

Selective catalytic oxidation by heterogeneous transition metal catalysts

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SELECTIVE CATALYTIC OXIDATION BY HETEROGENEOUS TRANSITION METAL CATALYSTS

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ABSTRACT

The reaction mechanisms of two transition metal catalysed reactions are discussed: epoxidation of ethylene production and vinylacetate. In addition short reference will be made to methanol and CO oxidation. The surface reactions are related to the corresponding reactions in organometallic complexes. Also a relation between surface science model studies and surface reactivity will be made. Elementary surface reaction steps on surfaces will be highlighted; subsequently the main mechanistic issues in oxygen CH and OH bond activation will be described.

1. Introduction

Three large scale selective oxidation processes are based on heterogeneous metallic catalysis. The epoxidation of ethylene, catalysed by silver, produces oxirane, which is an important intermediate to the manufacture of glycol or polyols. Silver is also used as a catalyst for the oxidative dehydrogenation of methanol to formaldehyde. The third process is the production of vinylacetate by oxidative coupling of ethylene and acetic acid catalysed by palladium. Whereas some of these processes are more than fifty years old, there is still a considerable need to further improve their yields. Only recently it has become possible to formulate a mechanistic basis to these reactions. This will be the subject of this chapter.

The reaction temperatures for these three processes are moderate. Two other important oxidation processes concern the oxidation of NH_3 to NO , the Ostwald process and the selective oxidation of CH_4 to synthesis gas. These reactions proceed at temperatures higher than 600°C and are catalysed by noble metals as Pt or Rh. The catalytic surface activates NH_3 or CH_4 . The product distribution of these processes is mainly determined by gas phase radical reactions. Reactions that also should be mentioned are the oxidation of SO_2 to SO_3 by Pt and the oxidation of CO to CO_2 . This reaction has been extensively investigated, mainly for fundamental reasons, and occurs for instance in automotive exhaust catalyst systems. Low temperature hydrocarbon conversion catalysis is also of interest in the context of automotive exhaust catalysis.

Here we will focus on the reactivity of transition metal surfaces of relevance to low temperature selective oxidation processes. Another chapter deals with the high temperature oxidation reactions.

As explained in chapter 10, the oxidation mechanism of vinylacetate formation is not yet completely clear. One possibility is that it is related to the homogeneous Wacker reaction^{1,2} as will be explained later; the alternative is a surface reaction on large Pd clusters. According to the latter proposal, the large Pd clusters that are found in the reaction mixture activate ethylene to an adsorbed vinyl fragment that reacts with adsorbed acetate to vinylacetate.

The activation of the CH bonds in ethylene will be discussed in section 3. On silver it initiates total combustion, the non-selective reaction in the ethylene epoxidation reaction.

For the ethylene epoxidation reaction³ comparisons have also been made with homogeneous systems, but main fundamental advances have been due to model catalyst surface science studies.

Recent advances in the understanding of the reactivity patterns of adsorbed oxygenates to transition metal surfaces are providing a molecular basis to a mechanistic description of selective oxidation reactions⁴.

This lecture will discuss the mechanism of selective oxidation based on information from surface science studies as well as on the reactivity of organometallic complexes. We will first describe the elementary steps of the corresponding catalytic reaction cycles and then discuss in some detail essential reaction steps.

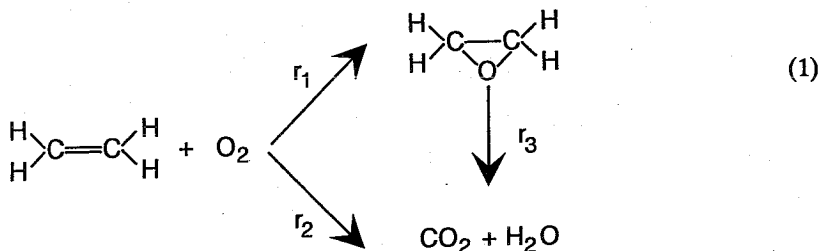
2. Reaction mechanisms

2.1. Ethylene epoxidation by silver (3)

The epoxidation reaction proceeds at 250 °C over a Ag catalyst. The selectivity of the catalyst strongly depends on catalyst composition and the presence of chlorine containing hydrocarbons in the gas phase (~ ppm).

