Formation of surface-peroxocompounds

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SURFACE-PEROXOCOMPOUNDS

PROEFSCHRIFT

DOOR

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DIT PROEFSCHRIFT IS GOEDGEKEURD DOOR DE PROMOTOR
PROF. DR. G.C.A. SCHUIT

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GENERAL INTRODUCTION

The catalytic oxidation of aromatics and olefins is the
base of certain important chemical processes. Examples
are:

 - The preparation of phtalic-anhydride from naphta-
   lene.
 - The preparation of maleic-anhydride from benzene.
 - The oxydehydrogenation of butene by which butadiene
   is formed.
 - The simultaneous oxidation and ammoniation of pro-
   pene by which acrylonitrile is formed.

That these are indeed important processes will be evi-
dent from table 1, quoted from "Hydrocarbon Processing"
(1) in which the yearproduction of these products in
the U.S. is given.

table 1

Product	Productions in millions of kg				% petro-chemical
	Actual		Estimated		
	1964	1965	1966	1967	
P.Z.A	255	275	305	340	55
M.Z.A	54	59	67	76	30
Butadiene	1120	1220	1320	1400	100
Acrylonitrile	270	350	420	500	100

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The catalysts that are used for these oxidation reactions are inorganic oxides such as:

- transition metaloxides (V_2O_5, MoO_3)
- oxides of metals with a filled d shell (SnO_2, ZnO)
- or combinations of both types (Bi_2O_3/MoO_3)

The catalysts have a double function.
- Firstly, the acceleration of the oxidation reactions, and consequently conversion at lower temperatures.
- Secondly, the improvement of the selectivity.

For instance: At the oxydehydrogenation of butene to butadiene two reactions occur:

   i.   The total oxidation of butene

$$C_4H_8 + 6\ O_2 \rightarrow 4\ CO_2 + 4\ H_2O$$
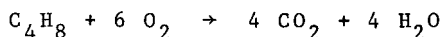
  ii.   The formation of butadiene

$$C_4H_8 + \tfrac{1}{2}\ O_2 \rightarrow C_4H_6 + H_2O$$
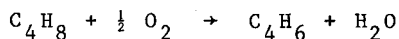
A good catalyst must lower the reactiontemperature thereby diminishing the total oxidation, and promote the selectivity for the butadiene formation. That lowering of the reactiontemperature alone is not sufficient can be seen from the following examples.
When MnO_2 is used as catalyst, an almost complete conversion of the butene occurs already at $250^{\circ}C$ but only a few percents of butadiene are formed. So MnO_2 is an active but not a selective catalyst.
However when Fe_2O_3 is used as a catalyst, a complete conversion of the butene does not occur below $350^{\circ}C$ but even then about 60 percents of butadiene are formed. So Fe_2O_3 is less active but much more selective than MnO_2.

To explain these differences in selectivity and activity it is often supposed that the oxydehydrogenation of

butene takes place according to the following reaction-
diagram (figure 1) (2) (3).
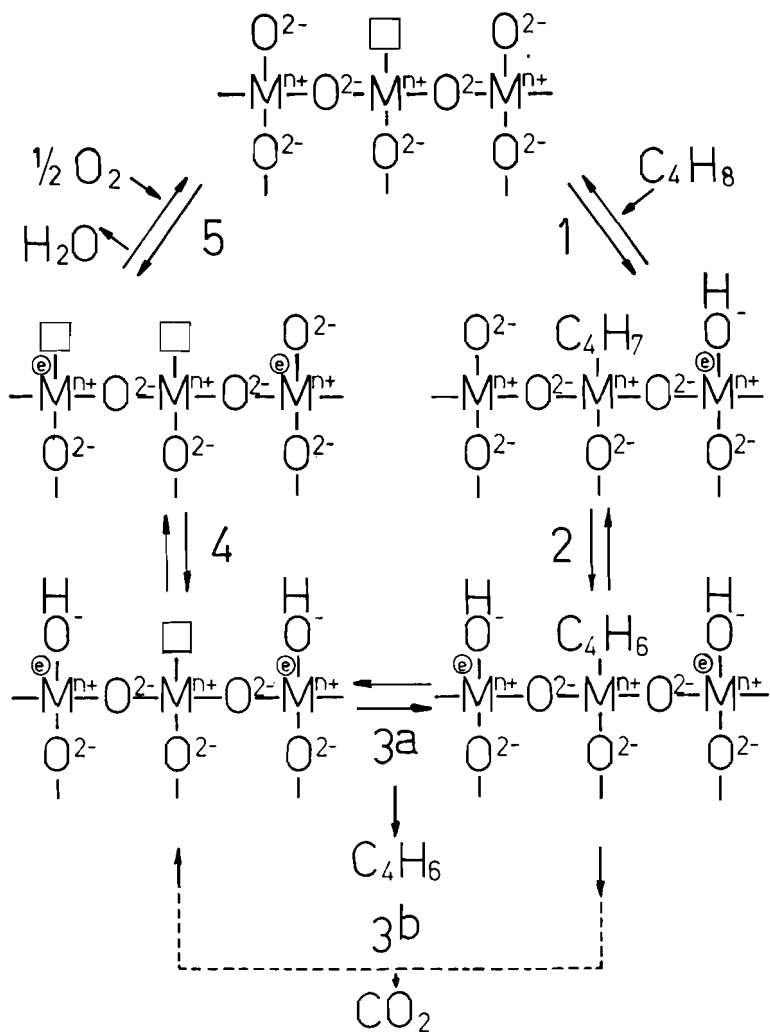
figure 1   Reactiondiagram of the oxydehydrogenation of
            butene.

In this reactiondiagram the following steps can be dis-
tinguished.

1. The butene molecule donates a hydrogen atom to an
   oxygen ion from the metaloxide lattice, forming an
   allylic radical that is bonded on an anion vacancy
   at the surface of the metaloxide.

2. The allylic radical donates a second hydrogen atom
   to the metaloxide, by which a butadiene molecule is
   formed.

3. Now there are two possibilities:
   a. The butadiene molecule desorps from the surface
      or,
   b. More hydrogen atoms are donated to the oxygen
      ions of the metaloxide lattice forming higher
      oxidationproducts and finally carbondioxide.

   In both cases the result is a partly reduced me-
   taloxide with hydroxylgroups on the surface.

4. A water molecule is formed from two hydroxylgroups
   on the surface. This watermolecule desorps from the
   surface.

5. The partly reduced metaloxide is reoxidated by oxy-
   gen from the gasphase thus restoring the original
   situation.

There are several arguments for the correctness of this
reactiondiagram. One of the strongest arguments is,
that even without oxygen in the gasphase, oxidation of
butene occurs. Therefore the only function of the oxygen
is to reoxidize the metaloxide as indicated as step 5 in
the reactiondiagram. This metaloxide is partly reduced
by accepting hydrogen atoms from the olefin, followed

by the dehydroxylation. Therefore the differences in reactivity between the metaloxides used as catalyst can be explained by the different reducebilities of these metaloxides.

From experiments by Verheijen (4) it is evident that there is relation between the activity and the reducebility of the metaloxide. As a measure for the reducebility of the metaloxide he applied the change in enthalpy of the reaction:

$$MeO_n \rightarrow MeO_{(n-1)} + \tfrac{1}{2} O_2 + \Delta H_{red}.$$
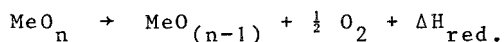
and as a measure for the reactivity the temperature that is necessary to oxidize 50% of the butene. He then finds the relation as shown in figure 2.
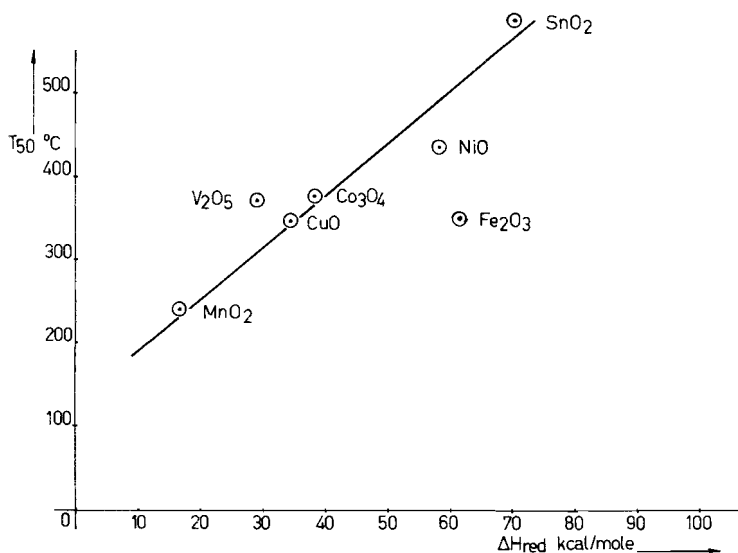
figure 2   Relation between the reducibility and the reactivity of some metaloxides.

The oxides with a small value of ΔH_{red}. (MnO_2, CuO) thus show a high activity. The principal reactionproducts are CO_2 and H_2O in this case, and therefore these metal-   **13**

oxides cannot be used for the butadiene formation. To
arrive this product one has to use metaloxides with a
value of ΔH_{red}, that is not too low, for example Fe_2O_3
and NiO. It is true that such oxides are less active
than MnO_2 and CuO but besides CO_2 and H_2O a relatively
large amount of butadiene is now formed.

By using oxides with higher values of ΔH_{red} one should
expect a smaller activity. And indeed ZnO (ΔH_{red} =
83 kcal/mole). TiO_2 (ΔH_{red} = 69 kcal/mole) and SnO_2
(ΔH_{red} = 70 kcal/mole) show little activity at least if
no oxygen is present in the reactionmixture. If oxygen
is present however these oxides also show a strong
oxidation by which principally CO_2 and H_2O are formed.
A possible explaination for this effect is the forma-
tion of surface peroxocompounds when oxygen is brought
into contact with the slightly reduced metaloxide (step
5 of the reactiondiagram) which peroxocompounds may be
expected to possess a strong oxidating action. Indeed
Kokes (5) and Khazansky (6) could observe the formation
of peroxocompounds on ZnO and TiO_2 respectively, by
EPR. Measurements performed by van Hooff and Cornaz (7)
at the Technological University of Eindhoven agree
herewith, but show at the same time that the system is
more complicated then was proposed by Kokes and Kha-
zansky.

Therefore we started an investigation, the results of
which are given in this thesis.

THE PRINCIPLES OF THE MEASUREMENTS

II.1.   Introduction

We want to investigate what happens at the surface of a
slightly reduced metaloxide when it is brought into
contact with oxygen.
In particular we want to have an answer on the question
if oxide (O^{2-}) is the only oxygencompound that is form-
ed or that other oxygencompounds are also formed. This
could take place according to the following equations:

$$1. \quad O_2(g) \quad\quad \rightarrow \quad O_2(ads) \quad ^*$$

$$2. \quad O_2(ads) + e \quad \rightarrow \quad O_2^-(ads) \quad ^*$$

$$3. \quad O_2^-(ads) + e \quad \rightarrow \quad O_2^{2-}(ads)$$

$$4. \quad O_2^{2-}(ads) + e \quad \rightarrow \quad O^{2-}(ads) + O^-(ads)^*$$

$$5. \quad O^-(ads) + e \quad \rightarrow \quad O^{2-}(ads)$$
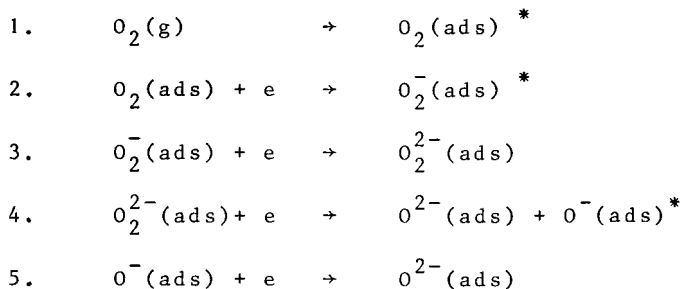
With the totalreaction:

$$6. \quad O_2(g) \quad + 4e \quad \rightarrow \quad 2\ O^{2-}(ads)$$
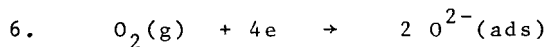
Four methods to give a decisive answer are cited in
literature.

1. The study of the photoadsorption and desorption of
   oxygen by metaloxides. (8) (9)

2. The study of the exchangereaction

$$^{16}O_2 + {}^{18}O_2 \quad \rightleftharpoons \quad 2 \ ^{16}O \ ^{18}O \qquad (10) \ (11)$$
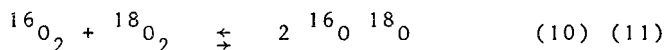
3. Measurement of the Infra Red absorption of compounds adsorbed at the surface.

