

Industrial catalytic partial-oxidation processes

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INDUSTRIAL CATALYTIC PARTIAL-OXIDATION PROCESSES

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INTRODUCTION

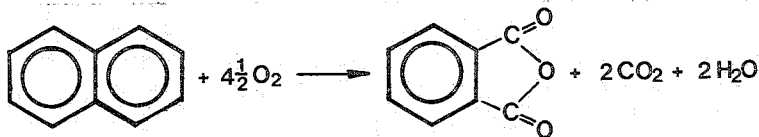
Catalytic partial-oxidation reactions are of considerable importance in the chemical industry. Roughly speaking the industrial partial-oxidation processes can be divided into two groups,

- i. reactions in the gasphase proceeding at high temperatures over solid catalysts,
- ii. reactions in solution catalyzed by soluble inorganic complexes, and thus confined to lower temperatures.

We shall in the following only discuss the first group and of all processes in this group we will ultimately focuss the attention on the acrylonitrile process.

Survey of the field of the high temperature partial-oxidation process

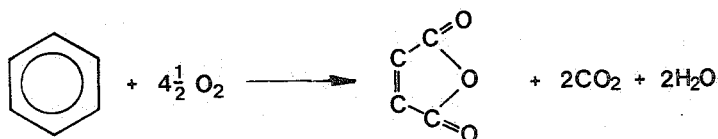
1. One of the oldest processes in this group is the oxidation of naphthalene to phtalic-anhydride.



The catalyst is V_2O_5 , supported on some low surface area, highly porous support. Because of the large amounts of heat evolved, the transfer of heat away from the reactor is of vital importance; for this reason the reactor is either a multitubular reactor or else a fluid bed reactor.

An interesting detail is that the catalyst contains K_2SO_4 that apparently causes the V_2O_5 to be in the liquid state in the pores of the support

2. A similar process is the conversion of o-xylene to phthalic-anhydride.
3. The oxidation of benzene to maleic-anhydride.



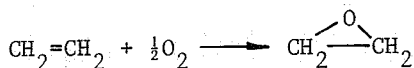
Reactors applied are of the multitube type and the catalyst is a mixture of V_2O_5 and MoO_3 on a support.

4. The oxidation of methanol to formaldehyde. This is a typical oxidative dehydrogenation. In the past the reaction



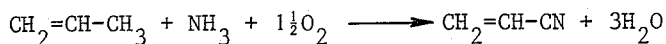
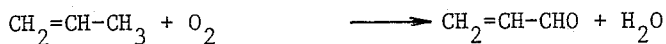
was performed on a copper metal catalyst but the more modern versions apply a $\text{Fe}_2(\text{MoO}_4)_3$ catalyst. Since the heat evolved is not so great as for the former three processes, a simple fixed bed reactor can be used.

5. The oxidation of ethene to ethene oxide.



The reaction is performed in a fixed bed reactor. The catalyst is Ag on a low surface area support; its selectivity is considerably enhanced by adding small amounts of chlorine containing compounds to the feed.

6. The oxidation of propene to acrolein and the ammoxidation of propene + NH_3 to acrylonitrile.



Both reactions are operated on a technical scale, the catalysts for both the oxidation and ammoxidation being quite similar (see later). The reactor for the ammoxidation is almost always a fluid-bed reactor; the oxidation of propene however is often performed in a fixed bed reactor.

Acrolein is rarely end product but usually oxidized in a second reactor to acrylic acid. The catalyst for the latter reaction consists of a mixture of transition metal molybdates.

It is noteworthy that the catalysts for these reactions are all oxides (even the Ag catalyst is in an oxidic state during operation) More often than not the catalyst consists of a mixture of oxides, or binary compounds of oxides. In most cases one of the oxides is a transition metal oxide.

Each reaction seems to need a special catalyst and a good catalyst for one process may be unsatisfactory for another. For instance, the V_2O_5 catalyst used for the selective oxidation of aromatics causes excessive combustion of propene, while the catalysts used for the latter process are not very active for the naphthalene oxidation. As to reactor technology it is not surprising that with the large amounts of heat to be transferred, reactors are usually of the fluid bed or multitube type.

CATALYSTS AND REACTORS

This lecture is almost entirely concerned with the catalysts for the partial oxidation reactions. Prof. Froment on the other hand will devote the greater part of his lecture to the design of the reactors for these processes and in particular to the problem of an adequate removal of the heat developed during the reaction. One might ask whether an ideal reactor designed for optimal heat transfer would not be sufficient to ensure that all partial-oxidation reactions could be performed using only one type of catalyst. Experience has shown that this is probable not feasible; we do not really know why.

