Heterogeneous molecular catalysis: Oxymoron or reality?

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Abstract

It has become common to call a molecular catalyst a single site catalyst. The intent is to stress that all sites of a molecular catalyst are identical in activity and selectivity. In this essay, three cases are examined. In each one the evidence is very strong that heterogeneous catalysts can be considered to be molecular catalysts. The first case is the cracking of alkanes on H-ZSM-5. The second is the oxidation of carbon monoxide on palladium. The third is ammonia synthesis on KMI, a multipromoted iron based commercial catalyst.

Keywords: Heterogeneous catalysis; Cracking; ZSM-5; Carbon monoxide oxidation; Ammonia synthesis; Iron; Palladium

1. The search for active centres in heterogeneous catalysis

Active centres, with the intended British spelling, were introduced by Taylor (Sir Hugh) in 1925 [1]. The concept was based on observations suggesting that catalytic surfaces contained sites or ensembles of sites called active centres, that were endowed with different activity in chemisorption and catalysis. If the science citation index were to go back that far in time, Taylor's paper might break all records, at least in heterogeneous catalysis.

Taylor did not specify the nature of active centres, except to mention as an example that certain atoms on a metal surface could be what we would call today highly coordinatively unsaturated. Why then was his paper so influential, for better or for worse? A plausible answer is that, if these centres exist, we should hunt for them. The hunting season started in 1925 and is still open. Even a partially successful hunt is a worthwhile achievement. On the down side, the very existence of active centres gave *heterogeneous catalysis* a bad reputation as a 'black art', very different from the science of *molecular catalysis* with *identical* active sites exhibiting optimum activity *and* selectivity. To promote heterogeneous catalysis to the rank of molecular catalysis, we must first identify active centres on solid surfaces and then build a surface with these active centres exclusively.

The purpose of this paper is not to review the many identified types of active centres on heterogeneous catalysts. Rather, it is to show that the hunt for a solid catalyst exposing exclu-

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sively identical active centres has been success-
ful in three selected, well-documented cases that
qualify heterogeneous catalysis as a *bona fide*
form of molecular catalysis. But first, let us
recall the full message of Taylor in his paper of
1925.

2. The message of Taylor

The message was not so much the idea of
active centres as quoted reverently by so many
who have not read Taylor's 1925 paper. The
critical and cryptic message was in two sen-
tences which I have cited repeatedly, in extenso
[2–4].

The first sentence reads: "There will be all
extremes between the case in which all the
atoms in the surface are active and that in which
relatively few are so active." The second state-
ment reads: "The amount of surface which is
catalytically active is determined by the reaction
catalyzed." Note that these are prophetic state-
ments, in the future tense, since there was no
experimental evidence at the time to support
them. The second statement, as it foreshadows
surface reconstruction, is truly remarkable. Both
statements will be illustrated and discussed in
this paper.

3. All surface sites are active but not equally so

This is the case between the two extremes of
Taylor. The literature on chemisorption reveals
that this is a frequent situation. This is the one
that has contributed to the reputation of hetero-
geneous catalysts as non-scientific as compared
to molecular catalysts. The question then arises
about the distribution of activity over the sur-
face or the distribution of binding energies of
probe molecules on surfaces by equilibrium ad-
sorption or calorimetry, and the distribution of
activation energies in activated chemisorption of
probe molecules. This information can be used
in obtaining a distribution of catalytic rates on

the different sites through the elegant formalism
of Temkin and co-workers, as summarized in
our monograph [5].

Besides this formalism, there exists an exper-
imental approach to deal with the distribution of
activity of surface sites: the isotope jump tech-
nique originated by Tamaru [6]. In its evolved
form, the technique consists of operating a cata-
lyst at the steady state, abruptly switching one
of the reactants from an isotopic composition to
another one, and measuring the relaxation time
of appearance of the new isotope in a reaction
product, while the reaction continues to proceed
at the steady state. If all sites are identical in
activity, the relaxation process is described by
an exponential curve with a single relaxation
time. If not, it is possible to extract a distribu-
tion of site activity from a deconvolution of the
relaxation curve [7,8].