4. Electron-Paramagnetic-Resonance absorption measurements. (12) (13)

This last method is considered especially in the present case. Three of the oxygencompounds mentioned above, indicated by an asterisk, are paramagnetic and since it is possible to detect very small amounts of these species by EPR spectrometry, this method was selected. Moreover EPR data are so specific that identification of the paramagnetic species is possible. To illustrate this fact the principles of the EPR method will be discussed in the next paragraph.

II.2.   Electron-Paramagnetic-Resonance-Spectrometry

The theory of this form of spectrometry is discussed in detail in many books and articles. (14)(15)(16)(17). Therefore it will suffice to describe only those principles, that are important for our investigation.

Remark.   The following notation will be used.
    - We shall place a dash under every symbol which stands for a vector.
    - We shall place a circumflex over every symbol which stands for an operator.

A paramagnetic species possesses a ground state that is at least twofold spindegenerated (Kramers doublet).

This degeneration is removed by an external magnetic field. The unpaired electrons present in the paramagnetic species cause a magnetic moment that can interact with the external magnetic field. This magnetic moment $\hat{\underline{\mu}}$ is the sum of the magnetic spinmoment $\hat{\underline{\mu}}_s$ and the magnetic orbitalmoment $\hat{\underline{\mu}}_1$.

In formula:

$$\hat{\underline{\mu}} = \hat{\underline{\mu}}_s + \hat{\underline{\mu}}_1$$

With:
$$\hat{\underline{\mu}}_s = -g_e\beta\hat{\underline{S}}$$

$$\hat{\underline{\mu}}_1 = -\beta\hat{\underline{L}}$$

In which: g_e = the spectroscopic splitting factor for a free electron with the value 2,0023.

β = the Bohrmagneton.

The interaction with the external magnetic field takes the form:

$$-\hat{\underline{\mu}}.\underline{H} = -(\hat{\underline{\mu}}_s + \hat{\underline{\mu}}_1).\underline{H} = \beta\underline{H}.(\hat{\underline{L}} + g_e\hat{\underline{S}})$$

The spinoperator $\hat{\underline{S}}$ in this equation is isotropic and therefore the interaction of the magnetic spinmoment with the external magnetic field is always independent of the orientation of this magnetic field. On the other hand the orbital operator $\hat{\underline{L}}$ is usually anisotropic as a result of the crystal field and the spin-orbit coupling. Therefore the interaction of magnetic orbitalmoment and external magnetic field will depend on the direction of the external magnetic field. Consequently the calculation of the total magnetic interaction is usually a complicated operation. However, Abragam and Pryce (18) show that this interaction can also be described via the introduction of a spinhamiltonian. In applying the spinhamiltonian we take no account of the interaction with the magnetic orbitalmoment but intro-

duce an anisotropic coupling between the magnetic spin-
moment and the external magnetic field of the following
form:

$$\hat{\mathcal{H}}_{spin} = \beta \underline{H} . G . \hat{\underline{S}}$$

in which G is the so-called g-tensor. The axes of this
g-tensor should coincide with the symmetry axes of the
system. Therefore the spinhamiltonian of a system with
rhombic symmetry has the following form:

$$\hat{\mathcal{H}}_{spin} = \beta g_x H_x . \hat{S}_x + \beta g_y H_y . \hat{S}_y + \beta g_z H_z . \hat{S}_z$$

and of a system with axial symmetry:

$$\hat{\mathcal{H}}_{spin} = \beta g_{/\!/} H_z . \hat{S}_z + \beta g_{\perp} (H_x . \hat{S}_x + H_y . \hat{S}_y)$$

For an axially symmetric system with a spindoublet as
groundstate an external magnetic field splits this
doublet into two new states. The difference in energy
between these states will depend on the orientation of
the external magnetic field. If the magnetic field is
in the z-direction the difference in energy will be:

$$\Delta E = g_{/\!/} \beta H$$

and when the direction is perpendicular to the z-axis
the difference in energy will be:

$$\Delta E = g_{\perp} \beta H$$

We may now induce transitions between these two states
by applying an oscillating magnetic field in a direc-
tion perpendicular to the permanent magnetic field. The
resonance condition for such a transition is:

$$h\nu = \Delta E = g \beta H$$

Using an external magnetic field with a field strength
of about 3500 Oersted and a g-value of about 2 this re-
sults in a frequency of about 10 GHz. In practice it is
more convenient to vary the magnetic field and maintain
the frequency of the microwave source constant.
In accordance herewith the spectrum is usually present-
ed as a relation between absorption and magnetic field-
strength for a given microwave frequency.
For instance, an axially symmetric system placed in a
magnetic field in the z-direction shows absorption if
the magnetic fieldstrength satisfies the condition:

$$h\nu = g_{\parallel} \beta H_{\parallel}$$

Is the direction of the magnetic field perpendicular to
the z-axis of the system the resonance condition be-
comes:

$$h\nu = g_{\perp} \beta H_{\perp}$$

By determining $H_{\parallel}$ and $H_{\perp}$ experimentally it is possible
to calculate the values of $g_{\parallel}$ and $g_{\perp}$ from which we can
obtain information about the crystalfield and the spin-
orbit coupling in the system.
Often the system does not have all its paramagnetic
particles similarly oriented with respect to the ex-
ternal magnetic field, as for instance in the case of a
polycrystalline material in which the crystallines are
randomly oriented. In that case absorption does not oc-
cur at one certain fieldstrength but in a range of
fieldstrengths. For instance the line shape of the EPR
absorption spectrum of a polycrystalline sample with
axial symmetry is as shown in figure 3. Nevertheless it
remains possible to determine the values of $H_{\parallel}$ and $H_{\perp}$
from these spectra as shown by Kneubühl. (19)
Summarizing we can say that it is possible to determine
the g-values of a paramagnetic compound from the line-

shape and position of its EPR spectrum. Often these g-
values are characteristic for a certain compound and
therefore it becomes possible to detect different co-
existent paramagnetic species.
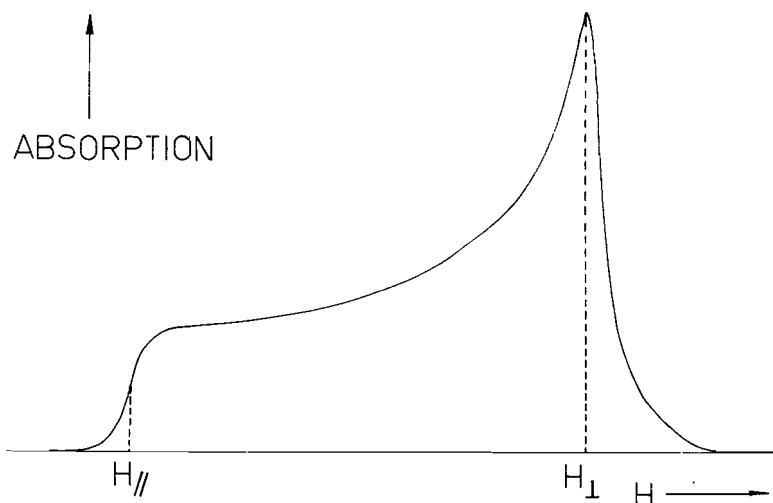
figure 3   EPR absorption spectrum of a polycrystalline
            sample with axial symmetry.

II.3.   Performance of the E.P.R. Measurements

In the previous paragraph we mentioned already that in
EPR spectrometry the sample is placed in a magnetic
field and is exposed to monochromatic radiation with a
fixed frequency. The EPR spectrum is then obtained by
measuring the absorption of this radiation as a func-
tion of the fieldstrength of the magnetic field. The
frequency ranges usually applied (X-band $\approx$ 10 GHz; Q-
band $\approx$ 36 GHz) preclude the use of detectiontechniques
known from other forms of spectrometry (Infra-Red,Visi-
ble and Ultra-Violet spectrometry). In this case we use
a so-called microwavebridge shown in the diagram of

figure 4.

```
                              ELECTRONIC
                               COUNTER

                                       TO AMPLIFIER

KLYSTRON              CRYSTAL DETECTOR

                 HYBRID T

   VARIABLE
   ATTENUATOR

                              CONNECTING
                              WAVEGUIDE
     FIELD
   MODULATOR

     MAGNET

  POWER SUPPLY

                                        CAVITY
                                        PROBE

                              MAGNET
```
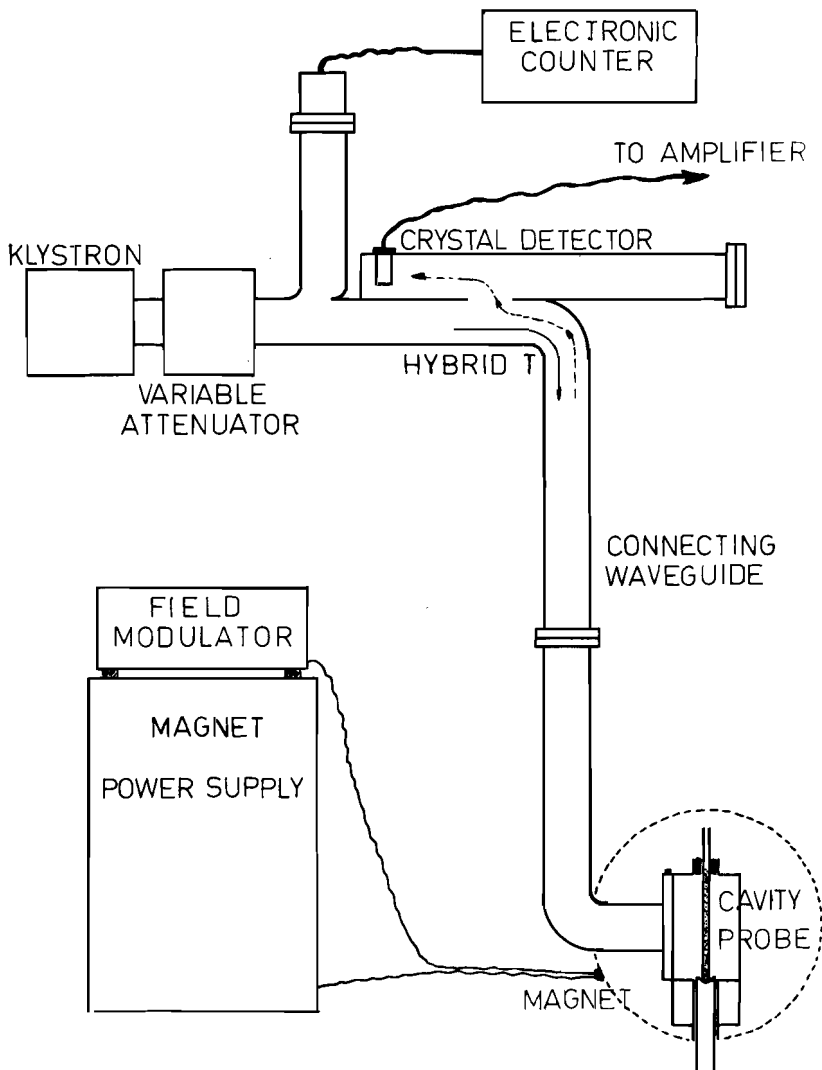
figure 4   Diagram of a microwavebridge.

The microwave radiation is produced by a klystron valve
and the microwaves are guided via a variable attenuator
to a cavity-resonator. The cavity serves to concentrate
the microwave radiation on to the specimen which is in-   **21**

serted through a hole in its centre. The frequency of
the radiation is so adjusted that it agrees with the
resonancefrequency of the cavity.In that case no radia-
tion is reflected and no power will then be fed on to
the crystal-detector. By varying the fieldstrength of
the magnetic field it becomes possible for the specimen
to absorb radiation. The resonance condition is then no
longer fullfilled and a part of the radiation will be
reflected. This radiation is fed on to the crystal de-
tector generating a signal that can be amplified and
registrated.The crystal detector used, has a high noise
level at low frequencies. Consequently we obtain an un-
favourable signal to noise ratio. To improve the signal
to noise ratio the magnetic field is modulated by an
oscillating field with a frequency of 100 kHz and a
small amplitude. The output of the crystal detector
then contains a 100 kHz component which is fed to a
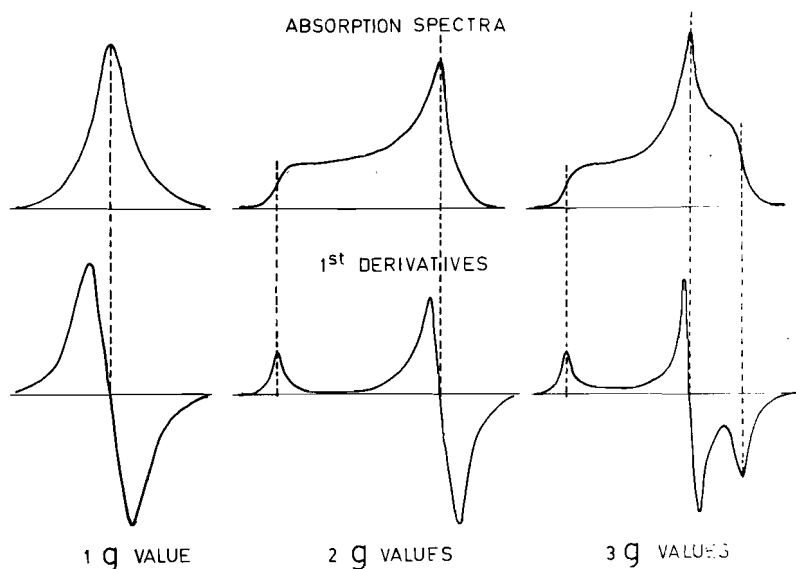
figure 5   EPR absorption spectra and first derivative
            variations of polycrystalline samples with
            1, 2 and 3 g-values.

narrow-band 100 kHz amplifier and from there to a
phase-sensitive detector. In this detector the ampli-
fied signal from the crystal is mixed with a reference
signal obtained from the 100 kHz oscillator in such a
phase that only the signal component arising from ab-
sorption within the specimen itself is passed on to the
d.c. amplifier. This method of phase sensitive detec-
tion is commonly used in a large variety of other
spectroscopic applications and has the great advantage
that the noise component present in the final signal
only depends on the band width of the recording stage.
Another result of this method of detection is the first
derivative variation that is obtained instead of the
absorption signal.Figure 5 shows us typical EPR spectra
of polycrystalline powders with 1,2 and 3g-values.