We can however offer some plausible reasons. One of the more attractive suggestions is that although all are oxidation reactions, their mechanisms may be different. For instance, breaking an aromatic C-C bond in the oxidation of naphthalene may need a basically different reaction path, with different types of intermediates as the epoxidation of ethene. Indeed this is not so strange an assumption since V_2O_5 and Ag are widely different types of catalysts.

However, suppose that we might succeed in classifying the various oxidation reactions into types that have related mechanisms, we

still remain confronted with a choice as to the best catalyst from a family such as for instance that of the molybdate catalysts. Now, partial oxidation means that the introduction of only a few oxygens should be fast while a further introduction should be slow. 'Fast' and 'slow' might be translated into 'low activation energy' and 'high activation energy'. Let us now try to see whether we can fit such a concept into reactor theory: we shall do this in a superficial manner since Prof. Froment shall give a far more complete discussion later on.

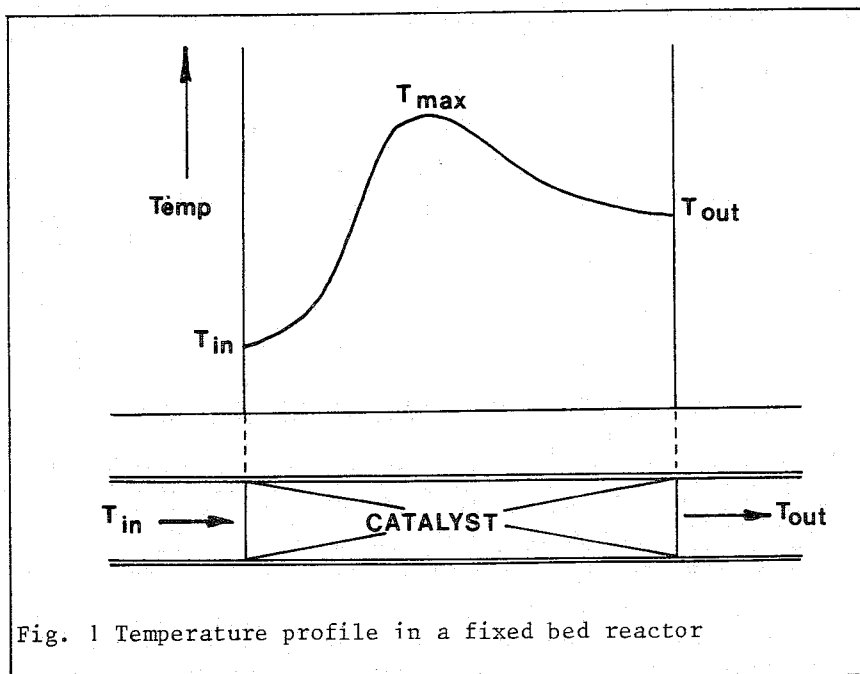


Fig. 1 Temperature profile in a fixed bed reactor

Consider first a single tube containing the catalyst (see fig. 1) The feed enters the reactor at the left side. Because of the exothermicity of the reaction heat is evolved and the temperature increases: simultaneously heat will flow out of the reactor in a direction perpendicular to the direction of the gasflow. There will now arise a competition between heat production and heat removal: the faster the latter the lower the temperature rise. Since heat production diminishes as the feed becomes exhausted, the axial temperature profile will be as shown in the figure. It will show a maximum somewhere along the axis and this maximum may be high and narrow or low and broad. (If it is high we call it a 'hot spot'). It is difficult a priori to predict the height of the peak the more so since we assumed above that there are two reactions, one that starts easily but has a low activation energy

and another that has a high activation energy. (Remember that we would like only the first to become operative.) Some qualitative information can be obtained by considering what might happen when the reaction is performed in a fluidized bed. The temperature in the fluidized bed reactor can be assumed constant over the entire length. We can however simulate the phenomena that lead to a 'hot spot' in the fixed bed by increasing the inlet temperature; we shall suppose that this temperature is equal to that of the cooling coils.

