be seen in Table 1.

Table 1 compares the effect of metals which differ in their activity and in their electronic structure, on the activity and the selectivity of iridium. Obviously, there is no correlation of the signs of the catalytic effect with the electronic structure of the additive, but the effects are very well understandable in terms of the variation in the ensemble size and composition. Sassen et al. [51] found, using EELS on single crystal planes (Pd, Pd–Cu) that (i) ethylidyne formation from ethene (or after H-redistribution, from ethyne)

can be slowed down by alloying and/or by carbonaceous deposits and (ii) ethylidyne is formed via ethylidene. This suggested that the strongly adsorbed species in the schemes above, can be those whose adsorption is accompanied by a simultaneous (multiple) dissociation of the C–H bonds, either in ethyne or in its half hydrogenated states.

The small size of effects due to the varying electronic structure of individual atoms in alloys (if the electronic structure varies at all) has been seen earlier, with hexane [52]. In that paper the Pd–Au and Ni–Cu systems were compared. In both cases, the addition of an inactive metal suppressed the total activity, suppressed the selectivity to hydrogenolysis and suppressed in the alloy the formation of larger Pd or Ni ensembles. Only in the case of Pd, the electronic structure changes by alloying ($4d^{9.7}5s^{0.3} \rightarrow 4d^{10}5s^0$) but the hydrogenation is suppressed also by alloying Ni with Cu. Thus, the ensemble size effects evidently dominate in the selectivity changes, also when the electronic structure undergoes a change.

Summarizing Section 4.2, the following can be said. The changes in the available ensemble size and, in the ensemble composition, dictate the selectivity changes. Expressed by terms of Eq. (3), the changes in ' N_i ', the numbers of sites suited for a certain reaction dominate the selectivity scene. This is a proper place to mention that my friend Wolfgang Sachtler not only stimulated my emigration to the Netherlands (to escape the occupation of the former Czechoslovakia by the former USSR) but he also initiated and stimulated the work on alloys.

Table 1
Effect of alloying IRIDIUM ($[\text{Xe}] 4f^{14}5d6s^2$)^a with the indicated metal [49,50]

Metal added	Effect on activation	Effect on selectivity	Electronic structure of the additive ^a
Ir +			
Cu	↓	↑	$[\text{Ar}]3d^{10}4s^1$
Au	↓	↑	$[\text{Xe}]4f^{14}5d^{10}6s^1$
Re	↓	↑	$[\text{Xe}]4f^{14}5d^56s^2$
Pt	↓	↑	$[\text{Xe}]4f^{14}5d^96s^1$

^aFree atom state.

4.3. Model catalysts for the naphtha reforming

For a long time, the research on alloys was mainly driven by theoretical interests (see e.g., Refs. [1–6,37,53]) and scientist's curiosity. However, the most important impulse for studies with alloys came later by the enormous industrial success of alloys ('bimetallics') in naphtha reforming [54]. The practical catalysts were combinations such as Pt–Re, Pt–Ir, Pt–Sn on Al_2O_3 with an acidified (Cl-containing) surface, sulfurized metals (Re, Ir) and, sometimes with still other additives being used. Fundamental research mentioned above in Section 4 produced results, which helped to understand what happens in the industrial reactor when the mentioned alloys are used as catalysts. The laboratory in Leiden made here also a contribution. Without going into details, a short list of conclusions, concerning the role of individual catalyst components, will be presented now, using Fig. 8 and some additional information concerning determination of acid sites, the effect of pyridine in the reaction mixture, etc. [37,55]. Inspecting Fig. 8, we observe the following.

(i) Addition of Re, Ir or Co to Pt/ Al_2O_3 (see the left column) catalysts causes an increase in selectivity to hydrogenolysis, accompanied by a parallel decrease in selectivity to isomerisation and cyclisation. (ii) When sulfur is added to the catalyst, the picture changes dramatically. Now isomerisation selectivity increases with additives in all cases. This is due to the acid-catalysed reactions on Al_2O_3 , which get the chance to manifest themselves, when the activity of the metallic component has been suppressed. (iii) Sulfur is preferentially adsorbed on the additive Re or Ir (this idea was first formulated by Wolfgang Sachtler). It suppresses all reactions on the Pt metal surface very strongly, except the hydro/dehydrogenations and, it stimulates the bifunctional mechanism by suppressing the formation on the metal of the strongly bound (by multiple C–H dissociation) intermediates, without influencing the number of acid sites [55]. In other words, the acid catalysed reactions on the