Thus, the first Taylor statement has now been
quantified, not only by the Temkin formalism,
but also by the powerful isotope jump tech-
nique. Other approaches have been suggested.
For instance, Kral proposed that the fraction of
surface sites that is catalytically active be called
the Taylor ratio [9]. This concept has not re-
ceived wide acceptance, probably because it is
usually qualitative. Indeed, is the activity of the
fraction of sites that is catalytically active the
same for all sites? Moreover, it is not clear how
the Taylor ratio should be measured experimen-
tally. The use of progressive poisoning of sites,
as proposed by Kral, is fraught with experimen-
tal difficulties. Indeed, it is essential to insure
that the successive pulses of poison, e.g., sulfur
on iron, are uniformly distributed in the catalyst
bed, as well as through each catalyst grain.

In conclusion, the kind of situation described
above is largely responsible for a recent answer
to the question: "Heterogeneous catalysis – still
magic or already a science?" [10]. The answer
was: still magic. The opposite answer comes out
strongly from a thorough study of catalytic
cracking of *n*-hexane on H-ZSM-5 (MFI) zeo-
lites, a case corresponding to one extreme of
Taylor's first statement.

4. All the atoms in the surface are active and equally active

This is the first part of Taylor's first statement, with one severe restriction, imposing *identical* activity of the atoms in the surface, atoms being meant to be *active sites* in currently accepted language. If the active sites differ in activity, the heterogeneous catalyst cannot be called a molecular catalyst in our understanding of the strict sense of the word.

In fact, Taylor's first case, with our restriction of identical activity, defines a heterogeneous molecular catalyst that necessitates a perfect single crystal with active sites that are sufficiently apart from each other so that they do not interact when bare or when covered with adsorbates. Such a situation exists in the case of zeolites such as silicalite with protonic sites. These sites were introduced by framework aluminum ions providing non-interacting molecularly known acid sites at sufficiently low concentrations of aluminum. Such catalysts were prepared and used by Haag in the catalytic cracking of alkanes [11]. This work may well be the first rigorous determination of a *true* turnover frequency (TOF). Indeed, the active acid sites were counted as corresponding to the number of aluminum ions in the zeolite. Their identity was shown by progressive poisoning as well as by the constancy of the TOF for hexane cracking as the content of aluminum increased over almost four orders of magnitude while remaining small enough for satisfying the condition of no interaction between them. This is shown in Fig. 1 by the linear increase in activity with aluminum content. The exhaustive investigation of Haag is the first rigorous demonstration of a heterogeneous catalyst functioning as a molecular catalyst over a set of identified and identical active sites. This achievement opens up the use of zeolitic catalysts as ideal systems to study various aspects of molecular heterogeneous catalysis. The so-called *black art* of heterogeneous catalysis should now be a misnomer of the past, not only qualitatively but also quan-
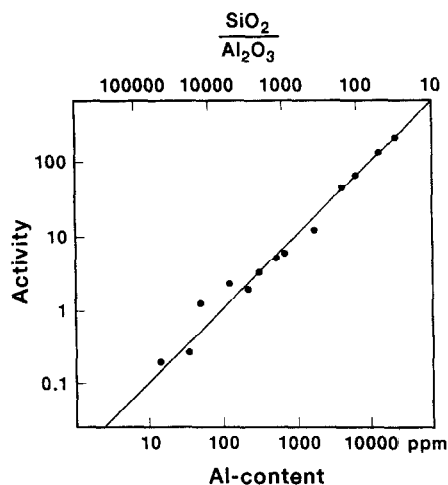

Fig. 1. Activity of H-ZSM-5 for cracking of *n*-hexane [11].

titatively. The example just discussed is particularly interesting, since no soluble molecule has ever been reported to crack alkanes in a catalytic mode. Zeolites offer an added asset not available with other heterogeneous catalysts, namely the possibility of shape selectivity [12]. Zeolites offer today the best examples of heterogeneous molecular catalysts.

5. Can metal catalysts behave as molecular catalysts?

Metallic catalysts are widespread in practice. But for theoretical studies they present the complication of all solid materials: *surface crystalline anisotropy*. Even the simplest metal surface, the (111) face of a face centered cubic structure, exposes different sites: a threefold hollow site, a bridge site and an on-top site. Relaxation and reconstruction effects on clean metal surfaces are important and are modified by chemisorption. Both attractive and repulsive interactions between chemisorbed species must be taken into account. Many of these features, including surface defects, change when a different crystal plane is exposed. In other words, can a pure metal surface function as a molecular catalyst? As a result of the knowledge accumulated over the past 30 years [12], the answer to

the question above would seem to be a resounding *no*.