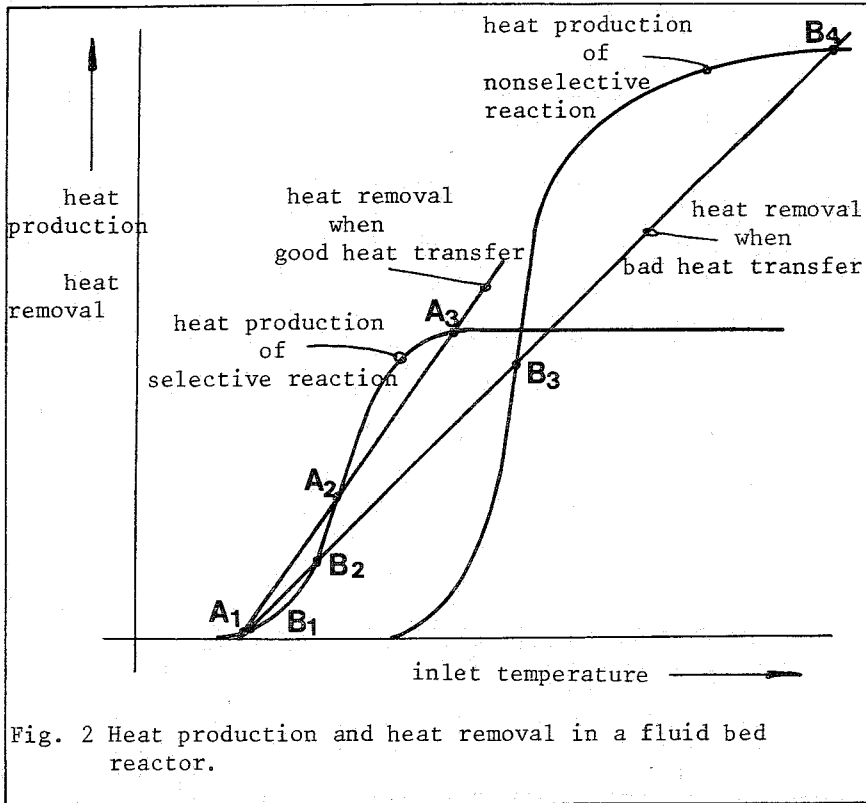


Fig. 2 Heat production and heat removal in a fluid bed reactor.

Fig. 2 gives a picture of the production of heat because of the reaction and of the heat removal because of heat transfer from reactor contents to cooling coils, both as a function of the inlet temperature. The rate of the reaction increases exponentially with this temperature (Boltzmann-Arrhenius factor) and so does the heat produced. However, there is an upper limit to the rate given by the total amount of feed introduced per unit of time; the curve is therefore sigmoidal. The heat removal is supposed to

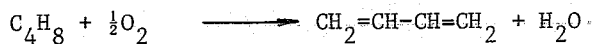
be linear in ΔT , the difference in reactor temperature and cooling temperature, resulting in straight lines in the figure. The slope of these lines depends on the extent of the heat transfer. (The better the heat transfer the steeper the line.) The intersections between the two lines indicate the states where there is equilibrium between the heat production and the heat removal. Normally there are three of these intersections (A_1 , A_2 and A_3) of which two (A_1 and A_3) correspond with stable states and one (A_2) with an unstable situation. Consequently there is either a reaction with low conversion (A_1) or another with almost complete conversion (A_3). If however, the heat transfer is bad the heat removal line also intersects the heat production line of the non-selective reaction and consequently the reaction 'runs away' to give complete non-selective oxidation (B_4). The morale of the story is that we cannot engineer a commercial selective oxidation process using a catalyst that intrinsically tends to complete combustion. On the other hand even if we are in the fortunate possession of an adequate catalyst with the property of being selective for partial oxidation we usually still need a careful and adequate engineering to make full use of this property. The engineering will be dealt with by Prof. Froment. While we shall try to understand how to devise appropriate catalysts for the special case of the propene oxidation and ammoxidation catalysts.

THE OXIDATION AND AMMOXIDATION OF PROPENE

The oxidation is performed in the temperature range between 400-500°C with a gas mixture of propene and air with an air/propene ratio of about 8. A fraction of the propene is combusted to CO_2 (CO) and H_2O (non-selective oxidation) but the main reaction is the selective oxidation to acrolein



Related reactions are the oxidative dehydrogenation of butene to butadiene



and the ammoxidation of propene



which is also basically a dehydrogenation.

Without a catalyst and depending on the temperature there is either hardly any reaction or a non-selective and 'deep' oxidation. The task of the catalyst therefore is not only to increase the rate but at the same time to limit the depth of oxidation i.e. to

make the reaction more selective.

Metal Oxide	T _{50%} °C	Selectivity %
MnO ₂	~ 250	< 10
Fe ₂ O ₃	~ 400	~ 50
SnO ₂	~ 500	~ 20
Bi ₂ O ₃ /MoO ₃	~ 375	> 90

Table 1 Activity and selectivity of some metal oxides for the oxidation of butene-1.