The Ag particles are supported on a wide porous α -Al₂O₃ support and the catalyst is promoted by addition of alkali, especially Cs.

The kinetics of the reaction consists of two parallel reactions and a consecutive reaction:



Total combustion of ethylene can occur by a direct competitive combustion of ethylene, r_2 , or a consecutive reaction of epoxide, r_3 .

Ethylene epoxide itself has been demonstrated to be converted with a very low rate by silver. However the ethylene epoxide molecule can become isomerized to the aldehyde by acidic protons on the support. The aldehyde has a high rate of combustion by silver to CO_2 and H_2O . The role of alkali is amongst others the suppression of the presence of acidic protons on the support and hence to reduce the rate of the consecutive reaction r_3 .

The moderating chlorine containing hydrocarbons, e.g. vinylchloride are combusted by silver and chlorine becomes deposited on silver. Chlorine containing molecules have to be added continuously to the reactant feed, because chlorine is removed from it by a reaction with ethylene.

Chlorine adsorbed to the silver surface enhances the initial rates ratio r_1/r_2 . There have been many different proposals concerning the mechanism of epoxide formation. All of them have in common that adsorbed oxygen species of different reactivity are proposed to be present on the silver surface and one species is proposed to give the epoxide upon contact with ethylene.

According to one early proposal oxygen can be adsorbed in the molecular or dissociated form to silver. Only molecular oxygen is proposed to give the epoxide, atomically adsorbed oxygen gives total combustion of ethylene. Since 6 atoms of oxygen will burn one ethylene molecule to CO_2 and H_2O , 3 adsorbed O_2 molecules can produce 6 ethylene epoxide molecules from 6 ethylene molecules. A seventh ethylene molecule then has to be used to remove the 6 oxygen atoms left on the silver surface. According to this proposal the maximum ethylene selectivity of the reaction can never exceed 6/7. Modern epoxidation catalysts, however, exceed this value.

Another proposal, now generally accepted, is based on the strong dependence of the selectivity on silver surface oxygen coverage. The selectivity of the epoxidation reaction is found to have its optimum value when the $\text{O}_{\text{Surf.at}}/\text{Ag}_{\text{Surf.at}} \approx 1.0$. This implies a surface composition close to AgO . Since only half of the oxygen can reside on the external surface, the other half of the oxygen atoms has to be located in subsurface positions. At this high oxygen concentration, the O-Ag bond energy is low and O behaves electrophilic. There is no barrier for oxygen insertion into the ethylene π bond (figure 1).

Total combustion proceeds by activation of the C-H bond of ethylene, as has been demonstrated using deuterated ethylene. At low surface coverage adsorbed oxygen atoms behave nucleophilically and attack the slightly positively charged ethylene hydrogen atoms. Empty vacancy sites next to adsorbed oxygen are needed to stabilize the resulting C_2H_3 species.