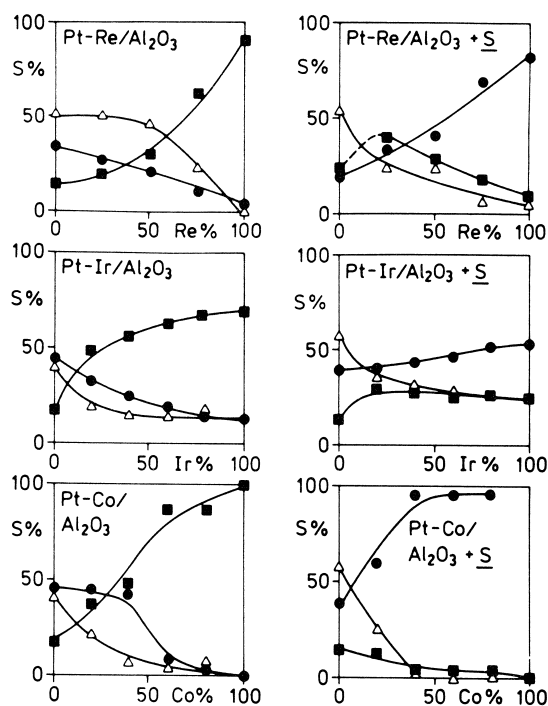


Fig. 8. Selectivity in the reactions of *n*-hexane at 620 K, at standard reaction conditions as a function of catalyst composition. Left: catalyst unmodified by sulfur. Right: modified by sulfur. ■ Hydrogenolysis; ● isomerisation; △ cyclisation.

alumina surface receive more of the weakly bond unsaturated species created on the metal, when the metal is sulfurized. The latter conclusions have been arrived at upon measuring also the particular rates, next to selectivities [55].

The message from this all is again, very simple. The dominating effect of the combined additives (Re, Ir, Co and sulfur) on the industrially used Pt/ Al_2O_3 catalyst, is to modify the active centres on Pt in such a way that the undesired reactions on the Pt surface are eliminated and the desired acid-catalysed reactions on Al_2O_3 get more chance [55].

5. Selectivity in syngas reactions

Methanol synthesis (worldwide), Shell Middle-Distillate Synthesis in Malaysia, and the gasoline synthesis in Sasol/SAR, are at the

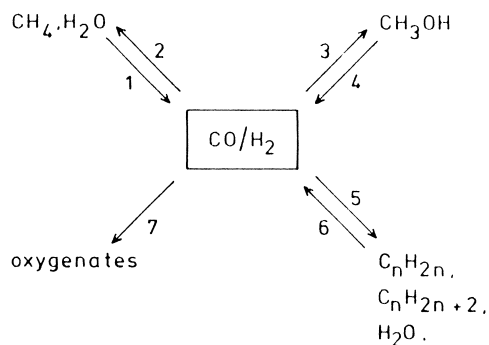


Fig. 9. Reactions of syngas on metal containing catalysts. Reactions (1), (2) and (5), (6) can be catalysed also by pure metals; reaction (7) to alcohols and most likely the reactions (3) and (4) require a promoted metal as a catalyst.

moment the examples of operating applications of syngas reactions. However, it is a deep conviction of your author, that ‘the time’ for this theoretically very interesting network of reactions, ‘is still to come’.

Syngas reacts, in principle, along the lines, shown in Fig. 9. It was for us in Leiden extremely attractive to make an attempt to identify the factors determining the selectivities in reactions (1) to (7), in Fig. 9. Typical catalysts are for (5): promoted Fe or Co; for (3): Cu–ZnO/Al₂O₃ and for (7): Co or Rh + transition metal oxide/SiO₂. The question is—why it is so? It was most interesting to establish what has to be done with one and the same catalyst to direct it to either reaction (5) or (3) or (7). This has been done with a rhodium-based catalyst. It was found that pure hydrocarbons are produced (reactions 2, 5) when rhodium is used as pure, unmodified. From studies on other metals we know (see below), that large ensembles of metal atoms are necessary to dissociate CO and the dissociation of CO is the first and necessary step of the prevailing mechanism of hydrocarbon synthesis [37,56–58]; this is behind the first conclusion. Methanol is produced best with Rh/MgO catalysts, when the preparation ensures a high concentration of unreduced Rh ions in the reduced catalysts [59]. Higher alcohols (C₂₊) are produced when Rh (or e.g., Co) is

properly promoted; for this reaction Rh ions are not required.