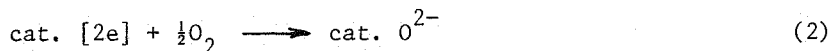
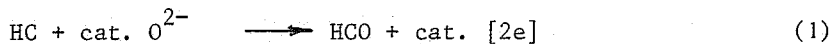
Table 1 shows how activities and selectivities for the butene-butadiene reaction are changing with the oxide used as a catalyst. The activity of the catalyst is given in terms of the temperature where 50% of the butene is oxidized within a certain residence time. The selectivity is expressed as the percentage of butene oxidized to butadiene. MnO₂ apparently is very active; 50% of the butene is already oxidized at 250°C. However, the selectivity is very low (~5%). A less active oxide Fe₂O₃ needs a temperature of around 400°C to obtain 50% conversion but is more selective (butadiene selectivity of about 50%). However, if a truly selective catalyst such as the combination of Bi₂O₃ and MoO₃ (or Bi-molybdate) is tried the activity is about comparable to that of Fe₂O₃ but the selectivity is far superior. What then is the reason for these differences?

REDOX-MECHANISM (Mars-Van Krevelen mechanism)

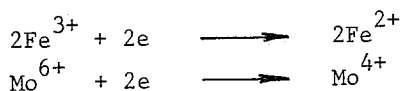
Mars and Van Krevelen concluded from experiments on the oxidation of naphthalene over V₂O₅ that catalytic oxidation reactions most often take place in two steps viz.

1. a reaction between the oxide and the hydrocarbon in which the hydrocarbon is oxidized and the oxide reduced, followed by
2. an oxidation of the reduced oxide to re-establish the initial state.

In a condensed notation (HC = hydrocarbon)



The two electrons [2e] might be donated to one or more cations such as for instance:

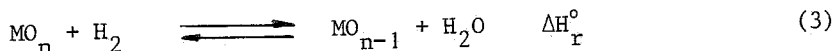


It is sometimes assumed that they are actually placed in the conduction band of the solid.

Intuition tells us that oxide catalysts with a weak metal-oxygen bond will easily donate oxygen to the hydrocarbon which means that donation already occurs at relatively low temperature; such catalysts therefore are probably active. It also means however, that donation may occur in numbers of oxygens that are greater than we require for our purpose: the catalyst is then also non-selective. If the catalyst follows an orthodox Mars-Van Krevelen pattern it should not be of great importance whether oxygen gas is present or not provided oxygen depletion of the catalyst does not interfere. Typical examples of such catalysts are Ag_2O or MnO_2 .

On the other hand, oxidic catalysts with strong metal-oxygen bonds are not readily reduced and need high temperatures to do so: they are not active and because of the high temperatures also non-selective. Examples should be for instance TiO_2 or SnO_2 .

Catalysts that are both reasonably active but also selective represent compromises: as Sachtler and De Boer postulated they are oxides with intermediate metal-oxygen bond strengths. Such oxides are Fe_2O_3 ($\rightarrow \text{FeO}$) and MoO_3 ($\rightarrow \text{MoO}_2$). To show this we define the bond strengths thermochemically as being equal to the reaction enthalpy



If we now plot $T_{50\%}$ for the oxidation of butene-1 to butadiene as a function of ΔH_r° we find fig. 3a showing a nice fit. To illustrate the selectivity pattern we choose an intermediate temperature and plot the % conversion to butadiene as a function of ΔH_r° (fig. 3b). At low ΔH_r° we should expect considerable but predominantly non-selective conversion. At high values conversion should be low and because of the high temperatures needed for conversion also quite non-selective. At intermediate values we expect to find a maximal selective conversion and this is indeed what happens. The maximum is situated for this particular reaction approximately at ΔH_r° is 0-10 kcal/mole. i.e. The metal-oxygen bond $\text{MO}_n \rightarrow \text{MO}_{n-1} + \frac{1}{2}\text{O}_2$ should be around 50-60 kcal/mole⁻¹. However, even here conversions are not particularly selective. If on the other hand we apply Bi_2MoO_6 a binary oxide we find a similar activity ($T_{50\%}$) but a far superior selectivity. Characterization of metal-oxygen bond strengths as given in eq. (1) when applied to Bi_2MoO_6 leads to ambiguities: which bond strength do we choose Mo-O-Mo, Mo-O-Bi or Bi-O-Bi? Let us as a rough assumption consider