Yet, in the next two sections (Sections 6 and 7), we shall attempt to show that for two reactions on two different metals, catalytic behavior of the metal approximates closely or very closely that of a molecular catalyst. The reactions will be, respectively, oxidation of carbon monoxide and ammonia synthesis. In the first case, the rate of reaction depends only in a subtle way on surface crystallographic anisotropy. In the second case, the opposite is true. The rate of reaction varies considerably with crystalline anisotropy, but the reaction reconstructs the surface so as to expose only the most active equivalent sites.

6. Oxidation of carbon monoxide on palladium

This is a bellwether, much studied, reaction in heterogeneous catalysis. The era of surface science for that reaction on palladium single crystals opened up with an often-quoted study by Ertl and Koch [13]. They measured the steady-state rate of CO_2 formation between 300 and 900 K on the (100), (110) and (111) faces of Pd single crystals, as well as on a Pd polycrystalline wire (Fig. 2). They concluded that "no crystal plane specificity exists for this reac-
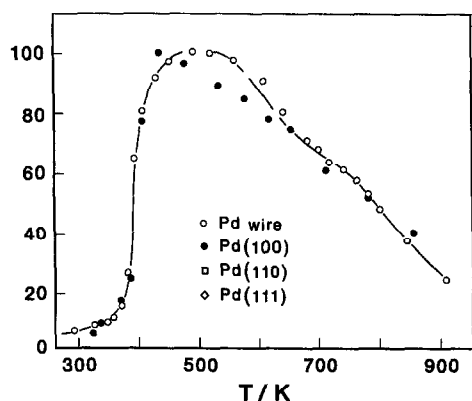
Fig. 3. TOF (s^{-1}) for CO oxidation $(p_{O_2}/p_{CO}) = 1.1$ on Pd clusters and supported on sapphire [14].

Fig. 2. Relative rate of CO oxidation on three low index planes of Pd single crystals and a polycrystalline wire [13].

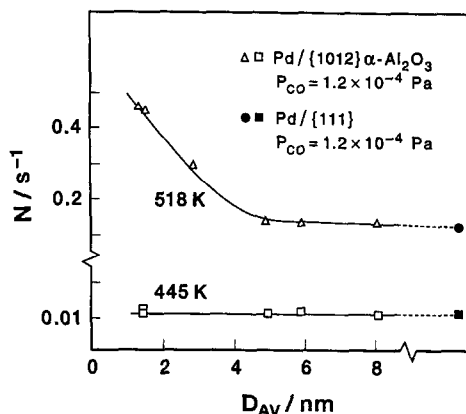tion system". In the discussion of this paper, they reported that the open planes (210) and (311) "showed almost identical behavior with the more densely packed planes". They concluded again that "for this system, the structural factor is only of minor importance".

Subsequently, Ladas et al. measured the rate of CO oxidation per Pd atom exposed on palladium clusters grown in UHV on a single crystal surface of sapphire at the partial pressures of CO and O_2 used by Ertl and Koch: they found no effect of cluster size for clusters with average particle diameter equal to 1.5, 2.8, 4.9, and 8.0 nm as determined from transmission electron microscopy or TPD of CO [14]. This result was obtained at 445 K on collections of clusters with a narrow size distribution. As seen on Fig. 3, rates were in good agreement with that obtained on Pd(111) by Engel [15]. It was concluded [14] that, at 445 K, the rate was insensitive to structural differences expected on clusters in the size range examined, a conclusion similar to that of Ertl and Koch. At 518 K, a higher TOF was found on the smaller clusters (1.5 and 2.8 nm) than on the larger ones (4.9 and 8.0 nm). This puzzling effect was later explained quantitatively by the surface diffusion of CO molecules adsorbed on sapphire, providing a secondary flux of CO to the clusters, in addition to the flux of CO striking the clusters directly from the gas phase [16]. While this

Table 1

Oxidation of CO on Pd(100) and Pd(111) at $p_{CO} = 1$ Torr and $p_{O_2} = 0.5$ Torr, ΔH isosteric heat of adsorption of CO/kcal mol^{-1}; E_a: apparent activation energy/kcal mol^{-1}; TOF: turnover frequency (s^{-1}) from Figs. 1 and 2

	ΔH	E_a	TOF (s^{-1})	
			$T = 465$ K	$T = 570$ K
(100)	29 ± 2	29.4 ± 0.3	0.6	200
(111)	25 ± 2	28.1 ± 0.3	0.4	110

effect of *reverse spillover* is beyond the theme of this paper, it is mentioned here as an example of yet another complicating factor that can be encountered in catalysis by supported metal clusters.