The idea expressed in the paper [56], that Fischer–Tropsch synthesis of hydrocarbons requires large ensembles for CO dissociation, has met first a great resistance in the literature, but it seems to be generally accepted now. The sum of positive and negative (!) reactions on the paper [56] promoted this paper to the ‘citation classics’ of Current Contents (June 1987).

The conclusion that positive ions, cations of Pd, Pt, Rh and, perhaps of Cu too, are the centres of methanol synthesis was mainly based on these results: (i) The activity in CH₃OH synthesis is proportional to the concentration of Pd present as (unreduced) Pdⁿ⁺ in the MgO promoted, SiO₂-supported catalysts (see Fig. 10) [25]; (ii) The positive charge on Pd stabilizes formyl (HCO), the potential intermediate of the methanol synthesis. The presence of a basic promoter (e.g., MgO) stabilizes Pdⁿ⁺. Promoter can also stabilize CO adsorption; upon this, it acts by its charge (point charge does the same as a cation), through-the-vacuum side of the catalyst, but not through-the-metal [60,61]; and (iii) Hindermann et al. [62] added the third

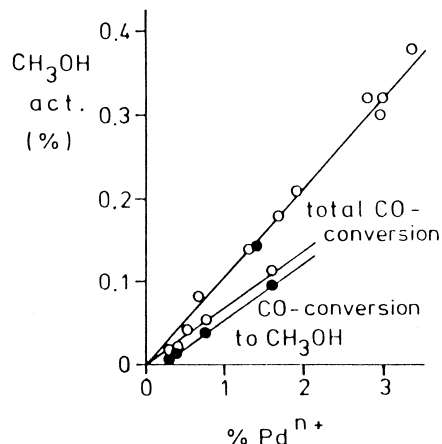


Fig. 10. Activity (yield) in CH₃OH formation at 488 K (defined as total conversion × selectivity × 10⁻²) as a function of the relative (to the total Pd content) of Pd extractable by acetylacetone under standard conditions (most likely Pdⁿ⁺); Upmost line—Mg promoted; middle and lowest line—La-promoted catalysts.

strong argument: the activity in methanol synthesis is proportional to the surface concentration of formyl groups, the assumed intermediates, which are stabilized on Pd^{n+} centres.

With regard to the Cu/ZnO catalysts, the following conclusions can be drawn. A high activity and stability of the catalysts is only achieved and maintained, when CO_2 is added to the syngas. This can be either explained by an assumption that a formiate (HCOO^-) is the necessary intermediate, or one can speculate that $2\text{Cu}^0 + \text{CO}_2 \rightarrow \text{Cu}_2\text{O} + \text{CO}$, whereby formation of formyl ($\text{Cu}^{(+)}\text{HCO}$) is again possible.

Although the three arguments (i)–(iii) (above), form a very convincing and self-consistent picture, this idea is not (yet) generally accepted. In particular, with regard the potential extension of this idea to the copper-catalysts (compare Ref. [63] with Refs. [26,64]), many people make objections against it.

The group in Strasbourg [65] solved the problem how the promoters induce the way to higher alcohols. In this direction, the main contribution from Leiden was the finding that the promoter can be created from the support, by the action of the precursor of the metallic components (e.g., chlorides dissolve V_2O_4 and bring—through the solution— VOCl_2 on the precursor and the metal surface) [66]. Interesting to see was that almost all commercial silicas contained so much impurities, that after leaching with the metal precursors (chlorides, nitrates), these silicas release so much promoters that the Rh catalysts made with these silicas are efficient catalysts for ethanol synthesis. (Only Aerosil (Degussa) appeared to be a clean support) [67,68].

Research described above has lead to a picture of an active Rh-catalyst ($\text{M} = \text{Rh}$) with identification of various active sites, as in Fig. 11 [63,69].