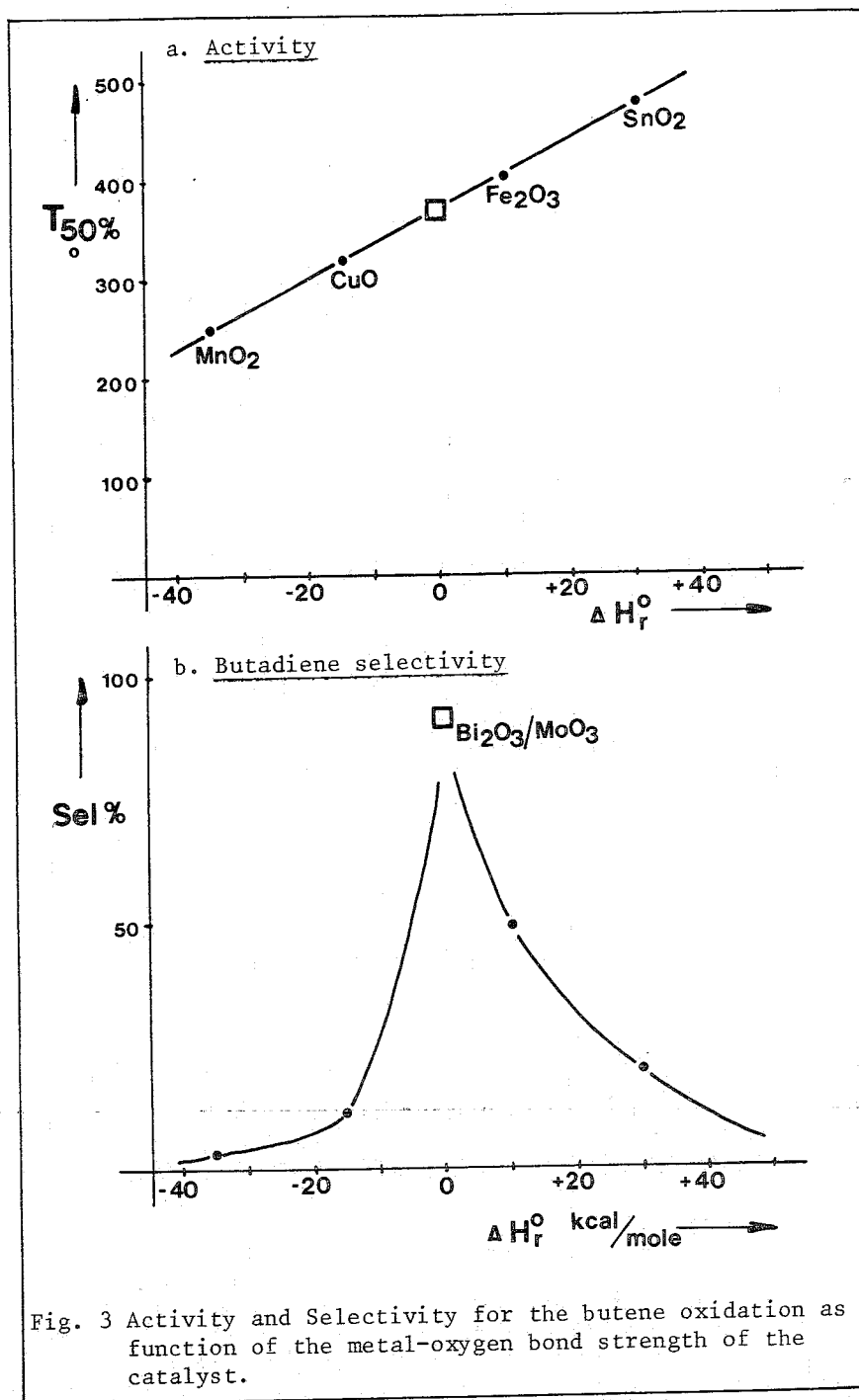
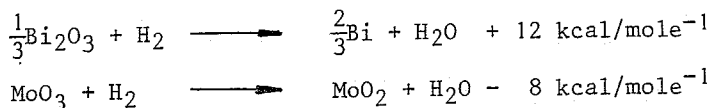


Fig. 3 Activity and Selectivity for the butene oxidation as function of the metal-oxygen bond strength of the catalyst.

Bi_2MoO_6 as a mixture of $\text{Bi}_2\text{O}_3 + \text{MoO}_3$

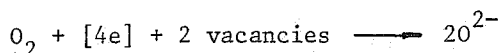


We should then tend to the belief that Bi_2MoO_6 should indeed be among the most selective catalysts but not so very much different from Fe_2O_3 ($\Delta H_r^0 = + 11 \text{ kcal/mole}$).

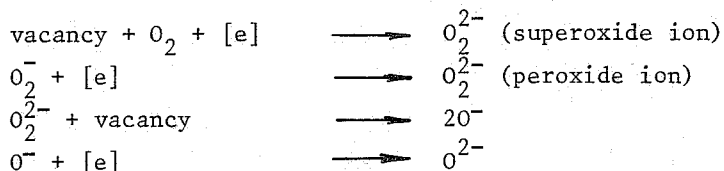
So, although thermochemistry might provide valuable initial directions there must be something else something, probably connected with kinetic factors, that ultimately defines the class of very selective catalysts. The coming pages are almost entirely concerned with this aspect. Before beginning to do so, however, let us draw the attention to two problems already hidden in what has been said before.