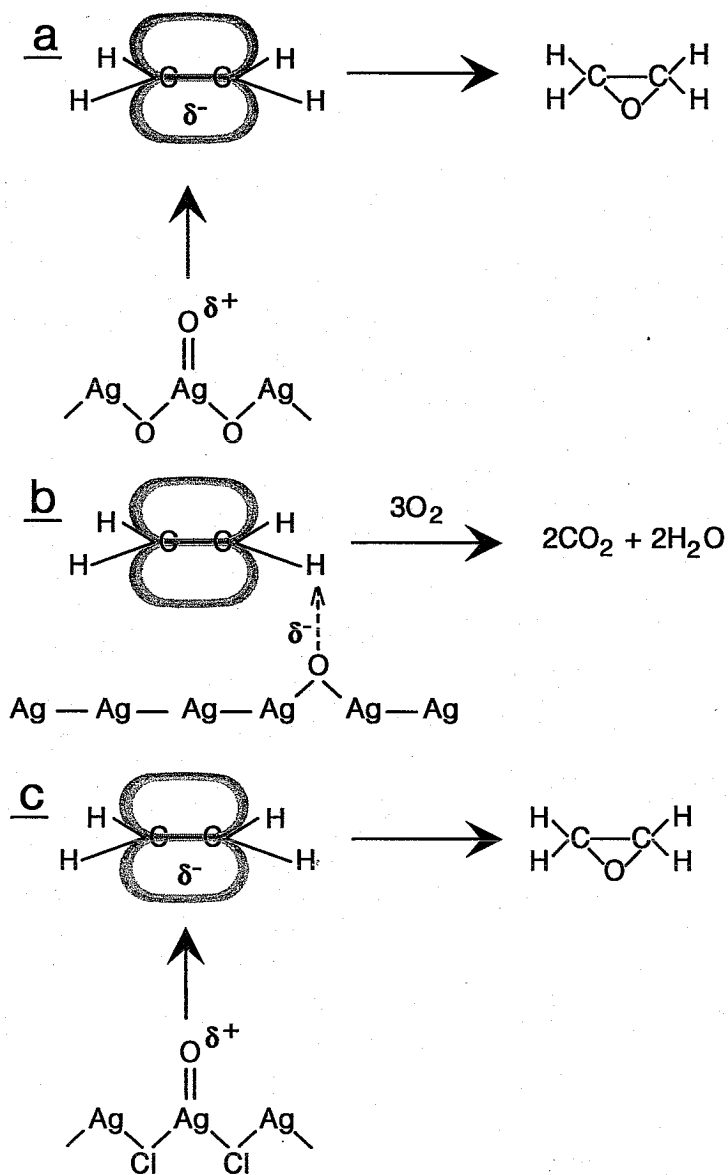


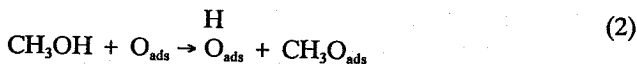
Figure 1

At the reaction temperature the surface will only be partially covered by oxygen. This would give a low selectivity. Chlorine adsorbs strongly to Ag. It can take over the role of subsurface oxygen. It will reduce the O-Ag bond energy of the oxygen atoms that share also a bond with Ag (see figure 1). Whereas in the epoxidation reaction molecularly adsorbed O_2 does not play a role, the question of the importance of molecularly versus atomically adsorbed oxygen in substrate activation is a recurring motive in selective oxidation.

Two examples are known for molecularly adsorbed O_2 to play a role in oxidation. One example is the oxidation of SO_2 by molecularly adsorbed O_2 on silver³. The other example is the activation of NH_3 (6) on Mg, Zn or Cu by molecularly adsorbed O_2 . In the case of low temperature NH_3 activation, convincing occurrence of a transient intermediate with molecular O_2 has been proposed.

2.2 Methanol oxidation

The methanol oxidation reaction catalysed by silver, proceeds at a temperature (~ 500 °C) such that the adsorption equilibrium of adsorbed oxygen is shifted to the gas phase. Hence oxygen can only be adsorbed on defects of silver gauze. Methanol adsorbs only weakly to silver, but will dissociate by a reaction with adsorbed oxygen.