II.4.   Intrumentation for the EPR Measurements

For measuring the EPR spectra we used a VARIAN EPR
spectrometer type V 4500 A together with a X-band ($\nu \approx$
10 GHz) or a Q-band ($\nu \approx$ 36 GHz) microwavebridge. To
modulate the magnetic field a 100 kHz fieldmodulating,
unit was used.
Most of the measurements were done with the X-band
microwavebridge in combination with a multipurpose
cavity. In this cavity the variable temperature acces-
sory was mounted by which it is possible to measure in
the region of about $-160^{\circ}C$ to $+300^{\circ}C$.The maximum dimen-
sion of a specimen that can be measured in this way is
a diameter of 4 mm outerside.
A Hewlett Packard microwave frequency converter type
2590 B in combination with the electronic counter type
5245L and a plug-in unit type 5253B was used for micro-
wave frequency measurements.
The magnetic field-strength could be measured with an
AEG Kernresonanz magnetfeldmesser type 11/5045/6.   **23**

MEASUREMENTS WITH TITANIUMDIOXIDE (ANATASE)

III.1.   Preparation of titaniumdioxide (Anatase)

Two   modifications of   titaniumdioxide   are known;   the
rutile- and the   anatase modification.   From these, the
rutile modification   is   the   most   stable one and   the
anatase modification only exist below 600°C. Above this
temperature anatase is transformed in rutile.
From work of Stone and   Khazansky it   is known that the
formation of surface-peroxocompounds   takes   place much
easier   on   anatase   than on rutile;   actually this   is
confirmed by our measurements.   This   difference in ac-
tivity can be ascribed   in first instance   to differen-
ces in surface area.   By following   a   special prepara-
tion method   is it possible   to prepare titaniumdioxide
with the   anatase modification   and   a specific surface
area of about 40-60 m^2/g whereas titaniumdioxide rutile
samples usually possess smaller surface areas.   Next to
a large surface area it is important that the titanium-
dioxide is very pure.   Small amounts of impurities, for
instance of iron, vanadium or manganese can disturb the
EPR measurements very strongly.

Since titaniumdioxide   that   satisfied   these   require-
ments was not obtainable,   it   was prepared in the fol-
lowing way:

$TiCl_4$ (Riedel-de Haen 140-12)   was   distilled in a dry
nitrogen   current,   from   a   vessel filled with   copper
turnings.   After repeating this procedure twice the re-
24   sultant purified   compound   (b.p. 135.7^{o}C) was added to

water at 0°C. Subsequent to a hydrolysis with ammonia
the resulting precipitate was filtered, washed until
no Cl⁻ could be observed in the wash water and dried
at 120°C. The product was white and X-ray diffraction
data showed that the product possesses the anatase
crystal structure. The specific surface area was 46.3
m^2/g.

III.2. Pretreatment of the $TiO_2(A)$ samples

The pretreatment of the $TiO_2(A)$ samples is intended to
obtain a slight reduction; subsequent reoxidation then
may form surface-peroxocompounds. Following the reac-
tion diagram as described in chapter 1 the reduction
should take place by a reaction with 1-butene. Indeed
this is possible, but the same result can be obtained
by pumping off the titaniumdioxide at a pressure below
10^{-3} Torr and a temperature of 500°C. Because of its
simplicity the last manner of reduction was chosen.
Evidently it is advantageous if reduction and reoxida-
tion of the sample and subsequent EPR measurements
could be observed using the same sample tube.
In the previous chapter it has already been mentioned
that the maximum outside diameter of the sample tube
that can be inserted into the variable temperature
dewar is 4mm. Therefore the maximum inner diameter of
this tube is about 3mm and this space is too narrow for
effective pumping of the metaloxide powder. To meet
these difficulties we constructed the apparatus shown
in the figures 6 and 7.
The sample tube that can be inserted into the variable
temperature dewar is indicated by A and B designates a
bulb in which the sample can be heated and evacuated.
By turning over the sample can be carried from B to A.
An amount of gas can be stored in the bulk C. This gas
can be brought into contact with the sample by opening
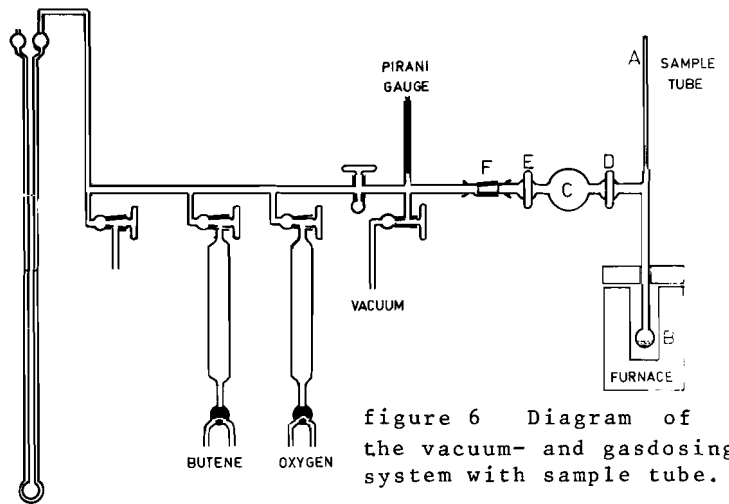
figure 6   Diagram   of
the vacuum- and gasdosing
system with sample tube.
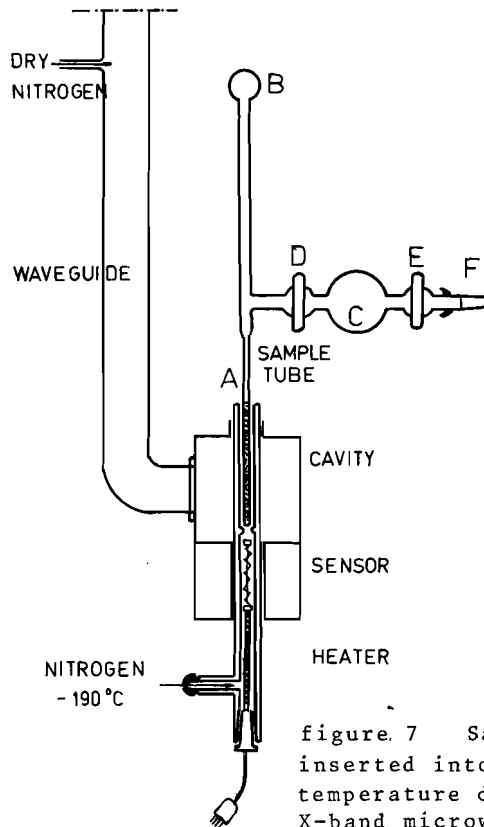
figure. 7   Sample   tube
inserted into the variable
temperature dewar of the
X-band microwavebridge.

tap D. Tap E and ground joint F serve for the coupling
to the vacuum- and the gasdosing system.
The following procedure was standard:
About 500 mg of TiO_2(A) are brought into bulb B through
tube A that is not yet closed. Tube A is then closed
by melting after which the sample tube is connected to
the vacuum- and the gasdosing system (figure 6). The
pressure is reduced below 10^{-3} Torr and the sample is
heated at 500°C during 2 hours. Tap D is then closed
and the sample is cooled to roomtemperature. Vessel C
is then filled with gas that can be brought into con-
tact with the sample at a later stage. After closing
tap E the sample tube is disjointed from the vacuum-
and gasdosing apparatus and after turning over brought
in the variable temperature dewar of the EPR spectro-
meter (figure 7).

The EPR spectra of the samples pretreated in this way
are shown in figure 8.
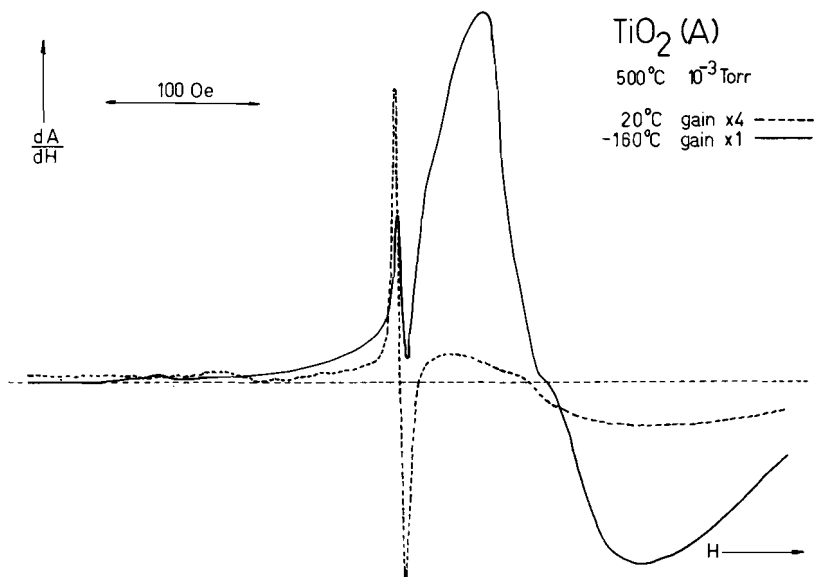
figure 8   EPR spectra of pretreated TiO_2(A) at dif-
            ferent temperatures.

at $20^{\circ}C$ the EPR spectrum shows a sharp symmetrical signal with g = 2.0021. At $-150^{\circ}C$ also a broad asymmetrical signal with g_{av} = 1.96 becomes visible. It is evident that the titaniumdioxide acquires weak semiconducting properties.

These facts can be explained in the following way:

By heating the TiO_2 at reduced pressures molecular oxygen is formed out of the oxygen ions according to the following equation.

$$2 \; O^{2-} \quad \rightarrow \quad O_2(g) + 4 \; e$$
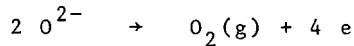
There are two possibilities for the position of the electrons in the lattice.

    i.   An electron is taken up in an empty 3d-orbital of a Ti^{4+}-ion, which hereby changes into a Ti^{3+}-ion.

   ii.   An electron is located at an oxygenvacancy of the lattice, forming a socalled F-centre.

The Ti^{3+}-ion as well as the F-centre are paramagnetic and could therefore give rise to EPR absorption. It is known that EPR signals derived from Ti^{3+} can only be observed at low temperatures because of spin-lattice relaxation. The g-values mentioned in literature vary from 1.95 to 1.97.

On the other hand F-centres give rise to sharp EPR signals already at room temperature with g-values only slightly different from g_e = 2.0023. It therefore is obvious that the g = 2.0021 signal can be ascribed to an F-centre and the low-temperature g = 1.96 signal to a Ti^{3+}-ion. The conduction can be explained by electronjumps from one site to another, for instance from Ti^{3+} to Ti^{4+}, typical for n-type semiconductivity. The jump probability is enhanced by an increase of the Ti^{3+} concentration.

28 Summarizing we can say that F-centres and Ti^{3+}-centres

are formed in the lattice by a slight reduction of the TiO_2(A).