One, rather obvious point is that the Balandin 'Volcanocurve' as reproduced by Sachtler and De Boer for oxidation reactions with the ΔH_r^0 (eq. 3) as parameter, of course changes its position with the reaction envisaged. Even for oxidative dehydrogenation reactions that appear similar such as $\text{C}_4\text{H}_8 \rightarrow \text{C}_4\text{H}_6$ and $\text{CH}_3\text{OH} \rightarrow \text{H}_2\text{CO}$ the curve must be somewhat different because $\text{Fe}_2(\text{MoO}_4)_3$ is a weak catalyst for the first but an active catalyst for the second. While $\text{Bi}_2(\text{MoO}_4)_3$ is active for both. For an entirely different reaction such as the oxidation of C_{10}H_8 to phthalic anhydride the need for many and aggressive oxygens in the catalyst is fairly obvious and the fact that the maximum shifts to the far left where we find V_2O_5 is not entirely unsuspected.

Another complication is that the redox mechanism often operates in the Mars-Van Krevelen manner but not always. Indeed, it is even somewhat surprising that it works so often. In the reoxidation of the catalyst the process occurring is



However, it is far from selfevident that the four electron transfer is concerted. It could - and often does - occur stepwise, for instance



The intermediates in this chain, the superoxide ion, the peroxide and O^- are very reactive species that have a tendency at the higher

temperatures to interact with the hydrocarbon in a non-selective manner. This means that the oxide in the presence of O₂ behaves quite differently than in its absence. Compounds such as TiO₂ and SnO₂ are not very active in the absence of oxygen but become quite virulent in a non-selective manner when there is oxygen present. Now, two of the intermediates viz. O₂⁻ and O⁻ can be detected by electron spin resonance; and these have indeed been found as surface species for the two oxides (among others) but not on the typically highly selective ammoxidation catalysts.

REACTION MECHANISM FOR THE CATALYTIC OXIDATION OF PROPENE TO ACROLEIN

The hydrogen atoms in an olefin at carbon positions next to a double bond may be supposed a priori to be relatively easily dissociated because their removal leads to allylic structures (carbocation, radical or carbanion) that are resonance stabilized. Consequently, if an olefin becomes involved in a substitution reaction such as oxidation the evident focus of the attack is on the 'allyl hydrogens'. Already very early in the study of the catalytic oxidation reactions it was postulated by Sachtler that the first step in the network of catalytic oxidation reactions consisted in the formation of an allylic structure. Kinetical evidence and measurements of isotope effects by Adams and Jennings showed that it was even the rate determining reaction. A most important detail in the mechanism was revealed by Sachtler's ¹⁴C labelling experiments (fig. 4) which showed that not only should there be an allyl but the way of bonding of the allyl to the surface should leave the terminal carbon atoms equivalent since they have an equal chance of collecting an oxygen.

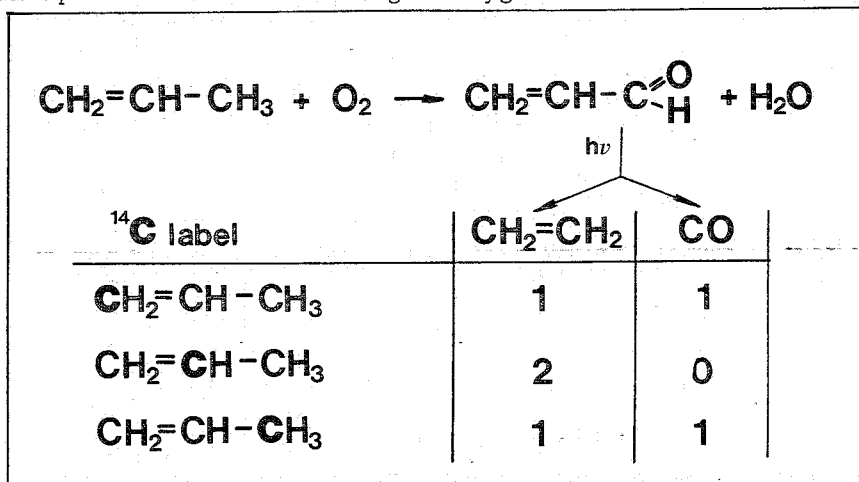


Fig. 4 Schematic representation of Sachtler's ¹⁴C-labelling experiments.