Summarizing the presented results and ideas in this section, one can make a preliminary conclusion that the selectivity to reactions (1) to (7) in Fig. 9, is dictated by the structure and

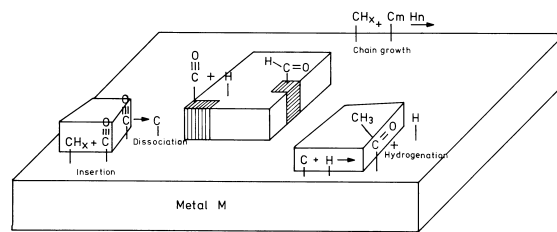


Fig. 11. A schematic model of a surface active in the synthesis of C_{1-} and C_{2+} -oxygenates. Base- and active metal particle M (Rh, Ru, Co ...) attached to a support (not shown). Blocks of promoting oxides (transition metal oxides, as optimal for C_{2+} -oxygenate formation, basic metal oxides, as optimal for CH_3OH synthesis) are shown, the black spots indicate the position of the active metal ions (M^{n+}) stabilized by the promoter.

composition of the active site: a large metal atom ensemble is needed for (1), a metal ion bearing formyl (zero valent metal is supplying hydrogen atoms) is necessary for (3) and the site on the metal–promoter interface is required for (7). In terms of Eq. (3), the selectivity is determined by ‘ N_i ’s’, the respective numbers of active centres for particular reactions.

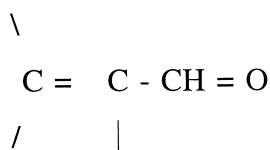
6. Promoted metals in hydrogenation of unsaturated aldehydes and ketones

Catalytic research in the Netherlands was, for a long period of time, oriented to oil processing industry and to the ‘catalysts’ (much more than to ‘reactions’) of these huge operations. Only slowly started (in about 1989) the reorientation of research to the so called ‘fine-chemical’ reactions. As it is usual in this world, this is in the meantime again one of the rails abandoned by the managers of the industry; and we can only add: definitely or for the time being?

Research concerning the fine chemical processes and their catalysts has a great opponent in the companies ‘book-keeper’. Money turnover taken per one single product is often so low, that 5% of it (an average what book-keepers want to spend on research in chemical industry) is not enough for supporting any reasonable research. Thus, only subjects of general charac-

ter, concerning the whole categories of products, have a chance to attract research money. It appeared that hydrogenation of conjugated double bonds in α,β -unsaturated aldehydes might be one of such generalized problems. Moreover, it is a nice selectivity problem.

Consider a molecule (a ‘substituted acrolein’); schematically:



Its interaction with metal surfaces starts through a weak adsorption, which is (i) a π -complexed C=C bond, or its di-sigma alternative and, (ii) a $\eta^1(\text{top})$ -coordination of C=O or, an α,β di-sigma, η^2 -adsorption through C=O. In all cases there is a shift of electrons from the molecule to the metal. Thus, strengthening of one weak chemisorption bond (for example, when going from one metal to another) strengthens the other bond, too. Obviously, the desired bonding to the metal through C=O must be selectively promoted. The Figs. 12 and 13 illustrate the most important information, obtained in a study of hydrogenation of substituted acroleins, on pro-

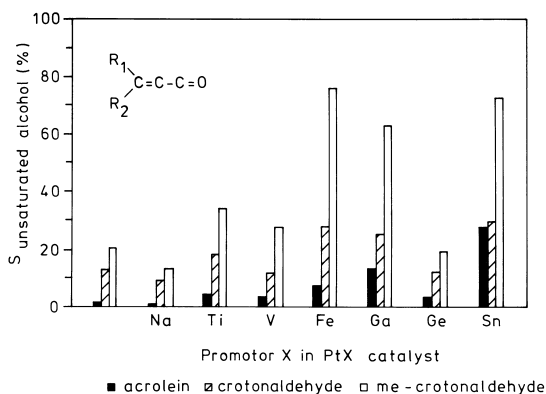


Fig. 12. Selectivity to unsaturated alcohols in hydrogenations of indicated α,β -unsaturated aldehydes. The used promoters are shown. The selectivity is higher when the C=C bond bears substituents.

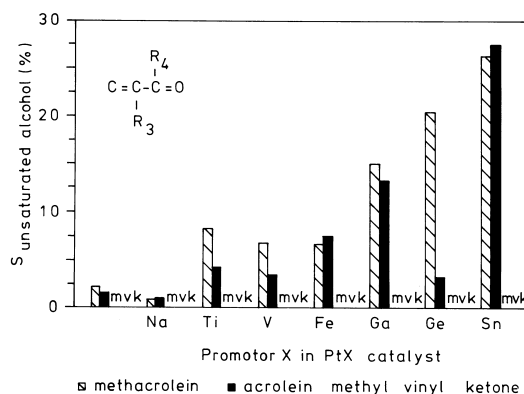


Fig. 13. Selectivity to unsaturated alcohols in hydrogenation of the indicated α,β -unsaturated aldehydes and ketone (methyl vinyl ketone). Notice the zero selectivity with unsaturated ketone!

moted Pt. The results can be summarized as follows [70–72].