III.3. Reaction of slightly reduced TiO_2(A) with oxygen

By opening tap D of the sample tube the pretreated TiO_2 can be brought into contact· with the gas present in bulb C, and any changes can be registrated by EPR measurements. When bulb C is filled with oxygen at a pressure of about 10 Torr the following changes can be observed after opening of tap D.

  i. The EPR spectra of the Ti^{3+}- and F-centres des-
      cribed above vanish rapidly and almost complete-
      ly.

 ii. The conductance of the sample diminishes strong-
      ly.

iii. A new EPR signal appears with g_{av} = 2.010 (see
      figure 9).
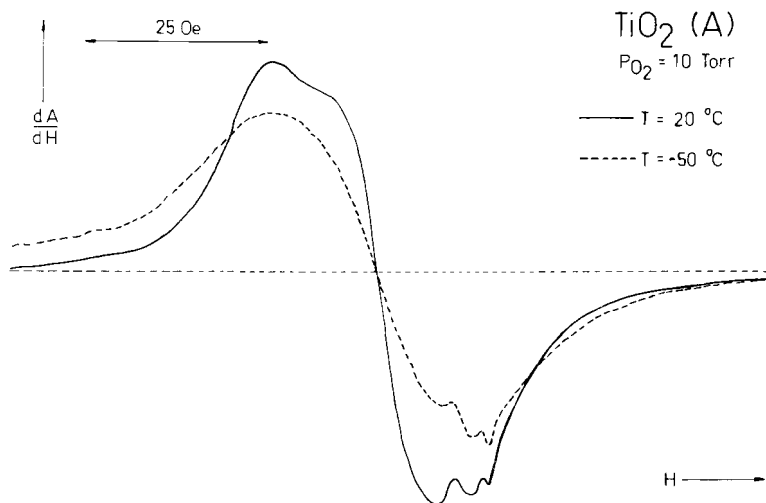
figure 9   EPR spectra of TiO_2(A) after addition of O_2,
           showing the increasing line broadening at
           decreasing temperatures.

Obviously the oxygen reacts with the electrons of the Ti^{3+}- and F-centres, forming new paramagnetical centra. The new EPR signal cannot be ascribed to molecular oxygen. A "forbidden transition" with g $\approx$ 2 is possible for oxygen but if the observed EPR signal is as signed hereto, then also transitions at higher magnetic fields corresponding to allowed transitions should be observed. No such EPR absorption were however observed. Therefore the signal must be caused by other paramagnetical oxygen compounds such as O_2^- and O^-.

The interpretation of the EPR signal is hindered by line broadening, increasing with lowering temperature. This line broadening is probably caused by an excess of molecular oxygen. Part of this oxygen is physically adsorbed at the titaniumdioxide surface. The physically adsorbed oxygenmolecules cause local, strongly varying, magnetic fields at the surface that in their turn cause the line broadening. At lower temperatures the amount of physically adsorbed oxygen increases and therefore also the line broadening increases. The heat of adsorption of this physically adsorbed oxygen is only small and therefore it is possible to remove it from the surface, whereas the chemisorbed oxygen remains adsorbed to the surface. Reducing the pressure below 10^{-1} Torr at $20^{\circ}C$ is sufficient to remove almost all physically adsorbed O_2, and an EPR spectrum recorded after outgassing indeed shows no line broadening (see figure 10).

The presence of 4 peaks indicates that this EPR spectrum consists of at least two different EPR signals. Measurements with different microwave power (figure 11) and at different temperatures (figure 12) give an indication that the three peaks at the low fieldstrength region form one signal and that the peak at the right belongs to another signal. The peak at the high field-

strength side is easily saturated while the other three are not.
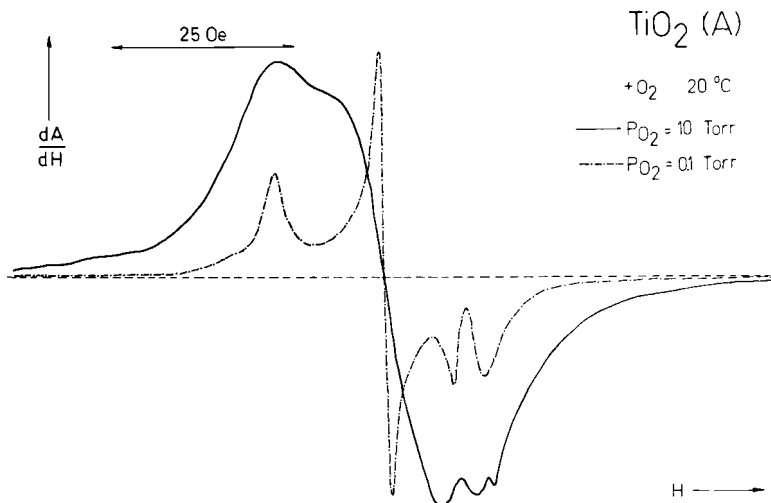
figure 10   EPR spectra of O_2 on TiO_2(A) before and after removing of physically adsorbed oxygen.
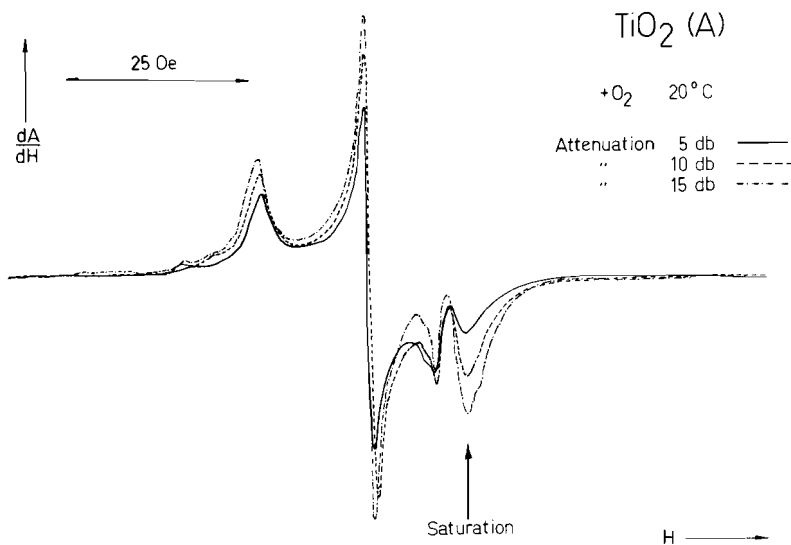
figure 11   EPR spectra of O_2 on TiO_2(A) obtained with different microwavepowers.

The explanation of the differences in saturation is the
following:
Increasing of the microwave power (or decreasing the
attenuation) in general leads to a proportional in-
crease of the absorption. If however the relaxation
mechanism of the system is slow with respect to the
vibration time of the microwave radiation saturation
occurs. In the latter case the relative increase of the
absorption is less than the increase of the power of
the radiation.

To illustrate the differences in saturation the three
spectra in figure 11 are drawn in such a way that the
left part of the spectrum remains almost equal in
signal intensity i.e. the signal strength is divided by
the power. The different sizes of the right part now
show that indeed saturation occurs in this region. A
similar conclusion is arrived by varying the tempera-
ture (see figure 12). Lowering of temperature causes a
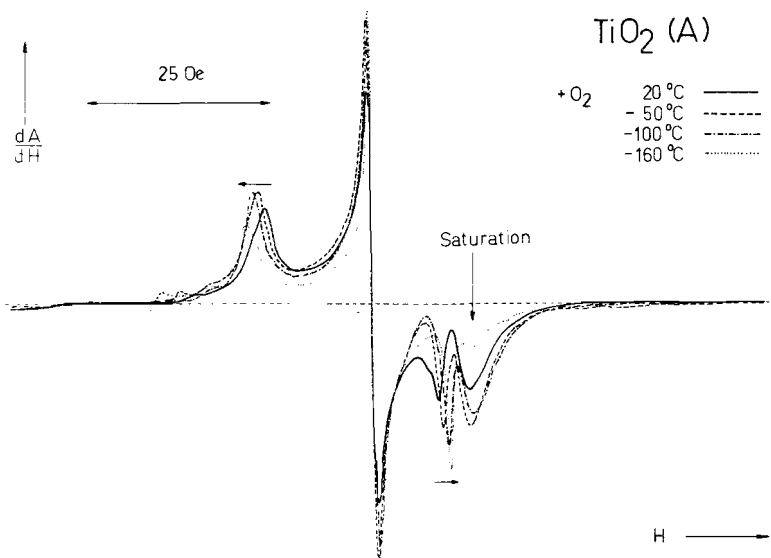
TiO_2 (A)

figure 12   EPR spectra of O_2 on TiO_2(A) obtained at
             different temperatures.

retardation of the relaxation mechanism favouring saturation.

These experiments indicate that the EPR spectrum indeed consists of two different signals. They do not however allow to completely clarify the form of these signals. The signal belonging to the three left peaks leaves the least doubt. This signal shows the form of a 3g-value signal as represented in figure 5. It is more difficult to detect the correct form of the signal belonging to the right peak, since it is partly overlapped by the former signal. As far as can be concluded from the figures 11 and 12 this signal has the symmetrical form of a 1g-value signal. If the two peaks at the left side are considered to be unperturbed by the 1g-signal the form of the 3g-signal can be deduced. The 1g-signal then can be drawn by subtraction. Figure 13 shows how on this assumption the EPR spectrum can be built up from the different EPR signals.
We distinguish:

a. The signal A; a 1g-value signal with g = 2.0028

b. The signal B; a 3g-value signal with g_1 = 2.019
g_2 = 2.010 and g_3 = 2.004 at 20°C

c. The signal C; a 1g-value signal with g = 2.0006

   This signal C is caused by the quartz-glass sample tube and occurs in all spectra.

This interpretation is in keeping with the EPR spectrum obtained with the Q band microwave bridge (figure 14). This spectrum can also be built up from the three above mentioned signals.

Summarizing we can say that when oxygen is brought in contact with slightly reduced TiO_2(A) a reaction takes

TiO₂(A)

25 Oe

$\frac{dA}{dH}$

$P_{O_2} = 10 \rightarrow 0.1$ Torr

$T = 20\ °C$

observed
EPR spectrum

H ⟶

signal A
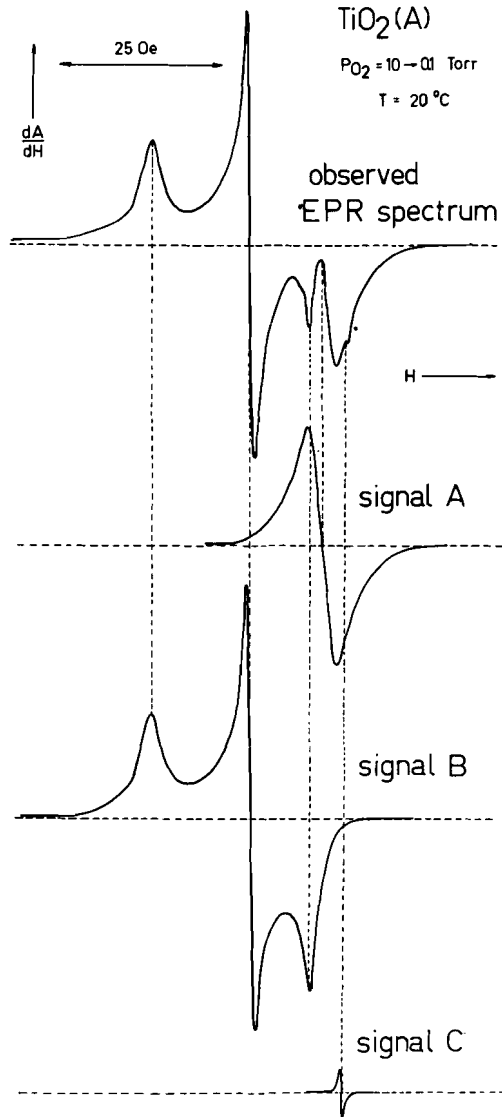
signal B

signal C

figure 13   Observed EPR spectrum of O_2 on TiO_2(A) and
the three EPR signals from which this spec-
trum can be built up.
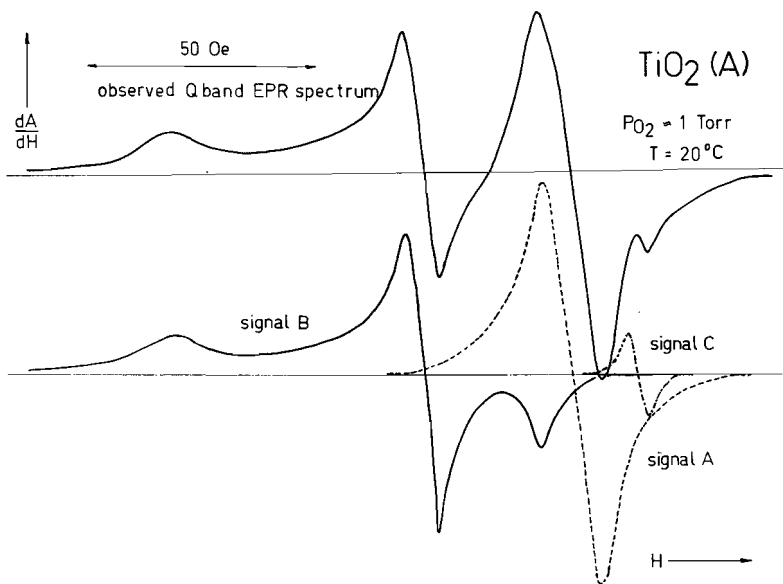
figure 14   Observed Q band EPR spectrum of O_2 on TiO_2(A)
            and the three EPR signals from which this
            spectrum can be built up.

place between the electrons of the Ti^{3+}- and F-centres
and the oxygenmolecules by which at least two new
paramagnetical compounds are formed. One of these com-
pounds gives rise to the 1g EPR signal A and the other
to the 3g EPR signal B.