This can be realized dissociating a proton from the CH_3 group, attaching the proton to an oxygen on the surface and binding the residual carbanion via acceptor π -bonding to a transition metal cation next to a surface anion vacancy. The π -bonding takes care of the equivalence of the terminal C-atoms while the interaction between the p-orbitals of the allyl and the d-orbitals of the transition metal cation causes the allyl to become bonded to the surface. Because of the $\sigma\pi$ -double bond there will occur some transfer of negative charge (electrons) to the cation equivalent to an incipient reduction. Simultaneously oxygen anions of the surface (fig. 5) will move towards the terminal C-atoms because it is at these atoms that the radical character is strongest. The initial steps in the heterogeneous catalytic oxidation are therefore reasonably well understood.

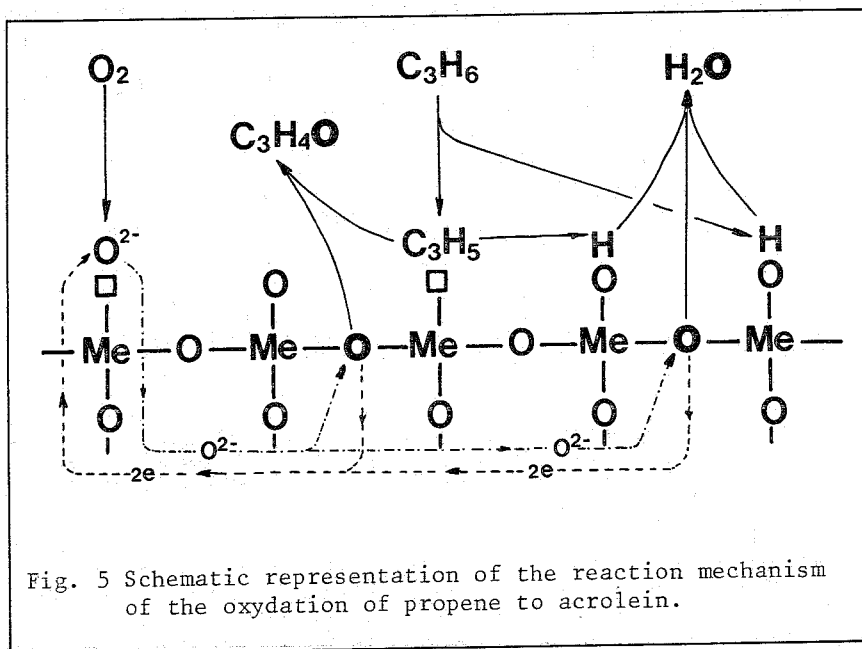


Fig. 5 Schematic representation of the reaction mechanism of the oxidation of propene to acrolein.

Our difficulties start when we have to explain why on some oxides or combinations of oxides the reaction stops whereas in non-catalytic gaseous oxidation the subsequent oxidation reactions are faster. Even for single oxides where the thermochemistry seems favorable for selective processes there remains a considerable amount of more extensive oxidation. One of the difficulties in explaining these observations is that we lack the necessary information as

to the nature of the subsequent steps in the more extensive oxidation.

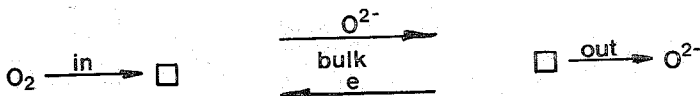
There is however a simple explanation for the extraordinary selectivity. Let us suppose that the oxygen ions of the oxidic catalyst can be classified in types, one of which contains only relatively small numbers of oxygens that however are very reactive. Their high activity combined with their small concentration cause the catalyst to be moderately active. However, in the absence of gaseous oxygen the selectivity should be very high since there are simply not enough oxygens in the environment of the allyl to allow a more extensive oxidation. Such a model was first proposed by Callahan and Grasselli and later on worked out in more detail by Grasselli and Suresh to explain the properties of their USb_3O_{10} catalyst. They could show that reduction of the catalyst by propene occurred in two different manners. A small amount of oxygen (A-oxygen) was rapidly removed and produced acrolein. By far the larger amount (B-oxygen) reacted only slowly but the products were CO and CO_2 . Another proof for the existence of small quantities of very active oxygen was given by Matsuura. The oxidation of butene is inhibited by its product butadiene and the activation of propene inhibited by acrolein. Oxidation catalysts adsorb butadiene and acrolein in an activated but strong adsorption (A-type adsorption). This adsorption can be eliminated by a small prereduction of the catalyst and is reestablished by an ensuing oxidation. The adsorption site therefore is an O^{2-} -ion and this ion must be the active oxygen otherwise adsorption would not inhibit the propene or butene oxidation. The surface concentration of the active oxygens is indeed surprisingly small: Matsuura found one active oxygen per 150 \AA^2 for $Bi_2Mo_2O_9$ but one per 1800 \AA^2 for USb_3O_{10} . While Grasselli considers the active oxygens as still belonging to the normal catalyst structure, Matsuura postulated that they are surface defects. He showed that Bi_2Mo_6 is not active but can be activated by adding small amounts of excess MoO_3 . Simultaneously herewith the A-type of adsorption (absent on pure Bi_2Mo_6) grows linearly with the activity.