(1) Substitution on the C=C bond (from acrolein to croton aldehyde, etc.) suppresses the bonding through this bond and increases thus, the desired selectivity to unsaturated alcohols. Substitution on the C=O bond (from aldehydes to ketones) eliminates the reaction on this bond. In competition with the C=C bond hydrogenation, the conjugated keto-group does not react at all (MVK, in Fig. 13).

(2) Promotion is not only by the cationic charge (alkali ions are inefficient promoters), certain orbitals must be available on the promoter's cation.

(3) Transition metal oxides are less efficient than the s,p metal oxides (Ga, Sn) presumably, because transition metal cations are active in π -complexing the C=C bond, which adsorption competes with the interaction of C=O with the same cation.

(4) A long discussion preceded the conclusion that one can speak, indeed, of promotion by cations and not of promotion by zero-valent metal atoms in corresponding alloys [72,73]. If one starts with an $\text{Pt}^0\text{-Sn}^0$ or $\text{Pt}^0\text{-Ga}^0$ alloy-state, the s,p metal is oxidized by the reactants in the initial stages of the reaction [72,73].

With the knowledge now available, it seems to be a safe conclusion, that the desired selectiv-

ity in the title reactions is entirely determined by the presence or absence of active sites formed by the metal and the promoter, on the boundary between them. The preliminary results [74] thus indicate that the promotion effect is again mainly due to the number of new sites (N_i) for the C=O hydrogenation and not due to the changes in E_{act} or due to other changes.

7. Deoxygenation reactions

In the industrial production of fine chemicals is an oxidation (insertion of oxygen/oxygenation) step involved in about 20% of the reactions. Selective removal of oxygen (deoxygenation) is applied in much less processes, but the fact that it comprises a mirror image of the oxygenation step is, amongst others, also justifying research on deoxygenation. The theoretical interests (see Section 3) are, of course, always there.

Molecules studied in Leiden are shown in Fig. 14. Their common feature is that in the adsorbed state (proton-free or deprotonized) they have *two* equivalent oxygen atoms from which *only one* has to be removed. Removing one of the two oxygen atoms can be also performed by classical organic chemistry. In the case of nitrobenzene this can be done by a two-step reduction–oxidation process. First, by adding HCl and Zn, nitrobenzene is reduced to phenylhydroxylamine, which is, thereafter, oxidized by chromium salts. For 1 kg nitrosobenzene is

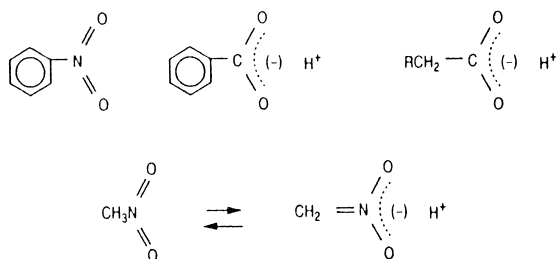


Fig. 14. Some reactions interesting as subjects of studies on deoxygenation by oxides.

about 3 kg solid waste produced, containing, amongst others, chromium. Carboxylic acid can be deoxygenized (reduced) to aldehyde by first ('making oxygens unequivalent') converting it with e.g., phosphorus pentachlorides, into its chloride and subsequently by reducing the acid chloride (on Pd catalysts) to aldehyde. Waste is again stoichiometrically produced. A continuous catalytic process is in both cases more economic, when the waste (solids plus diluted HCl) disposal is expensive as it already is.