The above studies were carried out at low total pressure of the order of 10^{-6} mbar. Under these conditions the rate of reaction of CO and O_2 on palladium surfaces is not affected much by structural details of the surface. This conclusion remains valid at much higher total pressures of up to 10^2 mbar [17] with a comparison of identical TOF values on Pd(100) and (110) as well as on a commercial catalyst Pd/γ-Al_2O_3) as shown on Table 1.

This very detailed recent study by Goodman et al. [18,19] of the reaction on Pd(100) and Pd(111) at high pressure bears on the conclu-

Fig. 5. TOF (s^{-1}) for CO oxidation on Pd(111) [19].

sion of Ertl and Koch when they say that "for this system, the structural factor is only of minor importance".

The results of these studies are shown in Figs. 4 and 5 and summarized in Table 2. The values of TOF at the upper and lower temperatures of these studies differ by a factor of about two for the (100) and (111) faces. As to the (110) face, the value of TOF is practically identical to that on the (100) as shown on Fig. 8 of Ref. [20]. The work of Goodman et al. [18,19], shows small but complex effects of surface coverage by CO, as it changes with

Fig. 4. TOF (s^{-1}) for CO oxidation of Pd(100) [18].

Table 2

Mole fraction of the products of reaction between 2-butyne and deuterium at 287 K on palladium [21]

2-butyne	$CH_3-C\equiv C-CH_3$	0.220
Cis-2-butene-2,3-d_2		0.772
Trans-2-butene-2,3-d_2		0.007
1-butene	$CH_2=CH-CH_2-CH_3$	0.000
Butane	$CH_3-CH_2-CH_2-CH_3$	0.001

temperature, pressure, and face exposed. As coverage changes, so does the heat of adsorption of CO. The latter seems to be the main factor affecting the rate of CO oxidation, although it is not the only one. These effects have to be sorted out, but a prudent conclusion is that the rate of oxidation of CO on Pd surfaces does not seem to be affected by changes in surface structure, except in a *subtle* manner, to use the word of Wayne Goodman. This conclusion is of course restricted to the conditions of the work discussed in this paper.

If this conclusion is granted, it becomes clear that on a polycrystalline array of palladium clusters of different size, the oxidation of carbon monoxide under the above conditions will take place at about the same rate on *all* exposed Pd atoms counted by a suitable technique that counts all the exposed Pd atoms, either selective chemisorption or electron microscopy. These surface atoms can be considered as identical in activity provided that the surface coverage is large enough that the free sites all find themselves in the same environment. This condition seems to be satisfied not only at high pressure [18–20], but also at low pressure [13,14]. This also appears to be true at low temperature with respect to chemisorbed CO and at high temperature with respect to chemisorbed oxygen, but this question of coverage must be clarified by further work. With the reservation of subtle differences in rate in the collection of exposed atoms, a typical supported palladium catalyst is a close approximation to a molecular catalyst for the oxidation of carbon monoxide.

This statement is reinforced if we consider catalytic selectivity rather than catalytic activity, since selectivity is frequently considered as the most important asset of molecular catalysts. The chemoselectivity and stereoselectivity of a supported palladium catalyst are shown in Table 2 for the deuteration of 2-butyne [21]. Table 2 shows very high selectivity at a high value of conversion.

Thus the surface of a supported heterogeneous metallic catalyst may expose a collection of *subtly* identical sites. The uniform behavior of palladium surfaces in the oxidation of carbon monoxide may be assisted by surface relaxation and/or reconstruction under reaction conditions as suggested in Ref. [17]. This idea corresponds to Taylor's second message: "the amount of surface which is catalytically active is determined by the reaction catalyzed." Convincing evidence for surface reconstruction as a result of reaction is discussed in Section 7.