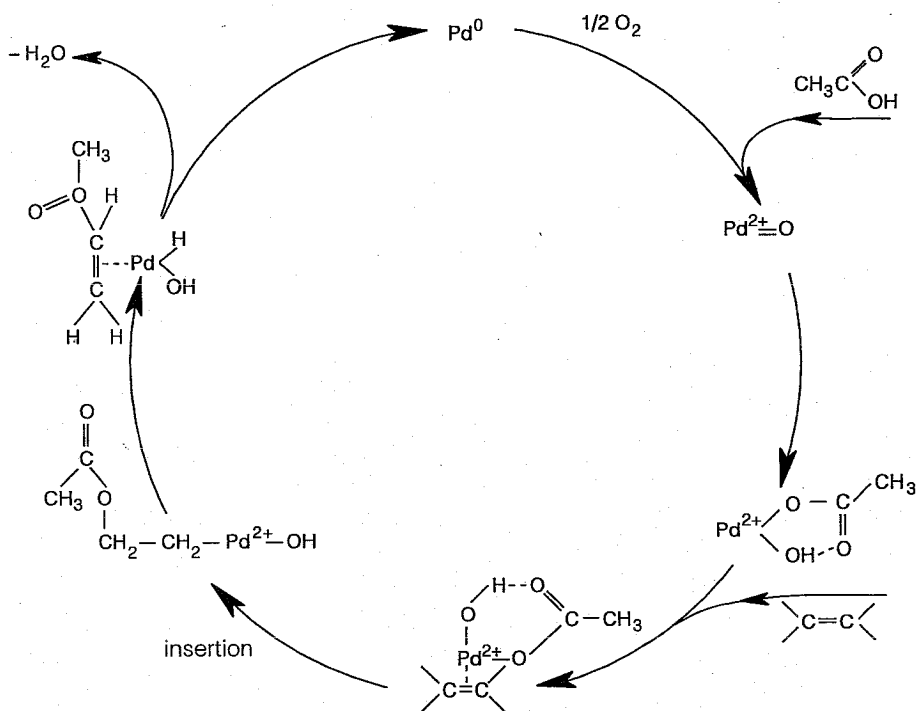


The adsorbed methoxy will desorb as formaldehyde.

2.3 Vinylacetate from ethylene and acetic acid

In the liquid phase a mechanism can be proposed that is analogous to the Wacker reaction. This is shown in figure 2.

The reaction concerns a redox cycle between Pd^{2+} and Pd^0 . In the Wacker reaction ethylene reacts with H_2O instead of acetic acid, and Pd oxidation is catalysed by Cu^+ . Cu^+ is a catalyst for Pd^0 oxidation, Cu^+ has only to change one valency, whereas oxidation of Pd requires two electron transfer and hence is more difficult.

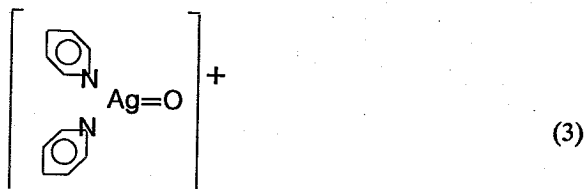


The vinyl acetate oxidation-redox cycle
(analogue Wacker)

Figure 2

The essential difference between the acetoxylation reaction and ethylene epoxidation is that insertion occurs by a nucleophilic attack between a negatively charged acetate ion and ethylene, with formation of ethyl acetate coordinated to the Pd^{2+} ion.

In the epoxidation reaction oxygen addition to the ethylene π bond occurs by an electrophilic attack, without stabilization of one of the ethylene carbon atoms. Interestingly it has been found that also in a homogeneous catalytic reaction epoxidation occurs by such a complex with electrophilic oxygen⁴: with Ag in a threevalent state.

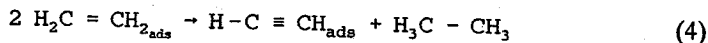


After the acetate insertion step, the ethyl acetate intermediate undergoes β C-H cleavage to vinyl acetate. Bond breaking of this CH bond is facilitated by the presence of the near polar C-O ester bond.

The other important steps are reductive elimination of acetic acid and oxidation of Pd^0 to Pd^{2+} . Except for the reoxidation step of Pd^0 (in acetoxylation Cu^{+1} is not applied), the other elementary steps are well known in organometallic chemistry. The reduced Pd forms metal clusters as in a metallic catalyst. Oxygen can dissociate on these clusters. The non-selective total oxidation of ethylene to acetic acid or combustion of acetic acid probably occurs on these metallic Pd particles. However, according to Moiseev (see chapter 10) the Pd surface also plays a role in the vinyl acetate reaction step.

Whereas Ag metal without adsorbed O will not activate CH bonds, the more reactive Pd metal can activate the CH bond of ethylene.

In the absence of hydrogen ethylene adsorption to Pd will lead to ethane formation by self hydrogenation and formation of carbonaceous residues in a reaction formally represented as:



Adsorbed acetylene is readily converted into CH_{ads} or C_{ads} and H_{ads} species. The partially hydrogenated 'C' species will readily react with adsorbed oxygen to produce CO or CO_2 .

Acetic acid interacts more weakly with palladium metal, but can become activated by coadsorbed oxygen as we will discuss later.