The problem of the continuous catalytic processes is (in both mentioned cases) how to achieve a high selectivity with a high yield. In other words, one has to know which factors determine the selectivity and the activity. It has been established in Leiden that the activity and the selectivity of the catalysts are controlled by the stability, in the reaction mixtures and under reaction conditions of oxygen vacancies. The Mars and van Krevelen redox cycle (see, Section 3, under (iii)) is initiated by the reducing molecule (H_2 in the feed or, the phenyl ring of nitrobenzene in a pure nitrobenzene feed) and the oxygen vacancy is replenished by oxygen of the donor molecule: nitrobenzene or carboxylic acid. When the metal–oxygen bond strength is too high, the steady state value of the net rate is low, because the number of active sites (oxygen vacancies) is low. When the metal–oxygen bond is too weak, then a high steady state concentration of oxygen vacancies arises and leads to a loss of both oxygen atoms: nitrobenzene reacts up to aniline [75], benzoic acid up to toluene [76], etc. The selectivity to aldehydes in the aliphatic acid reduction is influenced by a parallel running ketonization (from acetic acid to acetone, etc.) Ketonization occurs by two mechanisms: (i) via ketenization, (ii) via thermal, radical like decomposition of bulk carboxylates (or surface-carboxylates). Ketenization under (i) requires that the catalyst surface dehydrogenates (finally dehydrates) the acid molecule and this initiation step can be suppressed when the catalyst surface is all time hydrogenated up to its saturation. Therefore, addition of a metal such

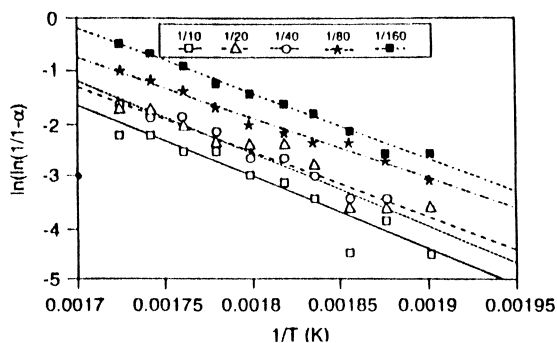


Fig. 15. Reaction of acetic acid on Pt/TiO₂ diluted by TiO₂. Arrhenius plot of a function which expresses the first order reaction constant (with respect to acetic acid) as a function of temperature and overall conversion (the total amount of TiO₂ in the reactor increases when going up along the y-axis).

as Pt to a (mainly) ketonization catalyst as TiO₂, saturates the surface of TiO₂ by hydrogen spill-over and converts this oxide from a ketonization to an effective deoxygenation catalyst, producing aldehydes selectively [77–79]!

When a ‘mixed’ metal-oxide catalyst Pt/TiO₂ (or Fe/FeO, Fe₃O₄) is used, a question arises, what is the role of individual components. Robert Pestman has nicely proven that Pt, covered upon reaction in hydrogen/acid mixtures by carboxylate, still produces atomic H, but does not induce other reactions. Deoxygenation occurs on the TiO₂ surface, in which oxygen vacancies have been created by hydrogen. Robert used a formal kinetic equation for a reaction of first order to calculate the rate constant (from the $\ln[\ln(1 - \alpha)^{-1}]$ vs. T plot, with α being the conversion) and evaluated the apparent activation energy for a series of catalysts which all contained the same amount of Pt and a varying amount of TiO₂. The apparent pre-exponential factor, comprising the number of active sites, increased with an increasing amount of TiO₂ added [78,79], while the apparent activation energy remained the same. This can be seen in Fig. 15. Thus, the selectivity to either ketonization or deoxygenation depends on the number and properties of the active sites; the active sites for deoxygenation being the oxygen

vacancies; necessary in a Mars and van Krevelen cycle.

With the nitrobenzene-to-nitrosobenzene reactions, identification of active sites went even further. It could be established, that with the catalysts of spinel structure A(II)B₂(III)O₄, A being the tetrahedrally and B-octahedrally coordinated cation, the B-site must be occupied by a reducible cation (cation of variable valency, such as Co or Mn) and this cation forms the active site. Actually, it is the oxygen vacancy associated with the cation [80–82]. This is illustrated by Fig. 16, from the thesis by Sylvia Meijers. Notwithstanding the fact that the steady state number of active sites (oxygen vacancies) is controlled by energetic factors (metal–oxygen bond strength, activation energy of reduction/reoxidation), similar to other cases mentioned above, the selectivity is again mainly controlled by the factor ‘N_i’ in Eq. (3). When another parallel running mechanism is also possible (as ketonization and related reactions in the case of acids), the rate and the extent of the Mars and van Krevelen mechanism is the key to the selective reduction: a single oxygen vacancy removes a single oxygen atom [79].