7. Ammonia synthesis on iron

If the oxidation of CO on Pd is perhaps the best understood reaction proceeding at a rate that is least dependent on surface crystalline anisotropy, then the synthesis of NH_3 on Fe is certainly the most extreme known example of a reaction with a rate that is very different on five different faces of iron single crystals. The situation is unique in that the rate of synthesis is the rate of adsorption and desorption of nitrogen, the rate determining step, all the other elementary steps being in quasi-equilibrium. Next, the nature of the active site or centre has been identified beyond any reasonable doubt. Finally, as anticipated by Taylor, the reaction itself restructures the surface so as to expose the most active centres.

First, the importance of surface crystalline anisotropy was demonstrated in Somorjai's laboratory by measuring the rate of reaction at ~ 20 bar on the (111), (211), (100) (210) and (110) faces of iron single crystals [22]. Areal rates are shown in Fig. 6. Rates on the (111) and (211) faces are larger by an order of magnitude than on the (100) and (210) faces, and larger by a factor of about 600 than on the (110) face. The two faces with the highest values of rate, corresponding to a TOF of about 10 s^{-1}, are the only ones exposing C_7 sites, i.e., surface atoms with a coordination number equal to 7. The identification of C_7 sites as Taylor's likely *active centres* in ammonia synthesis was made earlier in a study by Mössbauer effect spec-
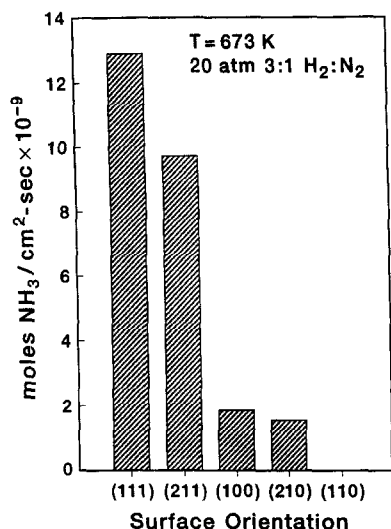
Fig. 6. Areal rates of ammonia synthesis on Fe single crystal faces [22].

troscopy of iron clusters supported on MgO. Details of several investigations at Stanford on the catalytic and magnetic anisotropy of these iron surfaces were reviewed in a single paper [23]. In particular, it was shown that the Néel surface magnetic anisotropy of superparamagnetic iron clusters changes by pretreatment of the clusters in ammonia, leading to an increase in surface C_7 sites. The change also led to an increase in TOF for the ammonia synthesis. The restructuration of the iron surface of iron by nitrogen had been shown previously by Brill et al. on an iron tip in a field electron microscope [24]. The restructuration led to the appearance of (111) faces on the tip. Brill and Kurzidim also reported that the catalytic activity of iron for ammonia synthesis was higher when Fe_3O_4 was reduced to iron with NH_3 than with H_2. This increase was attributed to the preferential (111) orientation of the reduced surface [25]. Since the (111) face exposed C_7 sites, the identification of the active centres as C_7 sites is strongly supported by work prior to Somorjai's study of NH_3 synthesis on single crystals, but Somorjai's results are a direct proof of this identification.

The work of Brill et al. and the Stanford

results suggest reconstruction by nitrogen, but more strongly by ammonia. A large single crystal of Fe, exposing a face different from the (111) face, has not been reported by Somorjai to restructure to the (111) face. Will an ammonia synthesis catalyst do so?

The answer is in the affirmative, as shown by Fig. 7, which summarizes one of the most revealing studies in catalysis by metals [26]. All data of Topsøe et al. are from Ref. [26] except the value of TOF for the 30 nm Fe clusters [27] and the Fe(111), for which the experimental value [28] was extrapolated to the conditions of Topsøe et al. [29].

The data points along the curve pertain to Fe/MgO with cluster size plotted on the horizontal axis, the sites for TOF values having been counted by selective chemisorption of H_2 and CO. The marked effect of cluster size on TOF reflects the marked effect of single crystal orientation on areal rate. Indeed, chemisorption of CO has been shown by the extensive classical work of Emmett and co-workers to count all of the iron atoms exposed [30]. From the paper of Topsøe et al., about the same is true for H_2 chemisorption. The data along the curve of Fig.
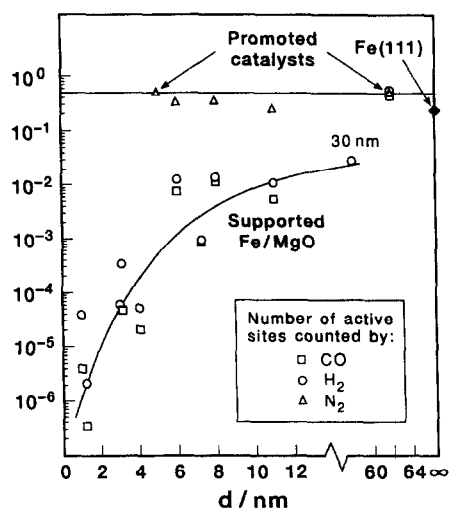