III.4. Reaction of the chemisorbed oxygen with 1-butene

In the introduction we expresses an expectation that
peroxides on the surface should give rise to a strong
oxidizing action on hydrocarbons such as olefins. To
test this the bulb C of the sample tube was filled
with 1-butene at a pressure of about 20 Torr with the
help of the gasdosing apparatus. If by opening of tap
D this 1-butene was brought into contact with a tita-   **35**

niumdioxide sample on which oxygen is chemisorbed it
is observed that indeed a reaction occurs as shown by
a change in the EPR spectrum.
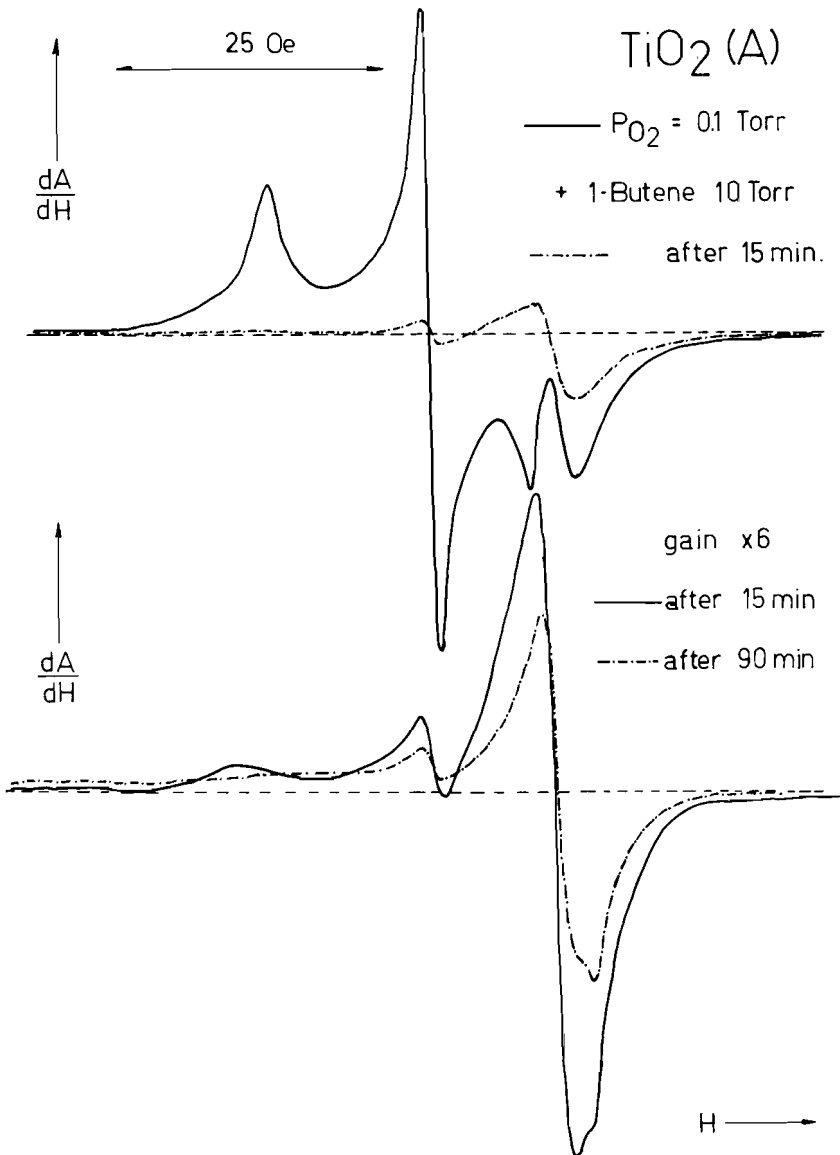
figure 15   Changes in the EPR spectrum of O_2 on TiO_2(A)
after addition of 1-butene.

Figure 15 shows the EPR spectra before and after the
addition of 1-butene at 20°C. It can be clearly seen
that the 3g-value signal (signal B of figure 13) rapid-
ly decreases and vanishes almost completely after a
reactiontime of about 90 minutes. At the same time
the signal A diminishes in intensity but at a rate
that is considerably lower. The oxygen compound respon-
sible for the signal B is therefore more active for
the oxidation of 1-butene. than is the oxygen compound
responsible for the signal A. In fact the activity of
B is so high that already a reaction occurs at room
temperature. The strong oxidizing action of the sur-
face peroxocompounds therefore appears justified by
these experiments. Another supposition that becomes
verified by these experiments is that the second EPR
signal might be a symmetrical 1g-value signal. The EPR
spectrum recorded 90 minutes after the addition of
1-butene shows besides a weak signal B a symmetrical
signal A. It is therefore proven that there are indeed
two surface oxygen compounds with the EPR properties
deducted before. However we do not know which oxygen
compounds cause these EPR signals. To give a decisive
answer to this question we performed experiments in
which slightly reduced $TiO_2(A)$ was brought into con-
tact with other gases then oxygen. The two following
paragraphs give the results obtained with NO and N_2O.

III.5. Reaction of slightly reduced $TiO_2(A)$
       with nitrogen monoxide

In the same manner as mentioned in paragraph III.3 for
oxygen, slightly reduced $TiO_2(A)$ can be brought into
contact with nitrogen monoxide.   **37**

For this particular case the changes observed are:

i. The EPR signals of the Ti^{3+}- and F-centres dis-
appear.

ii. The conductance diminishes strongly.

iii. A new EPR signal with g_{av} = 2.003 appears (see
figure 16).
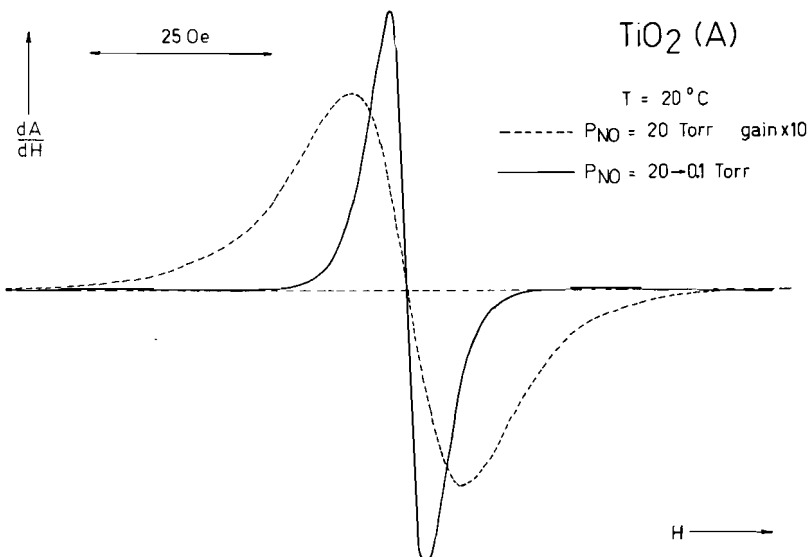
figure 16   EPR spectra of NO on TiO_2(A) at 20°C before
and after removal of the excess NO.

Thus NO can also react with the electrons of the Ti^{3+}-
and F-centres and form new paramagnetical centres. The
new EPR signal shows a strong line broadening that de-
creases if the excess of NO is pumped off. The re-
maining signal is a symmetrical 1g-value signal with
g = 2.0028, exactly the same value given by the A
signal observed after addition of oxygen.
The EPR spectrum recorded at -150°C shows another
signal (see figure 17). This is a broad and a symme-
trical signal that strongly decreases in intensity when
38 the excess NO is pumped off. Therefore this signal is
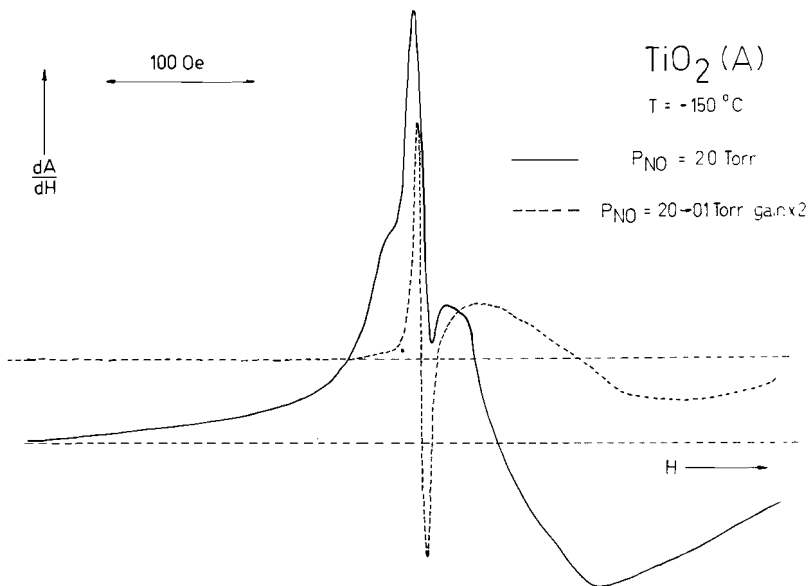
figure 17   EPR spectra of NO on TiO_2(A) at $-150^{\circ}C$ be-
             fore and after removal of.the excess NO.

caused by weakly adsorbed NO and not by chemisorbed NO
or a reaction product of NO.
Summarizing NO reacts with reduced TiO_2(A) but forms
only one paramagnetical compound giving rise to a sym-
metrical 1g-value EPR signal with g = 2.0028 similar to
the A signal also formed when oxygen is used. If after
the addition of NO and pumping off an excess of this
compound, oxygen is added the EPR spectrum does not
show any new signal. So under these circumstances O_2
cannot form paramagnetic compounds, its action being
limited to the line broadening accompanying physisorp-
tion.
Adding of 1-butene after the removal of excess of NO
causes only a small decrease of the EPR signal. Conse-
quently the paramagnetical compound that causes the
EPR signal reacts only very slowly with 1-butene in
good agreement with the observations from the oxygen
experiments.   **39**

III.6.   Reaction of slightly reduced TiO_2 (A)
with dinitrogen monoxide

Similar results as with NO are obtained after N_2O ad-
dition (figure 18). The EPR spectrum after the addi-
tion of this gas at a pressure of about 10 Torr does
not show any Ti^{3+}- and F signals but a symmetrical
1g-value signal with g = 2.0028, hence the same signal
as observed after addition of NO and also identical to
the A signal after addition of O_2. Again if the excess
of N_2O is pumped off and then oxygen added no change
in the EPR spectrum was recorded, but only line broade-
ning of the signal already present is observed.
Also the addition of 1-butene causes only very small
changes. In this case a little decrease of the EPR
signal can be observed.

TiO_2 (A)

T = 20 °C

P_{N_2O} = 15 Torr

25 Oe

$\dfrac{dA}{dH}$

H ——
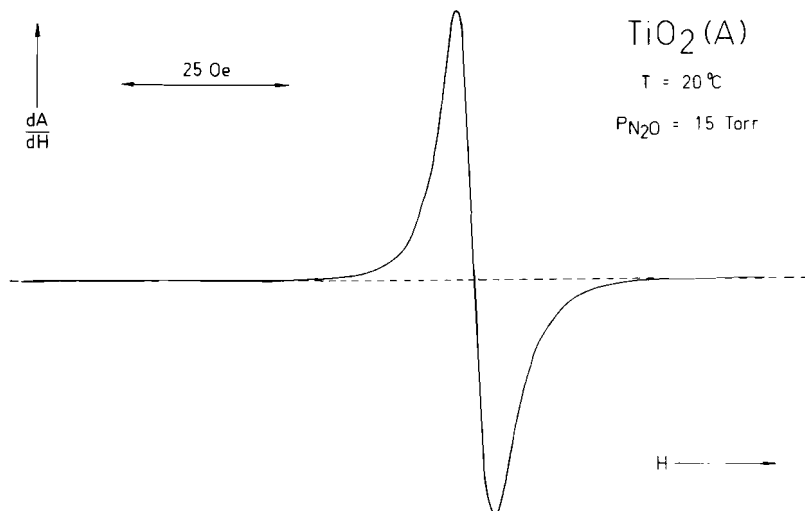
figure 18   EPR spectrum of N_2O on TiO_2 (A).

The most important results of the measurements with $TiO_2(A)$ are summarized in table 2.