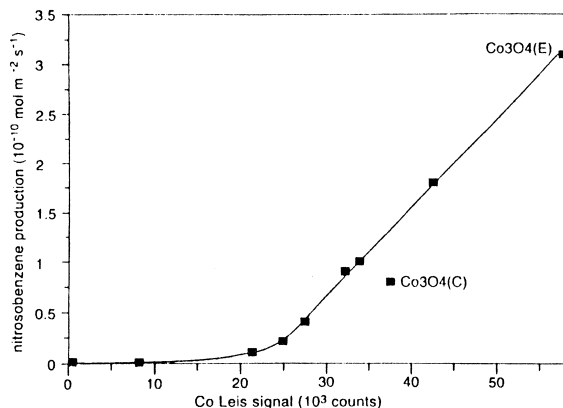


Fig. 16. Activity in the selective auto-reduction of nitro- to nitrosobenzene as a function of the surface composition of $(\text{Co}_{1-x})(\text{Al}_{2-x})\text{Co}_x\text{O}_4$ spinels. The surface composition is expressed in terms of the LEIS-signal intensity. Co₃O₄ (E, pure cobalt oxide and C, oxide containing sodium contamination accumulating on its surface).

8. Acid catalysed skeletal isomerisation of *n*-butene

For many years, the excellent paper by Brouwer [83] was a permanent topic of the course ‘Catalysis’ in Leiden. In a most straightforward manner, the author gathered there the arguments and made his impressive conclusion: C_4 hydrocarbons cannot isomerize! It was a real surprise when during one informal discussion Ruud van Hardeveld mentioned a paper [84] which claimed the opposite for olefines (van Hardeveld also explained the practical impact of that finding, if it were confirmed). Skeletal isomerisation of *n*-butene opens the way to a production of the much demanded methyl-tertiary-butyl-ether (MTBE). Therefore, Leon Gielgens started in Leiden immediately experiments to verify the results in Ref. [84] and he confirmed the conclusions! It was a very lucky coincidence that at that time in Leiden the freedom still existed to make use of the University-paid positions for a high-risk research (such as C_4 -isomerisation) and to change the topic of the PhD studies freely and opportunistically (other Grant Foundations believed in Brouwer’s paper too much and refused to give support).

The first problem solved, concerned the nature of active sites. Jindra Houzvicka has proven that the ‘condition sine qua non’ for a catalyst active in this reaction, is the presence of acidic-OH groups [85]. A moderate acidity (as of P-OH) appeared [86] to be more suitable than the strong one [86], since the strong acidity stimulated too much the side-product ($C_3^=$, $C_5^=$) formation. A clear cut conclusion with regard to the mechanism helped later to identify and define the features of an active, selective and catalytically stable catalyst for butene isomerisation. The identification of the operating mechanism is not a mere academic question, as we shall see immediately.

Brouwer’s paper [83] concerned the reactions occurring in liquid acids, but his conclusions were—by everybody—extended also to solid acids. Therefore, people looked for ideas which

would allow to circumvent the formation of primary carbenium ion, which was ‘forbidden’ according to Brouwer. A promising idea was that $C_4^=$ first dimerizes to an octene, this molecule isomerizes and after cracking it yields isobutene and other products. For example, 2,2,4 trimethylpentene ($TMP^=$) is split very selectively into two isobutenes. Another possibility is that (somehow) a small amount of isobutene is formed, it co-dimerizes with butene and via 2,2,4 $TMP^=$ is converted into two molecules of isobutene. The first mechanism was disproved [87] by a simple experiment. Product distribution of *n*-butene reactions was, for a number of catalysts, compared with a product distribution obtained from various octenes, the assumed intermediates. If octenes were the unique intermediates, these distributions should have been very similar. However, they were very (!) different, as can be seen in Fig. 17. Nevertheless, the dimerization mechanism is still believed by some to operate [88,89].

The co-dimerization mechanism has been excluded on different grounds. A series of molecular sieves was studied and it was found [90] that (i) the 8-member-ring (8MR) sieves are of very low activity, being obviously active only by their external surface, (ii) the 10-MR sieves are

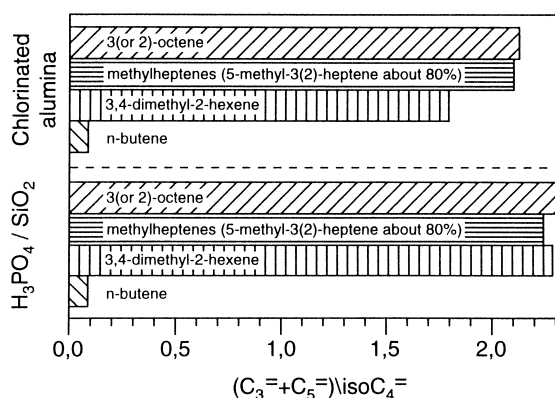


Fig. 17. A comparison of product distributions (here represented by the extent of side product formation) obtained with various hydrocarbons (indicated in the bars) as the feed on two open-surface catalysts. Notice, the difference between *n*-butene on one side and all octenes on the other side.