Fig. 7. Turnover rate (s^{-1}) for ammonia synthesis (673 K, 1 atm, stoichiometric mixtures) on Fe/MgO with Fe clusters of size d (nm), two multipromoted catalysts (arrows), and a (111) single crystal of Fe [26].

7 show that as cluster size increases, so does the value of TOF calculated on the assumption that all iron atoms are active sites in ammonia synthesis. Clearly, not all exposed atoms are equally active: as cluster size increases, so does the fraction of exposed iron atoms capable of catalyzing ammonia synthesis at a faster rate. This is why the data of Ref. [27], plotted on a curve similar to that of Fig. 7, were interpreted as indicating sensitivity of the rate to surface crystalline anisotropy.

But the crucial fact shown by the data points in Fig. 7 is that when TOF is calculated from chemisorption data for N_2 at high temperature, all shown TOF values are the same: there is no more any effect of cluster size on TOF. It was concluded by Topsøe et al. that N_2 chemisorption at high temperature counts only the more active sites.

The next most decisive result of Topsøe et al. consists of two points on Fig. 7 for the TOF measured on two multipromoted unsupported industrial catalysts. The one on the left is for an experimental catalyst, and the one on the right for a commercial catalyst. Both show TOF values practically identical to those of Fe/MgO catalysts. But the most interesting result is that for the commercial catalyst. Indeed, the TOF for the commercial catalyst is practically the same whether the number of sites is counted by H_2, CO, or N_2 chemisorption. This suggests that the commercial catalyst exposes only sites that are the best for ammonia synthesis. Turning back to Fig. 6, we come to the conclusion that the commercial catalyst exposes almost exclusively C_7 sites. This conclusion is strengthened by a calculation of the TOF as measured on Fe(111) surfaces [28] by extrapolating this value to the conditions of the work of Topsøe et al. [29]. The result of that extrapolation is shown on Fig. 7, as the point labeled Fe(111). Extrapolation is always risky, although this one has not been contested as yet. The strongest argument remains that TOF is practically the same whether sites are counted by CO, H_2 or N_2 (high temperature) chemisorption, the last method being

the one that counts the sites that are the most active in ammonia synthesis. This tells us that a commercial ammonia synthesis has been optimized to the extent that its surface exposes almost exclusively the C_7 sites that have been shown by work on single crystals of iron to be the most active ones in ammonia synthesis.

8. Conclusion I

The commercial ammonia synthesis catalyst is a molecular catalyst in the sense that approximately all of its sites are identical and are active centres based on C_7 sites. This surprising conclusion is based on a mechanism of surface adaptation, i.e., surface reconstruction, anticipated by Taylor and documented only much more recently. In the case of ammonia synthesis, reconstruction of iron surfaces under nitrogen or ammonia with formation of (111) facets was anticipated by a number of investigators [24–26]. The results discussed in this paper are compatible with the idea that an iron surface will be reconstructed to a surface exhibiting C_7 sites under conditions of ammonia synthesis if it can do so kinetically. This does not happen with large single crystals (see Fig. 6), but seems to happen with iron clusters of not too large a size and iron facets on promoted iron catalysts. Indeed, the data on Fig. 7 pertaining to the latter deal with catalysts that had been previously used in ammonia synthesis under commercial conditions [31]. The intuition of Taylor as to the role of the reaction in determining the fraction of active centres on a working catalytic surface was discussed by Boreskov to explain why areal rates for a variety of reactions on supported metals did not depend on the fraction of metal exposed, i.e., on cluster size [32].

We conclude that multiply promoted ammonia synthesis catalysts appear to be molecular heterogeneous catalysts in the sense that all working sites are identical with respect to TOF and that these sites have been identified molecularly as C_7 iron 'active centres'.