EPR RESULTS ON TiO_2

2 h 500 °C 10^{-3} Torr

$\boxed{TiO_2 \text{ reduced}}$

F center   g = 2.0021

Ti^{3+} center g_{av} = 1.96
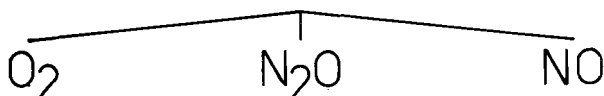
O_2	N_2O	NO
10 Torr 20 °C	10 Torr 20 °C	10 Torr 20 °C
Broad signal g=2.010	Narrow signal g=2.0028	Broad signal g=2.003
Linebroadening by physically adsorbed O_2	No linebroadening	Linebroadening by physically adsorbed NO
Removal of excess O_2	Removal of excess N_2O	Removal of excess NO
EPR spectrum consisting of 2 signals	EPR spectrum consisting of 1 signal	EPR spectrum consisting of 1 signal
signal A g = 2.0028	signal A g = 2.0028	signal A g = 2.0028
signal B $\begin{cases} g_1 = 2.0193 \\ g_2 = 2.0099 \\ g_3 = 2.0039 \end{cases}$	+ O_2 10 Torr no new signals linebroadening by O_2	+ O_2 10 Torr no new signals linebroadening by O_2
+ 1-Butene 10 Torr	+ 1-Butene 10 Torr	+ 1-Butene 10 Torr
signal B decreases rapidly signal A decreases very slowly	signal A decreases very slowly	signal A decreases very slowly

table 2   EPR results on TiO_2

The presence of the 3g-value signal in the EPR spec-
trum was already observed by other investigators (20)
(21). They ascribe this signal to O_2^- which is formed
at the surface out of a oxygen molecule by taking up
an electron of the slightly reduced TiO_2(A).

$$O_2 + e \rightarrow O_2^-$$

The g-value measured by them are:

a. Khazansky ; $g_1 = 2.020$, $g_2 = 2.009$ and $g_3 = 2.002$
b. Lu Tun Sin; $g_1 = 2.022$, $g_2 = 2.010$ and $g_3 = 2.003$

in good agreement with the values measured by us.

The 1g-value signal that occurs in the EPR spectrum
after the addition of O_2 and the only signal observed
if NO or N_2O is added instead of O_2 is not mentioned
in literature. A possible reason for this is that all
measurements described in literature were performed at
low temperatures at which saturation effects can occur.

Only Kwan (22) mentioned the possibility of the pre-
sence of O^- after the addition of O_2 to slightly re-
duced ZnO, supposed to give rise to a symmetrical EPR
signal with $g = 2.002$. This is in good agreement with
the A signal that we find after the addition of O_2 or
the EPR signal after the addition of NO or N_2O. Indeed
it is possible that out of O_2 as well as out of NO and
N_2O O^- is formed. This can take place according to
the following equations:

$\underline{O_2}$	$O_2 + e \rightarrow O_2^-$	signal B
	$O_2^- + e \rightarrow O_2^{2-}$	no signal
	$O_2^{2-} + e \rightarrow O^{2-} + O^-$	signal A
	$O^- + e \rightarrow O^{2-}$	no signal

NO

$$NO + e \rightarrow N + O^-$$ signal A

$$N + N \rightarrow N_2$$

$\underline{N_2O}$

$$N_2O + e \rightarrow N_2 + O^-$$ signal A
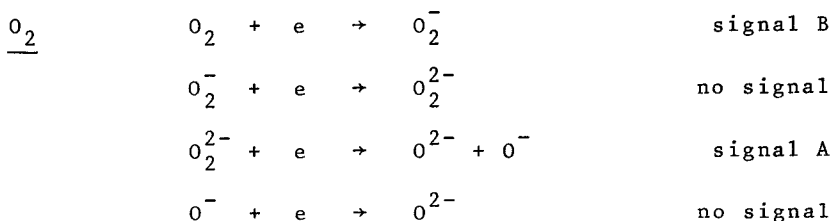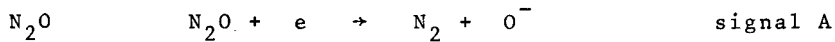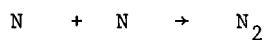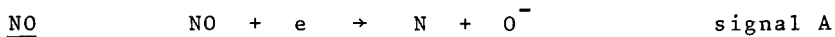
The decrease of the signal B after the addition of 1-butene points to the fact that the O_2^- ion that causes this signal reacts with the 1-butene.

Summarizing we can say that at the surface of slightly reduced $TiO_2(A)$ paramagnetical compounds are formed if O_2, NO or N_2O is added.

With O_2 these compounds are O_2^- and O^-; with NO and N_2O only O^-.

From these compounds the O_2^- reacts with 1-butene at room temperature.

MEASUREMENTS WITH ZINCOXIDE

IV.1.   Preparation of zincoxide

It is known that at the surface of slightly reduced
zincoxide also paramagnetical compounds are formed if
it is brought into contact with oxygen.

We studied this phenomenon in the same manner as we did
with titaniumdioxide.

For these experiments we needed very pure ZnO with a
large specific surface area. The commercially availa-
ble ZnO does not fulfil these requirements and there-
fore samples were prepared in the following manner:

A solution of $ZnCl_2$ (Merck 8816) is acidified with a
few milliliters of hydrochloric acid and heated at
about 70^oC. An aqueous solution of $(NH_4)_2C_2O_4$ (Merck
1192), to which an amount of ammonia is added equi-
valent to the hydrochloric acid,is also heated at 70^oC.
While stirring the oxalate solution is poured in-
to the zincchloride solution; a white precipitate of
$ZnC_2O_4 . 2H_2O$ is formed. This precipitate is filtered,
washed with hot water till no Cl^- is present in the
filtrate, and dried during 6 hours at 240^oC. The anhy-
drous zincoxalate was heated at 400^oC in an air stream
during 4 hours and ZnO is formed by thermal decomposi-
tion.

The product was white and had a specific surface area
44 of 14.7 m^2/g.

IV.2.   Pretreatment of the ZnO samples

The pretreatment of the ZnO was performed by heating
at 500°C under a pressure below 10^{-3} Torr during 2h.
The ZnO then becomes gray and somewhat conducting.
The EPR spectrum of the ZnO pretreated in this manner
shows two signals (figure 19); a weak symmetrical sign-
al with g = 2.0006   and a   stronger   symmetrical sign-
al with g = 1.96. The latter signal increases if the
temperature is lowered. Kokes associates it with a Zn^{+}
centre formed out of Zn^{2+} by trapping an electron. The
other signal is caused by the quartz glass sample tube.
The pretreatment of the zincoxide thus results in a
slight reduction. The released electrons can move free-
ly through the zincoxide as witnessed by the electrical
conductivity. However, part of the electrons is local-
ized at the Zn^{2+} ions and then causes an EPR absorp-
tion. At lower temperatures the amount of localized
electrons and also the EPR absorption increases.

IV.3.   Reaction of the pretreated ZnO with oxygen

If oxygen is added to the pretreated ZnO at 20°C up to
a pressure of about 10 Torr the electrical conduc-
tivity strongly decreases.Also the EPR spectrum changes
strongly (figure 19). The signal at g = 1.96 almost
disappears and at the low field side a new signal
occurs.
Thus oxygen reacts at the surface with the extra elec-
trons of the slightly reduced ZnO and forms one or
more paramagnetical compounds. The excess of oxygen
causes the usual line broadening. Pumping off this ex-
cess of oxygen down to a pressure of 0.1 Torr results
in a well detailled spectrum (figure 20).   **45**
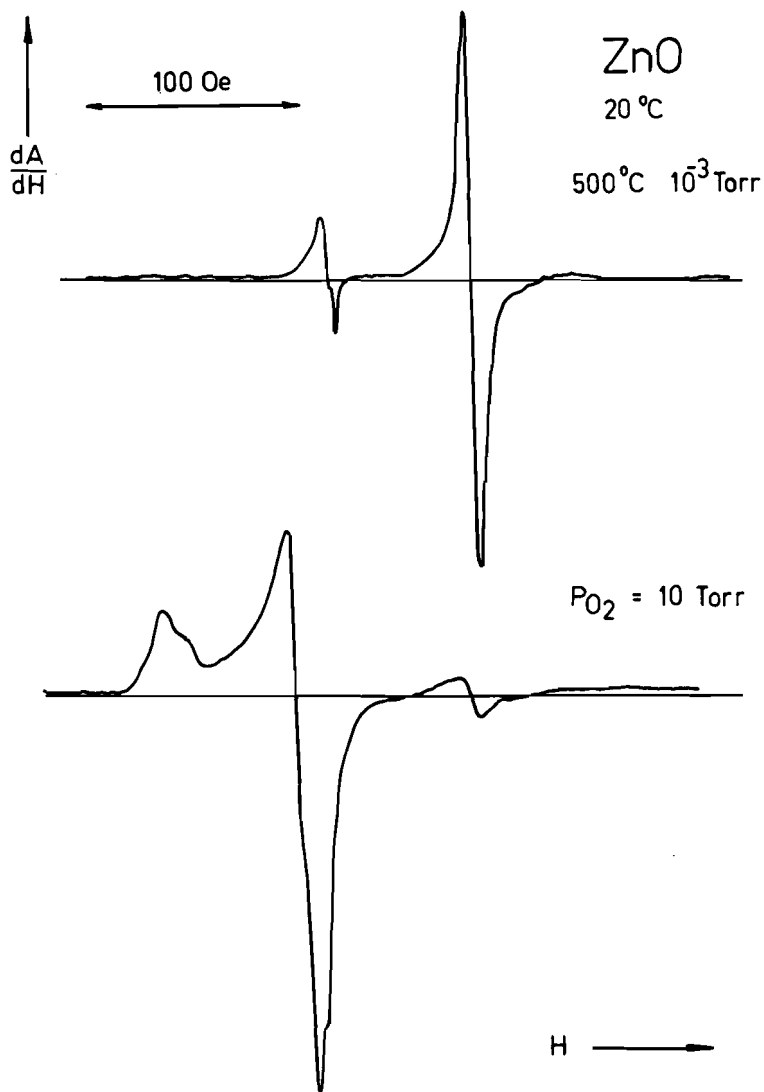
figure 19   EPR spectra of ZnO at 20°C before and after
             the addition of O_2.
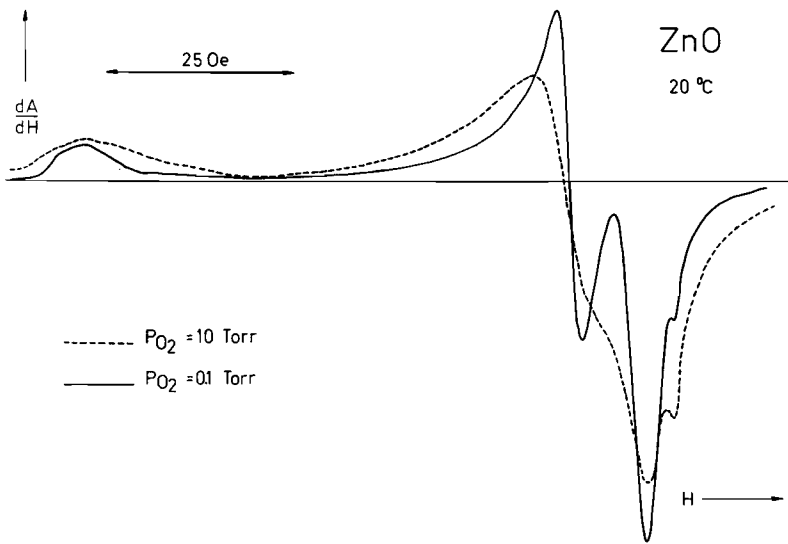
figure 20   EPR spectra of O_2 at ZnO at $20^\circ C$ before and
after removing the physically adsorbed oxy-
gen.

The weak signal with g = 2.0006 caused by the quartz
glass sample tube is clearly visible at the right hand
side.   The interpretation of the remaining and more im-
portant part of the EPR spectrum gives more difficul-
ties.   The two peaks at the left indicate the presence
of a 3g-value signal. The right side of this signal
coincides however with another signal. If we suppose
that the second signal is a 1g-value signal this re-
sults in the form of these signals given in figure 21.
The g-values that can be computed from this are:

        signal A: g = 2.0023

        signal B: g_1= 2.051, g_2 = 2.009, g_3 = 2.002

The situation is in good agreement with that observed   **47**

for titaniumdioxide and can be explained on similar lines.
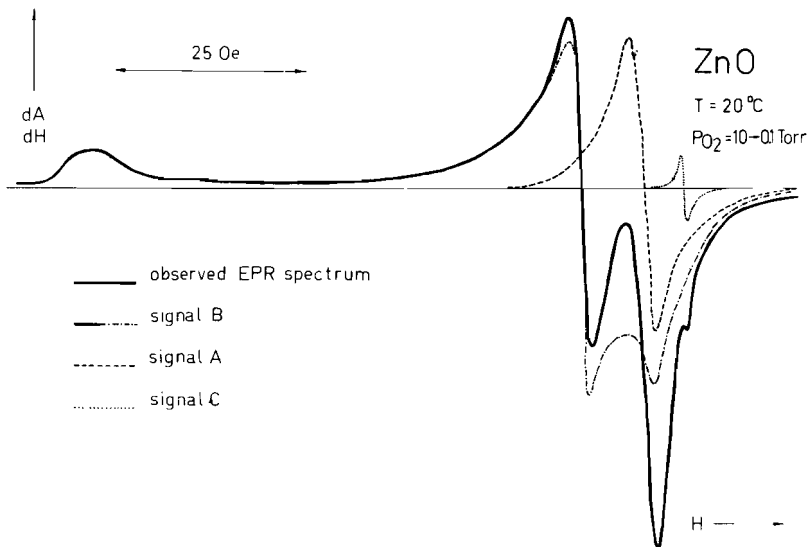
figure 21   Observed EPR spectrum of O_2 on ZnO and the three EPR signals from which this spectrum can be built up.