2.4. CO oxidation

The recombination of adsorbed O atoms and CO to give CO_2 occurs readily on most transition metals. The slow step is the dissociation of adsorbing O_2 into adsorbed oxygen atoms. At low temperatures the reaction order is negative in CO, implying that CO is Major Adsorbed Reaction Intermediate (MARI). This high surface coverage suppresses O_2 dissociation, for which at least two neighbouring vacant sites are needed.

The reaction rate shows a maximum as a function of temperature. The increase in reaction rate is due to the creation of surface vacancies. At higher temperatures the reaction rate starts to decrease, because then the adsorption equilibrium of CO is shifted towards the gas phase, and reaction becomes positive in the CO pressure.

Single crystal surface experiments have demonstrated an interesting surface reconstruction phenomenon⁹, that leads to oscillatory behaviour at low pressures.

The (100) surface of Pt reconstructs in a vacuum to a more stable surface in which the surface layer has the more dense (111) packing. The rate of O₂ dissociation on this surface is extremely low. CO, however adsorbs with a high rate, but destabilizes the (111) overlayer, so that the more reactive (100) layer is reformed. On this surface the O₂ dissociates rapidly. The reaction between CO_{ad} and O_{ad} occurs rapidly and the weakly adsorbing CO₂ desorbs. The surface free of adsorbate reconstructs to the stable (111) layer and the process repeats itself.

3. The reactivity of transition metal surfaces for oxidation reactions

3.1. Oxygen activation

The reactivity of small hydrocarbons with adsorbed oxygen has been extensively investigated by a number of groups^{4,10,11}

The oxygen molecule will dissociate on clear transition metal surfaces below room temperature. In order to accommodate the oxygen atoms large surface atom ensembles are required. Oxygen dissociation can become suppressed by the presence of adsorbed oxygen or other blocking coadsorbates. Hence the rate of dissociation of oxygen dissociation rapidly declines with surface coverage.

Because of the low reactivity of the noble metal surfaces as well as the group IB metals coadsorption of oxygen often has a promoting effect on hydrocarbon reactivity. It assists the dissociation of CH bonds. Due to their completely filled d-valence electron band, the IB metals, Cu, Ag and Au are least reactive.

With respect to oxygen the reactivity of Ag is intermediate between that of Cu and Au. On Ag as well as Cu adsorbed O₂ dissociates below room temperature, however O₂ will not dissociate on Au. The O_{ads}-Au interaction is too weak to overcome the O₂ bond energy. Cu has a higher reactivity than Ag. Whereas for instance NO will not dissociate on Ag, dissociation of NO on Cu occurs readily. Because of the high interaction energy with oxygen, and the resulting high temperature of oxygen desorption, catalytic dissociation of NO however is only possible at high temperatures in the absence of oxygen. Strongly adsorbed oxygen atoms will block surface ensemble sites necessary for NO dissociation.

Of recent interest is the reduction of NO by hydrocarbons¹² in excess oxygen catalysed by Cu or Co containing zeolites. In these cases no zerovalent metals are present, but metal-oxo-complexes. NO is oxidized to NO₂.

An intermediate formed by recombination with NO then probably reacts in a consecutive reaction with hydrocarbon to N_2 .

The high reactivity of most of the transition metals with respect to oxygen has as a consequence that oxidation catalysis will usually proceed on transition metal oxides instead of the metals. The catalytically active metals, silver and platinum remain bulk metals also during the catalytic oxidation reaction.

On reactive metal surfaces oxygen coadsorption can prevent decomposition of adsorbed molecules. On Mo (110) coadsorbed oxygen has been found to deactivate the metal surface and to stabilize adsorbed molecules¹³.

Also oxygen adsorption may lead to facetting of catalyst particles. Those surfaces will be stable during the catalytic reaction that have their lowest surface energy in the presence of oxygen. This usually is not necessarily the same surface that is most stable in the absence of adsorbed oxygen.

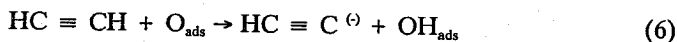
3.2. The activation of CH and OH bonds

Oxygen atoms adsorbed at low surface coverage to transition metal surfaces as, Ag, Pd or Rh are nucleophilic and act as Lewis basic atoms.