One more remark is necessary. When discussing the rigorous example of a heterogeneous molecular catalyst such as H-zeolite for cracking of alkanes, it was said that the sites should be identical and non-interacting. In the case of oxidation of CO on Pd or ammonia synthesis on Fe, interaction might be suspected because of appreciable surface coverage of Pd by CO at low T and by O at high T, and very high surface coverage of Fe by N. But in either case, remaining vacant sites have all the same environment and therefore identical interaction with their nearest neighbors. This is sufficient for preserving the identical activity of the vacant sites.

9. Conclusion II

Surface chemistry of solids is a treacherous field. With the analytical methods of surface science, qualitative, quantitative, and structural analysis of model catalysts have become possible down to the nanometric scale [33]. Studies on single crystals provide the standards by which work with heterogeneous high specific surface area catalysts can be assessed, as illustrated by our two examples.

In the first example, study of oxidation of CO at low pressure on model supported palladium clusters indicated insensitivity (*not* invariance) with respect to surface structure at low temperature [14]. This was in agreement with the earlier single crystal work of Ertl and Koch [13]. Anomalous behavior of the clusters at higher temperature could have been explained away by dependency of the rate on cluster size. The conflicting anomaly was later explained qualitatively and quantitatively by reverse spillover in the case of supported clusters [16].

Conversely, for the second example, early work on model supported iron catalysts indicated sensitivity to cluster size. This was interpreted as structure sensitivity because the TOF for ammonia synthesis was calculated by counting surface sites by a technique (chemisorption

of CO) known to count all surface iron atoms. Structure sensitivity of the reaction was then confirmed spectacularly by single crystal work [22]. The identification of the sites that were the most active by far was also confirmed by the single crystal work.

Next, when the sites were counted by chemisorption of nitrogen at high temperature, the TOF became independent of cluster size, since the rate determining step in ammonia synthesis is the chemisorption of nitrogen at high temperature. Finally, surface reconstruction during reaction came into play. This phenomenon was first recognized on platinum metals gauze used in the Ostwald oxidation of ammonia, and illustrated by *cauliflower* structures on photomicrographs [34], then transmission electron micrographs [35], and finally on the tip of a field election microscope at the atomic resolution level [24]. This phenomenon of surface reconstruction of iron surfaces during ammonia synthesis was evidenced by Mössbauer effect spectroscopy [23]. It accounts for the behavior of a working multipromoted industrial catalyst as a surface exposing only identical sites of identical activity [26,29] as befits a molecular catalyst.

This ultimate result is important for the future development of heterogeneous catalysis: first, because it illustrates how intuitions, working hypotheses, and indirect evidence can be clarified or guided by surface science techniques; second, because the technological advantages of heterogeneous catalysts *can be* preserved without sacrificing the advantages of molecular catalysts as a collection of identical single sites of uniform activity and selectivity.

These considerations are pertinent not only in theory, but also in practice. Indeed, if the iron based ammonia synthesis catalyst has been optimized, as suggested above, further process improvements at lower temperatures and pressures may be forthcoming, only if iron is replaced by another metal. This is in fact taking place.

The new generation of ammonia synthesis catalysts started with the report by Ozaki of

very active carbon-supported and potassium-promoted ruthenium catalysts [36]. Their development started at British Petroleum six years later with a high surface area graphite [37]. This was followed by the preparation of a Rb promoted Ru catalyst supported on the new carbon support[38]. Commercialization by M.W. Kellogg was pursued. After more than 950 days on stream, the new catalyst showed no sign of deactivation in a retrofitted plant. This result led to the construction of a low pressure, low volume grassroots commercial ammonia synthesis plant at Ocelot, Canada. This plant is scheduled to go on stream in 1996 [39].

The search for the nature of active centres on these new ruthenium catalysts for ammonia synthesis has already started. The practical goal is clear: to optimize the new ruthenium catalyst as another molecular catalyst.