The oxygen added causes the formation of two paramagnetical compounds

O_2^- which causes the B signal and

O^- which causes the A signal.

One may suppose that also O^{2-} and O_2^{2-} are formed. These compounds however cannot be detected by EPR spectrometry. To get an impression of the amounts in which the different oxygencompounds may be formed the following experiment was performed.

A pirani gauge was coupled to the sample tube described before enabling to measure the pressure in bulb

C, and the volumes of bulb C and the sample tube A + B
were determined. A known amount of ZnO (about 350 mg)
was brought into the sample tube. It was heated at
$500^{o}C$ at a pressure below 10^{-3} Torr during 2h. There
after tap D was closed and the sample tube was cooled
to room temperature. With the help of the gasdosing
system bulb C was filled with oxygen at a known pres-
sure. Tap E then was closed. By opening of tap D the
oxygen can be brought into contact with the ZnO present
in the sample tube and from the gas pressure indicated
by the pirani gauge the oxygen adsorbed can be cal-
culated. Simultaneously the amount of paramagnetical
particles formed at the ZnO surface can be determined
by comparing the observed EPR spectrum with an EPR
spectrum of a standard compound. The result of this
measurements was that on 1 gram ZnO with a specific
surface area of 14.7 m^2/g about 2×10^{17} O_2 molecules
are chemisorbed including about 2.5×10^{15} ($\approx 1.25\%$)
paramagnetical particles.

Thus the major part of the oxygen is bonded either as
O^{2-} or O_2^{2-} while only 1.25% produces O_2^- or O^-.
In another experiment O_2 was added stepwise up to
saturation and after each oxygen dosage the EPR spec-
trum was recorded (figure 22). It showed that the first
amounts of oxygen produce only a very small amount of
paramagnetical species. What is seen in the EPR spec-
trum is a small increase of the signal ascribed to O^-.
Following additions of oxygen lead to a further in-
crease of this signal but now also the signal ascribed
to O_2^- becomes observable. A strong increase of both
EPR signals occurs however at the final addition of
O_2. Further addition of oxygen give hardly any further
increase in either the amount of adsorbed oxygen or
the intensity of the EPR signals. This phenomenon can
be explained in the following manner:
The slightly reduced ZnO contains many - "extra" elec-

figure 22   EPR spectra of ZnO recorded after the addi-
             tion of increasing amounts of O_2.
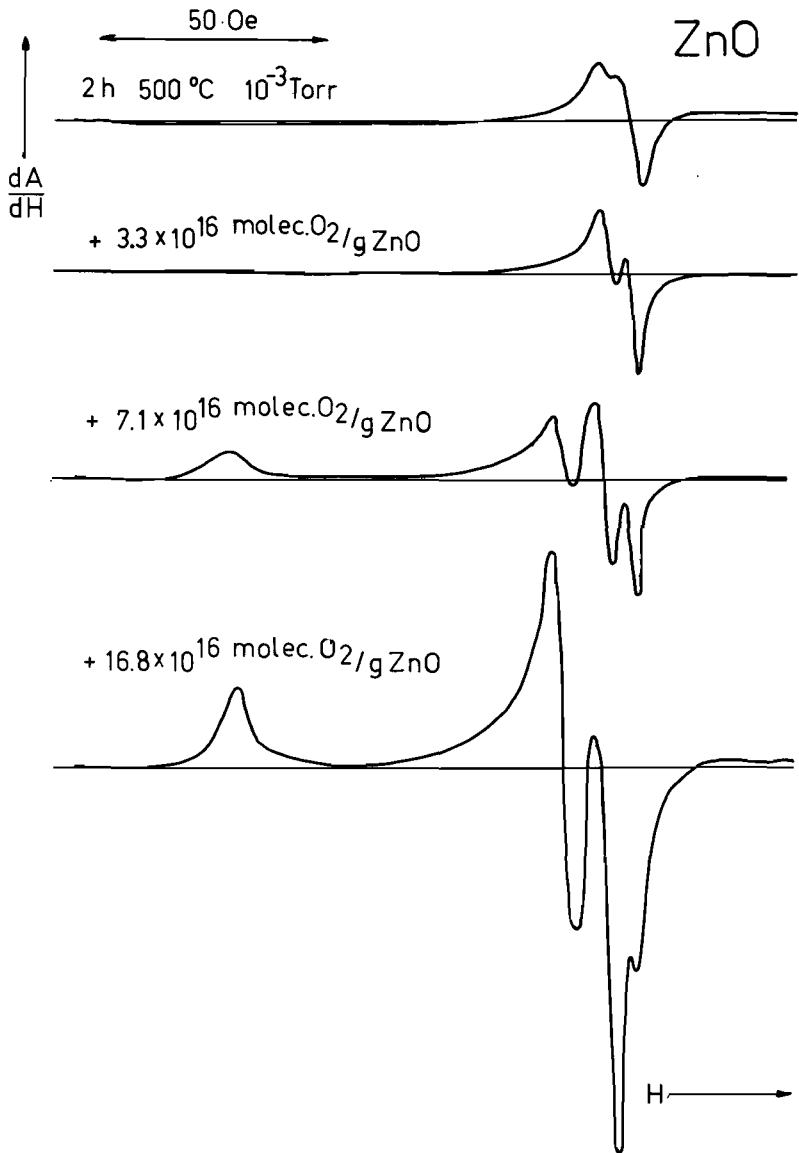
trons, part of these being – localized on Zn^{2+} ions
50 and the rest moving as conduction electrons through

the lattice. If it is brought in contact with O_2 mole-
cules the extra electrons react with this gas pro-
ducing in first instance O_2^-. However as a consequence
of the large amount of "free" electrons chances are
high that a second, a third and even a fourth electron
are picked up. The main product is therefore supposed
to be O^{2-} leading to a depletion of the extra elec-
trons. For oxygen molecules that make contact with the
surface at a later stage the chance for picking up
four electrons continually decreases. In that case al-
so O^- ions are formed and after a certain time also O_2^{2-}
and O_2^- ions.

IV.4. Reaction of the chemisorbed oxygen with 1-butene

If at $20^{\circ}C$ an amount of 1-butene is added to a sample
of ZnO at which surface oxygen is chemisorbed, the EPR
signal decrease (see figure 23).
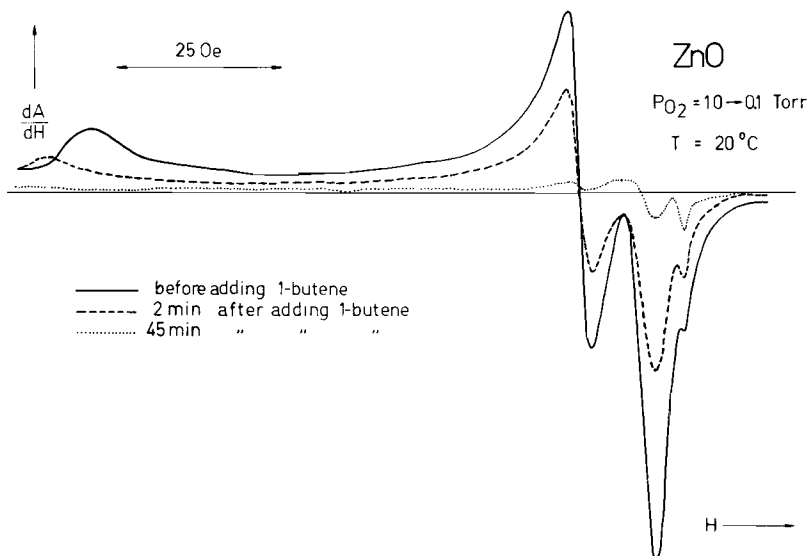
figure 23   Changes in the EPR spectrum of O_2 on ZnO
             after the addition of 1-butene.

The decrease of the signal B that is ascribed to O_2^- is
stronger than that of signal A ascribed to O^-.
Hence also for ZnO the O_2^- ions are more reactive for
the oxidation of 1-butene than the O^- ions.

IV.5. Reaction of N_2O and NO with slightly reduced ZnO

Next to O_2 it is possible to reoxidize the slightly re-
duced ZnO with N_2O and NO.
After adding an amount of one of these gases the ZnO
ceases to be electrically conducting and it shows an
EPR spectrum consisting of a symmetrical 1g-value sign-
al with g = 2.003. Again this signal corresponds to the
A signal observed after O_2 addition. Corroborating the
observations on TiO_2 also the observation that no new
signals are produced of O_2 is added subsequently and
that the only result of this addition is line broaden-
ing is in good agreement with the results reported
above.

MEASUREMENTS WITH TINDIOXIDE

V.1.   Pretreatment of the tindioxide

Besides on TiO_2 and ZnO the formation of surface per-
oxocompounds was also studied on SnO_2. For this we used
the commercially available SnO_2 (Baker Analyzed Re-
agent) that proved to be of satisfactory purity.It
possessed a specific surface area of 3.1 m^2/g.
It was pretreated by heating at $500^{\circ}C$ and a pressure
below 10^{-3} Torr during 2 hours. The SnO_2 then became
grayish and somewhat electrically conducting. EPR spec-
tra recorded at $20^{\circ}C$ and at $-150^{\circ}C$ show only a small
signal with g = 2.0006 caused by the quartz-glass sam-
ple tube (see figure 24).
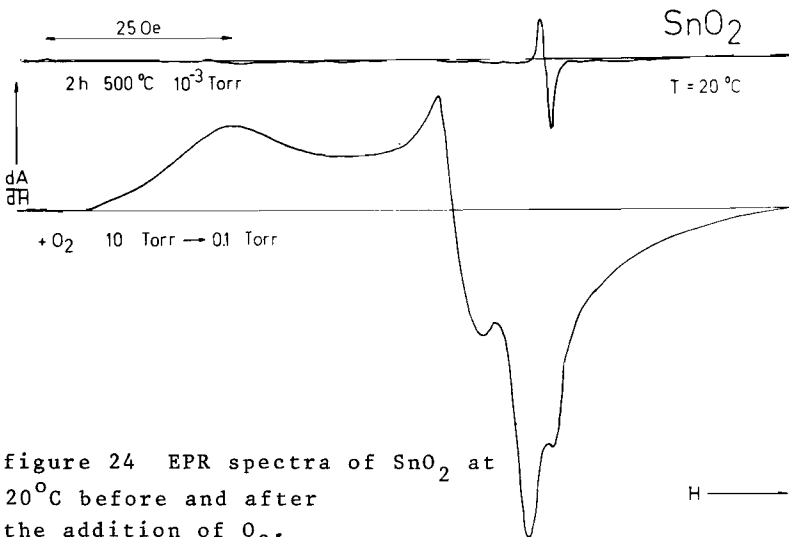
figure 24   EPR spectra of SnO_2 at
$20^{\circ}C$ before and after
the addition of O_2.

53

Obviously no paramagnetical centres are formed during
the reduction of SnO_2.

V.2.   Reaction of pretreated SnO_2 with oxygen and sub-
        sequently with 1-butene

If oxygen is added at $20^\circ C$ to the SnO_2 pretreated as
mentioned above, the electrical conductivity disappears
and paramagnetical compounds are formed at the surface.
The excess of oxygen however causes a strong line
broadening. After pumping off this oxygen a well re-
solved EPR spectrum can be recorded (see figure 24).
This spectrum is almost similar to the spectra that can
be obtained with ZnO and TiO_2. It is obvious to explain
this spectrum in the same manner.
At the surface of SnO_2 O_2^- and O^- are formed. The former
compound causes a 3g-value EPR signal with the follow-
ing g-values

$$g_1 = 2.028, \quad g_2 = 2.009 \text{ and } g_3 = 2.002$$

while the latter compound causes a 1g-value EPR signal.
The g-value of this signal cannot be determined ac-
curately from the EPR spectrum. If however 1-butene is
added the 3g-value disappears almost completely (see
figure 25) and only the 1g-value signal is left. The g-
value then measured is g = 2.0018.