Whereas acetic acid will mainly desorb molecularly from transition metals and at relatively low temperature, in the presence of coadsorbed oxygen acetate formation occurs readily.



Such Brønsted acid-Lewis base oxygen reactions are quite common. On Ag it has been shown that CH bonds, that are not activated by the clean metals, will react in the presence of oxygen:



Earlier we mentioned that the total combustion of ethylene is initiated by an analogous reaction to eq.7. In the presence of adsorbed oxygen also the methyl group of acetic acid may become activated, providing a pathway for the total combustion of acetic acid.

The CH bonds of the CH_3 group in propylene are also easily activated, because of resonance stabilization of the allyl formed upon CH cleavage.

Propylene will react with O_{ad} on Cu to acrolein¹² illustrating the preference of CH bond breaking in propylene versus oxygen insertion into the C-C π bond. At low oxygen coverage this reaction will compete with propylene oligomerization, at higher oxygen coverages consecutive reaction of acrolein will occur that will lead to total combustion.

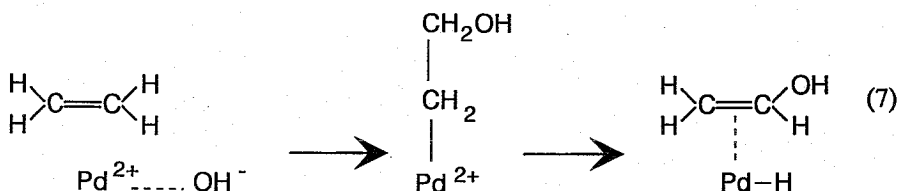
On the less reactive Ag surfaces it appears that with propylene oxygen insertion into the C-C π bond competes with methyl CH activation. The CH bond

of propylene epoxide reacts so rapidly, that propylene epoxide is only observed as a product when contact times are used of the order of msec¹⁵.

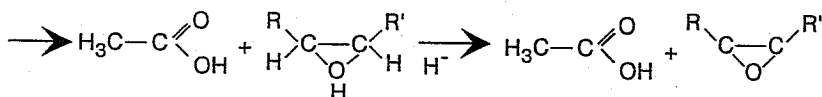
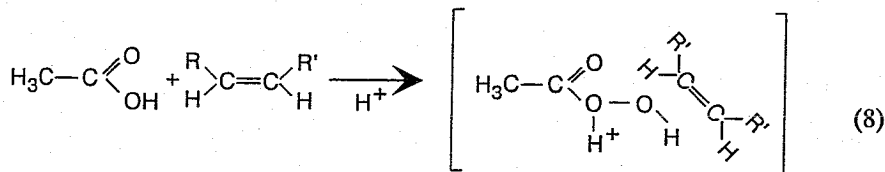
In case Ag is alloyed by Au, the oxygen concentration on the Ag surface is decreased. This enhances the nucleophilicity of the adsorbed oxygen atoms. It is found that the selectivity for ethylene epoxide formation is decreased, but that propylene now forms acrolein with high selectivity¹⁶. The reaction of aldehydes or alcohols with atomically adsorbed oxygen can lead to acetate formation. On the transition metals acetate decomposition will occur upon heating¹⁷. At lower temperature CO and O_{ads} formation occurs. At higher temperature the acetate tends to decarboxylate. Coadsorbed oxygen tends to suppress the low temperature decomposition path because of site blocking.

Only atomic oxygen adsorbed to silver gives epoxide formation by reaction with ethylene. On Pd or Rh aldehydes or ketones will be formed. In the presence of excess oxygen the main reaction will be total oxidation. The analogous homogeneous reaction of ethylene on Pd²⁺ is the Wacker reaction.

The steps in the homogeneous phase that lead to the aldehyde formation are:



The reaction is initiated by insertion of OH⁻ into adsorbed ethylene. Aldehyde formation results by consecutive isomerization of the vinyl alcohol, that is formed after β CH cleavage. According to mechanism 7, intermediate I has a strong σ metal-carbon bond comparable to that in adsorbed ethyl. The next step in intermediate I is β C-H bond cleavage. These reaction paths have to be contrasted with epoxide formation, that does not require stabilization of ethylene and is preferentially formed via electron-deficient oxygen species. This is illustrated by the following typical homogeneous epoxidation reaction:

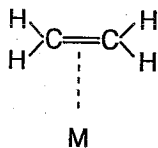


In reaction scheme eq.8 the proton is the catalyst that intermediates oxygen insertion from acetic peroxide into ethylene. Epoxidation occurs via intermediate formation of the electron deficient species II.