References

[1] H.S. Taylor, Proc. R. Soc. London A 108 (1925) 105.
[2] M. Boudart, A. Aldag, J.E. Benson, N.A. Dougharty and G.C. Harkins, J. Catal. 6 (1966) 92.
[3] M. Boudart, Adv. Catal. Rel. Subj. 20 (1969) 160.
[4] M. Boudart, in: G. Ertl, H. Knözinger and J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, Vol. 1, Section 1 (VCH-Weinheim), in press.
[5] M. Boudart and G. Djéga-Mariadassou, Kinetics of Heterogeneous Catalytic Reactions (Princeton University Press, 1984) ch. 4.
[6] K. Tamaru, Dynamic Heterogeneous Catalysis (Academic Press, London, 1968).
[7] M. de Pontes, G.H. Yokomizo and A.T. Bell, J. Catal. 104 (1987) 147.
[8] J.N. Nwalor and J. Goodwin, Topics Catal. 1 (1994) 285.
[9] H. Kral, Chem. Ztg. 61 (1967) 41.
[10] R. Schlögl, Angew. Chem. Int. Engl. 32 (1993) 381.
[11] W.O. Haag, in: J. Weitkamp, H.G. Karge and W. Hölderich (Eds.), Studies in Surface Science and Catalysis, Vol. 84 (Elsevier, 1994) p. 1375.
[12] C.B. Duke (Ed.), Surface Science: The First Thirty Years (North Holland, Amsterdam, 1994).
[13] G. Ertl and J. Koch, in: Proc. 5th Int. Congr. Catal., Vol. 2 (North Holland, Amsterdam, 1973) p. 969.
[14] S. Ladas, H. Poppa and M. Boudart, Surf. Sci. 102 (1981) 151.
[15] T. Engel, J. Chem. Phys. 69 (1978) 373.
[16] F.R. Rumpf, H. Poppa and M. Boudart, Langmuir 7 (1988) 722.
[17] L. Kieken and M. Boudart, Catal. Lett. 17 (1993) 1.
[18] J. Szanyi and D.W. Goodman, J. Phys. Chem. 98 (1994) 2972.
[19] J. Szanyi, W.K. Kuhn and D.W. Goodman, J. Phys. Chem. 98 (1994) 2978.
[20] X. Xu, J. Szanyi, Q. Xu and D.W. Goodman, Catal. Today 21 (1994) 57.
[21] E.F. Meyer and R.L. Burwell, Jr., J. Am. Chem. Soc. 85 (1963) 2877.
[22] G.A. Somorjai, Introduction to Surface Chemistry and Catalysis (Wiley Interscience, New York, 1994) p. 468.
[23] M. Boudart, H. Topsøe and J.A. Dumesic, in: E. Drauglis and R.I. Jaffee (Eds.), The Physical Basis for Heterogeneous Catalysis (Plenum Press, New York, 1975) pp. 337–360.
[24] R. Brill, E.L. Richter and E. Ruch, Angew. Chem. Int. 6 (1967) 882.
[25] R. Brill and J. Kurzidim, Colloques Int. CNRS 187 (1969) 99.
[26] H. Topsøe, N. Topsøe, H. Bohlbro and J.A. Dumesic, in: T. Seiyama and K. Tanabe (Eds.), Proc. 7th IRC, Kodansha, Tokyo (1981) p. 247.
[27] J.A. Dumesic, H. Topsøe, S. Khammouma and M. Boudart, J. Catal. 37 (1975) 503.
[28] N.D. Spencer, R.C. Schoonmaker and G.A. Somorjai, J. Catal. 74 (1982) 129.
[29] M. Boudart and D.G. Löffler, J. Phys. Chem. 88 (1984) 5763.
[30] P.H. Emmett, in: E. Drauglis and R.I. Jaffee (Eds.), The Physical Basis for Heterogeneous Catalysis (Plenum Press, New York, 1975) p. 18.
[31] H. Topsøe, personal communication.
[32] G.K. Boreskov, Geterogennyi Kataliz, Section 3.6 (Nauka, Moskva, 1988).
[33] M. Boudart, Z. Physik. Chem., in press.
[34] H.S. Taylor and E.K. Rideal, Catalysis in Theory and Practice (Longmans, London, 1919).
[35] J. Turkevich and G. Garton, J. Chim. Phys. 51 (1954) 515.
[36] A. Ozaki, K. Aika and H. Hori, Bull. Chem. Soc. Jpn. 44 (1971) 3216.
[37] J.J. McCarroll, J.T. Clark and S.R. Tennison, U.K. Patent 1,471,233 (1977).
[38] A.I. Foster, P.J. James, J.J. McCarroll and S.R. Tennison, U.S. Patent 4,163,775 (1981).
[39] S.R. Tennison, personal communication.