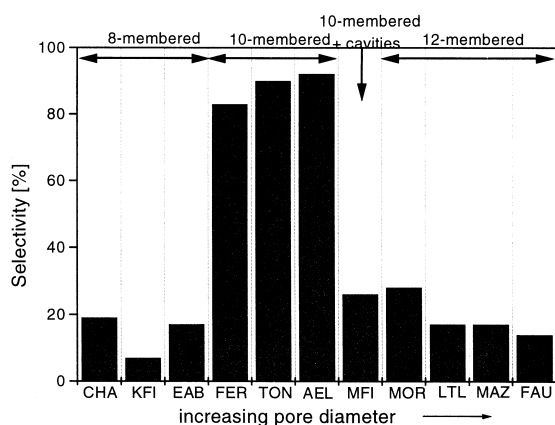


Fig. 18. Selectivity in the *n*-butene to isobutene reaction, for various molecular sieves (350°C, standard conditions).

the best option, except the cases when larger cavities are formed in crossings of channels, as with ZSM5 (iii) the 12-MR sieves and open surfaces are active but they deactivate too fast. Fig. 18 illustrates this comparison of molecular sieves. The most active and selective catalysts, the 10-MR-molecular sieves, cannot form TMP^{\ominus} in their pores, i.e., they cannot sustain the co-dimerisation mechanism. In this [90] and other papers [91] arguments can be found that di- or co-dimerisation is mainly a source of side products and these reactions should be suppressed.

This happens in the 10-MR sieves, by the space restriction round the active center.

9. Conclusions

A personal conclusion is easy to make. It was not difficult to stick to ‘catalysis’ as the field for scientific activities, all the 40 years. Catalysis offered by its multidisciplinary nature as many facets to study, as one could wish. Research, some results of which are presented above, was not long-term-planned (as fundamental research never is) and it is therefore more difficult to formulate a single scientific conclusion from the past 40 years. Nevertheless, one aspect of the selectivity studies emerges clearly: the selectivity is very much controlled by the presence or absence of active sites specific for a given reaction. Table 2 presents the overview (the first eight reactions are based on the L–H activation, the following three on the Mars and van Krevelen activation) on information gathered in this respect, by research in Leiden. However, a reader can hear it: ‘everybody knew that!’ There is nothing new under the sun, one says.

Table 2

Reactions and their active sites

Reactions	Site (optimal, or the most frequent one)
Hydrogenolysis of hydrocarbons metals	Large ensemble of metal atoms (N.B. only on Pt, the one-atom alternative [37] can prevail)
Isomerisation of hydrocarbons on metals	Large ensembles of metal atoms [37]; possibly with exception of Pt
Cyclisation of hydrocarbons on metals	Large ensembles of metal atoms (N.B. on Pt, one atom site alternative [37])
Hydrogenation of C=C on metals	Small ensembles, up to single-atom sites
Fischer–Tropsch synthesis of hydrocarbons	Large ensembles of metal atoms
Methanol synthesis on metal containing catalysts	Cooperation of M^+ (bearing intermediates) and M^0 (supplying H_{at}) sites
Oxygenates from syngas on metal containing catalysts	Cooperation of M^0 , large ensemble sites with the promoter sites binding the carbonyl group
Hydrogenation of C=O group, on metals	Cooperation of M^0 , small ensemble (single atom) sites with a promoter site binding the carbonyl group
Deoxygenation of nitro-benzene oxides	Oxygen single-vacancy; in spinels round the B-sites (trivalent cation in octahedral position)
Deoxygenation of aliphatic carboxylic acids, on oxides	Oxygen single-vacancy
Deoxygenation of aromatic carboxylic acids, on oxides	Oxygen single-vacancy
Ketonization of aliphatic carboxylic acids	Hydrogen abstracting (basic) sites on an oxygen-vacancy-lean surface

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