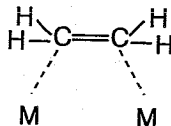
Also epoxide formation may occur upon reaction of ethylene with MnO^{3+} stabilized in a porphyrin¹⁸ or a TiO^+ species as present in Ti_2O_3 ¹⁹. Again illustrating the need for electron deficient oxygen.

Two factors contribute to the uniqueness of Ag. On Ag the CH bond will not be readily activated, whereas on the transition metal with a partially filled d-valence electron band CH bond activation will readily occur. In addition at high surface coverage the oxygen-metal bond energy has weakened, so that the weakly exothermic epoxidation reaction can occur.

Ethylene when adsorbed to a transition metal surface can have the π or di- σ adsorbed state:



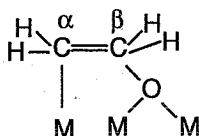
π adsorbed ethylene



di- σ adsorbed ethylene

di- σ adsorbed ethylene occurs preferentially on metals with spatially extended d-valence orbitals, as Pd or Pt.

The intermediate III²⁰



intermediate III,
metallocycle

can be considered the surface analogue of intermediate I. β CH cleavage and subsequent hydrogen addition to the C_α atom will produce the aldehyde. This appears to be the preferred alternative next to fragmentation on transition metals. In case no hydrogen activation occurs intermediate III could in principle give epoxide formation by formation of a $C^\alpha-O$ bond.

Formation of a metalocycle as intermediate III has been proposed to occur from adsorption of alcohols to transition surfaces^{10,17}. On Rh its decomposition gives CH_4 and CO. Aldehydes, however have been shown to be $CO \eta_2$ adsorbed. Their

decomposition leads to surface carbonaceous residues. On Ag dehydrogenation of the t-butyl alcohol, promoted by adsorbed oxygen has also been shown to give the epoxide. In this case a metallocycle as intermediate III could also be proposed. Epoxide formation is the preferred reaction path because of the absence of activated CH bonds.

Similarly coadsorbed on Ag norbornadiene and isobutylene have been shown to give the epoxide by reaction with atomically adsorbed oxygen¹¹.

On Ag the low reactivity with respect to CH activation may also result in interesting condensation reactions. Condensation of acetylene has been shown to give benzene.

Condensation of butadiene with surface atom oxygen on Ag has been shown to give ring closure and furfuryl formation²¹.

When ethylene adsorbs to a group VIII noble metal, its CH bonds become rapidly activated. This reaction has been extensively investigated with Surface Science techniques. Dehydrogenation of ethylene on the least reactive noble metals as Pd or Pt, may lead to adsorbed vinyl intermediates and will produce acetylene. On clean surfaces and in the absence of hydrogen adsorbed acetylene decomposes further to surface carbidic species.

Clearly in the presence of adsorbed oxygen these highly reactive species will lead to total combustion. Only when a surface is deactivated by the presence of coadsorbed intermediates one may expect that a reactive species as a vinyl species remains stable. Interesting examples by vinyl containing organic metallic complexes are known.

4. Summary

Surfaces, mainly metallic during oxidation catalysis, may become more reactive due to coadsorbed oxygen atoms. Especially the OH or CH bonds may react with basic oxygen atoms to initiate adsorbate activation with formation of OH_{ad} . However also the reactivity of molecules as CH_4 or NH_3 may be enhanced, because of cleavage of the CH or NH bond with formation of surface hydroxyls. These are important initiation steps in partial oxidation of CH_4 and NO production. The most important selective oxidation reactions catalysed by silver are ethylene epoxidation and methanol oxidation. Cu is a selective oxidation catalyst for the oxidation of propylene to acrolein.

Whereas oxygen adsorbed to Cu is nucleophilic, oxygen adsorbed to Ag can be electrophilic. On transition metals insertion reaction of olefins with atomically adsorbed oxygen leads to aldehydes or ketones.

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