Defects as the origin of the catalytic activity for the selective oxidation of olefins were first proposed by Sleight. He doped the Scheelite $PbMoO_4$ with small amounts of Bi to give $Pb_{1-3x}Bi_{2x} \square_x (MoO_4)$ where \square is a cationvacancy: the activity of doped catalysts grows linearly with x provided x remains small. A very interesting aspect of the doping is that variations such as $Pb_{1-2x}Bi_xNa_x (MoO_4)$ or $Pb_{1-3x}La_{2x} \square_x (MoO_4)$ remain inactive. This appears to show that an active molybdate catalyst needs Bi^{3+} -cations but also cation vacancies. Matsuura's active sites in Bi_2Mo_6 follow this principle because he assumes that the excess MoO_3 is incorporated in the Bi_2O_2 -layers by a replacement of $2Bi^{3+}$ -cations by a Mo^{6+} cation and a cation vacancy.

It is often assumed that the defects remain predominantly situated near or on the surface although this is not necessarily always true. (The doped Scheelites as prepared by Sleight have the defects uniformly dispersed over bulk and surface.)

However, for catalyst systems such as $\text{SnO}_2 + \text{Sb}_2\text{O}_4$ (Distillers), $\text{FeSbO}_4 + \text{Sb}_2\text{O}_4$ (Yoshino et al.) and even $\text{USbO}_5 + \text{Sb}_2\text{O}_4$ (Grasselli and Suresh) there are reasons to assume that the outer layers contain an excess of Sb. One of Grasselli and Suresh's catalysts was prepared by impregnating USbO_5 (active but not selective) with Sb to effect a surface enrichment of Sb. Indeed the catalyst became selective, presumably because of a formation of $\text{USb}_3\text{O}_{10}$ (selective on the surface. However, it soon lost its selectivity because the excess Sb diffused into the solid. SnO_2 is a reasonably active but non-selective catalyst (see before) but small amounts of Sb suffice to make it selective. Similarly, FeSbO_4 is active but non-selective; adding Sb_2O_4 causes it to become selective.

Together, all these observations appear to confirm that the 'isolated oxygen' is a relevant and valuable concept in explaining the selectivity of more prominent catalysts for olefin oxidation. It is however not entirely consistent with some other commonly accepted facts. One is the observation that products such as butadiene, acrolein and acrylonitril are adsorbed rather strongly and therefore remain attached for considerable time to the surface. Moreover, it is also generally observed that the reoxidation of the reduced catalysts is fast so that depleted sites are rapidly replenished. Experiments by Keulks and collaborators may perhaps be of relevance in this connection. They ran mixtures of C_3H_6 and ^{18}O -enriched oxygen over Bi-molybdate catalysts containing only ^{16}O . Following the ideas mentioned above viz. rapid replacement of oxygen earlier removed from the surface by oxygen molecules from the gasphase one would expect the ^{18}O to become observable in the products acrolein and CO_2 almost immediately. However, for a catalyst such as Bi_2MoO_6 almost the entire bulk of the catalyst has to be exchanged before the ratio's of gasphase ^{18}O and product ^{18}O have become equalized. Keulks' interpretation of this behaviour is that oxygen has to diffuse for a considerable length through the bulk from the site where it is incorporated to where the structural oxygen is going to be removed by the reduction. An appropriate model might then be



so that the entrance of O_2 is at a different site than the exit. Indeed, maintaining a spatial distance between the two sites has been occasionally proposed as an appropriate model to explain selectivity. It has also been postulated that entrance and exit are connected with the pair of cations as present in almost all

selective species. Sleight for instance assumes the oxygen to become removed from two MoO_4 -ions next to a cation vacancy while O_2 is entering via Bi. O^{2-} and electrons are travelling through the bulk from one cation to the other in opposite directions. Haber prefers the allyl to be formed on Bi and the oxygen to come in at Mo. Matsuura believes that formation of the allyl occurs on the Mo but that this migrate to Bi. The actual directions of migration of electrons and oxygen anions is therefore not clear but there is good reason to accept the concept of the two cations being separately operative in the two basic tasks of the catalyst viz. donation of O to the hydrocarbon and accepting oxygen from O_2 molecules: the catalyst is therefore truly bi-functional.