V.3.   Reaction of pretreated SnO_2 with NO and N_2O

NO and N_2O also form paramagnetical compounds at the
surface of pretreated SnO_2. The EPR spectrum of these
compounds shows a symmetrical 1g-value signal with g =
2.0019 being identical with the 1g-value signal formed
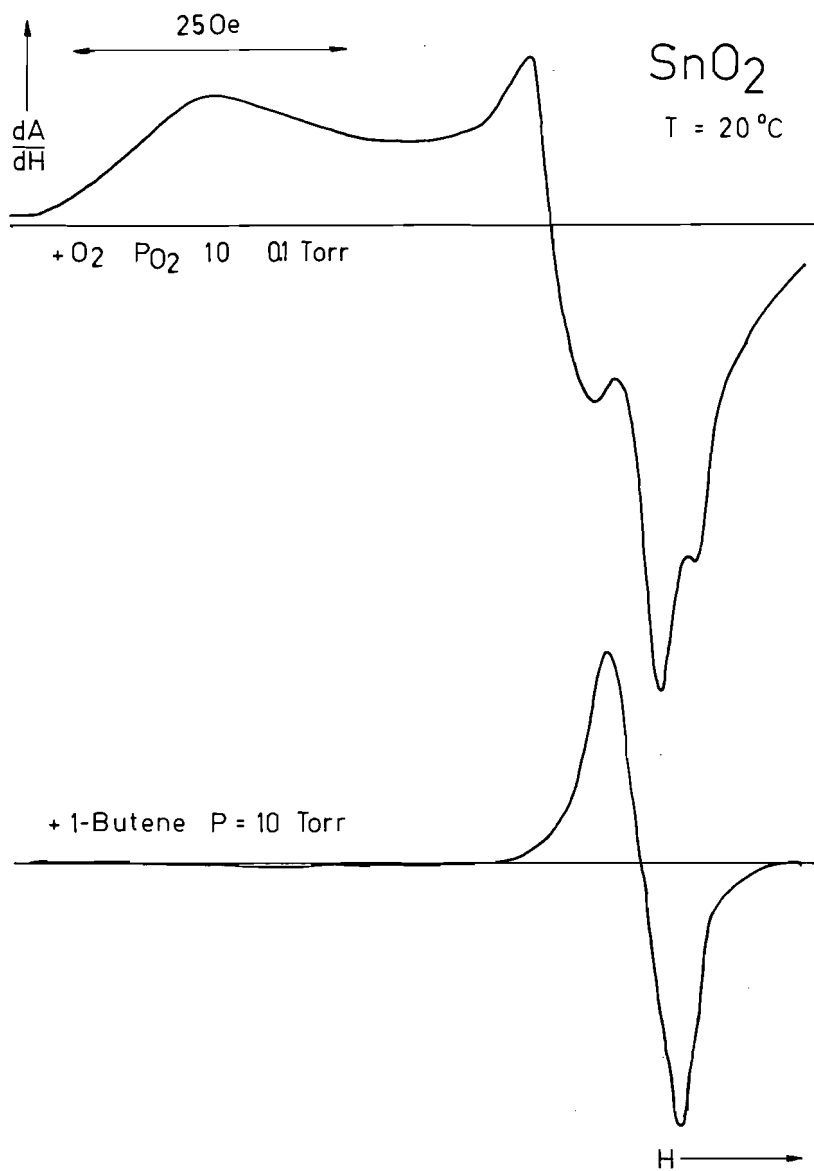
figure 25   Changes in the EPR spectrum of O_2 on SnO_2
            after the addition of 1-butene.

after the addition of O_2 and ascribed to O^-. Therefore
it is possible that O^- is formed out of NO or N_2O.   **55**

Subsequent addition of O_2 only causes line broadening but does not result in the formation of new EPR signals. The reaction of NO or N_2O with the extra electrons of the pretreated SnO_2 therefore is complete.

DISCUSSION

The EPR signals of O^- at the surface of the three me-
taloxides $TiO_2(A)$, ZnO and SnO_2 are almost identical
with respect to their form and g-value. In all cases
the signals are symmetrical with one g-value of

$$TiO_2(A) \quad g = 2.003$$
$$SnO_2 \quad g = 2.002$$
$$ZnO \quad g = 2.003$$

The O_2^- signals also show a similarity as to their shape
(see figure 26). One of the g-values however strongly
differs from oxide to oxide (see table 3).

table 3

	g_1	g_2	g_3
TiO_2	2.019	2.010	2.004
SnO_2	2.028	2.009	2.002
ZnO	2.051	2.009	2.002

For a free electron the g-value should be $g_e = 2.0023$.
Deviations of the actual g-values with respect to the
free electron g-value indicate the amount of coupling
between the magnetic orbitalmoment and the external
magnetic field. As already mentioned in chapter II this
is determined by the joint action of the crystalfield
and the spin-orbit coupling. The size of the deviation
of g_e therefore can be described by:

$$g_e - g = f\left(\frac{\lambda}{\Delta}\right)$$
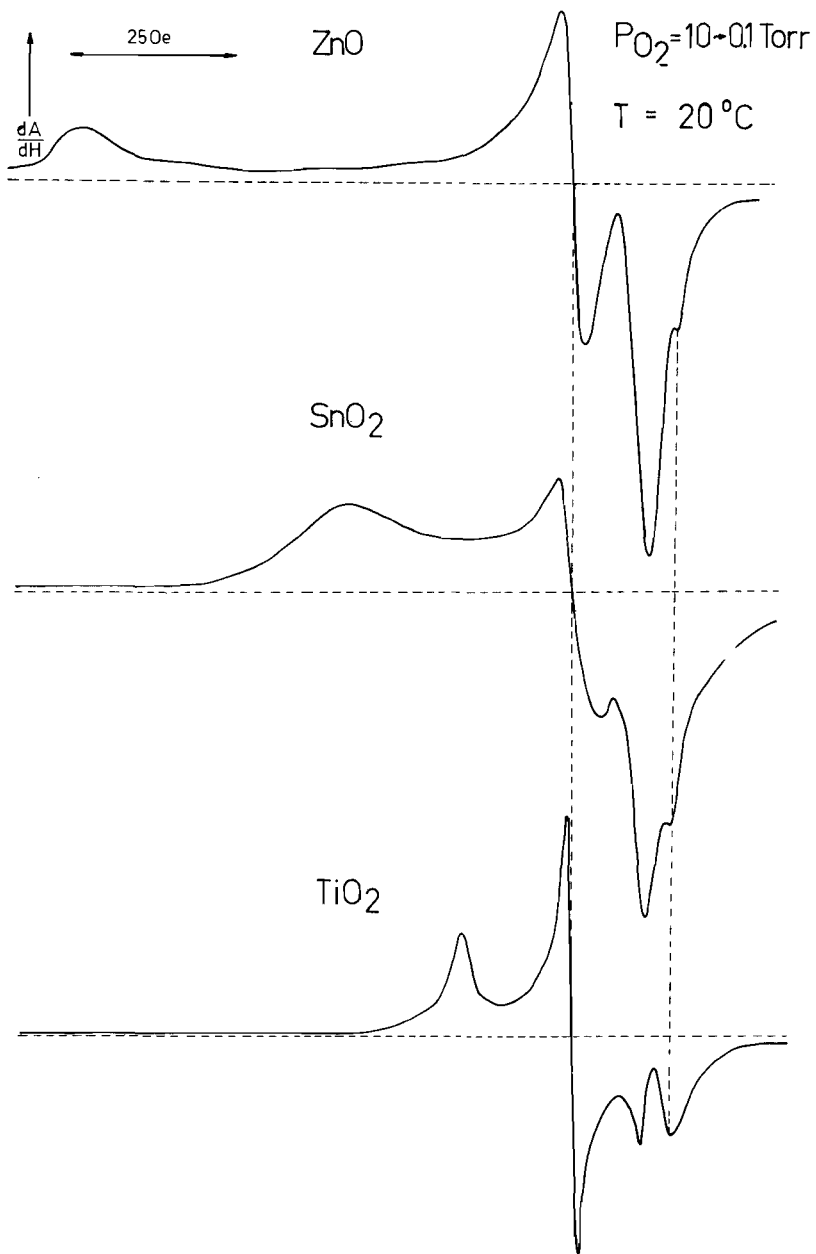
figure 26   EPR spectra of O_2^- and O^- present at the
surfaces of ZnO, SnO_2 and TiO_2(A).

in which: λ = spin-orbit coupling constant
            Δ = crystalfield splitting

To use this formula we have to know the structure of
the O_2^- ion at the surface of the metaloxide. The fact
that the EPR signal is characterized by three g-values
indicates that there is no axial symmetry in this sys-
tem. As a possible structure we could think of the
structure of the H_2O_2 molecule. Starting from this
structure we can arrive at the structure of the bonded
O_2^- ion by replacing one H^+ ion by a metalion of the
metaloxide lattice and removing the second H atom. (see
figure 27). In that case the unpaired electron is in an
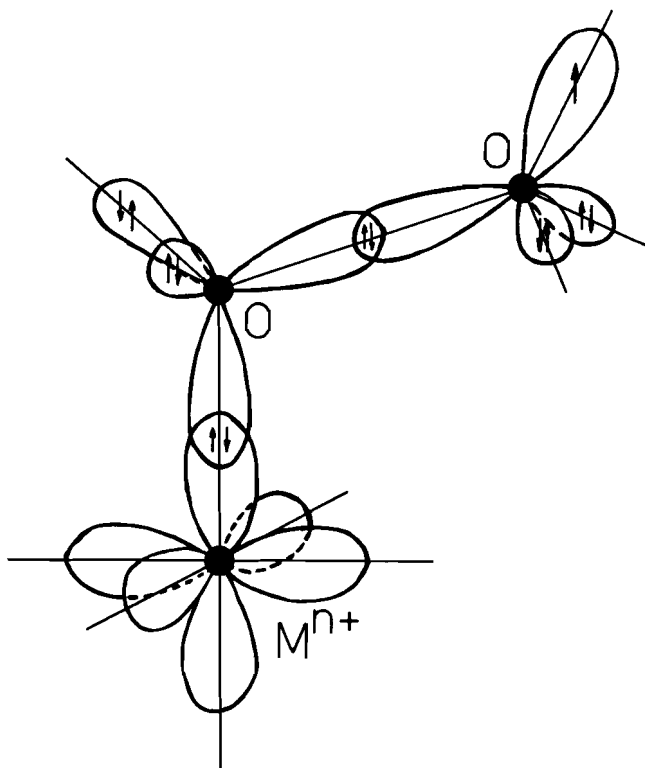
figure 27   Schematic picture showing spatial arrange-
             ment of the relevant orbitals in the bond
             between a metalion and the peroxoradicalion. **59**

oxygen orbital and the value of the spin-orbit coupling constant is therefore equal to $\lambda_0 = 151$ cm^{-1}. On the other hand the crystal-filed splitting is caused by the metalion to which the O_2^- ion is bonded. Its magnitude depends on the charge and the radius of the metalion. The charges and radii are:

	charge	radius
TiO_2	+4	0.68 A$^\circ$
SnO_2	+4	0.71 A$^\circ$
ZnO	+2	0.74 A$^\circ$

From this we can conclude that the crystalfield splitting shall increase in the sequence ΔZnO $<$ ΔSnO_2 $<$ ΔTiO_2 with the consequence that the difference $g-g_e$ is relatively small for TiO_2 and large for ZnO which is in agreement with the observed g-values.

Another point that needs an explanation is the reaction of 1-butene with the adsorbed oxygen compounds. As mentioned in the chapters III, IV and V the EPR signals of O_2^- present on the surfaces of respectively TiO_2(A), ZnO and SnO_2 strongly decrease if 1-butene is added at roomtemperature. Contrary hereto the EPR signals of O^- only show a small decrease. The first thing we want to know is the mechanism by which 1-butene reacts with the O_2^- ions and which reaction products are formed. We therefore performed a gaschromatographic analysis. In this way besides 1-butene only cis- and trans 2-butene but no oxidation products could be observed. A possible cause herefore is that only a relatively small amount of oxidation products is formed consequent to the small amount of peroxocompounds present at the surface. Moreover, these oxidation products may stay adsorbed at the surface. Another reason could be that not oxidation but **60** another type of reaction is responsible for the dis-
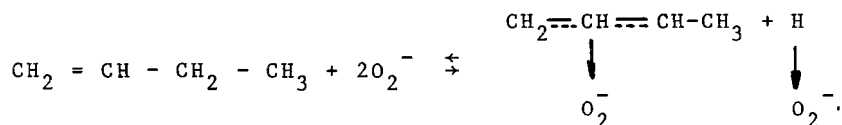
appearence of the O_2^- signal. That this is not the iso-
merisation reaction is clear from the fact that isome-
risation occurs at the same rate at the surface of an
outgassed metaloxide,on which no oxygen is chemisorbed.
Looking for compounds other than 1-butene that cause a
decrease of the O_2^- EPR signal we arrived at the fol-
lowing result:

> Propene and isobutene react just as 1-butene but
> ethene and hydrogen do not show reaction.

This suggest that the presence of a secondary or terti-
ary carbonatom is essential for a reaction with the O_2^-
ion, which points to the formation of a carboniumion
or an allylradical.
The formation of a carboniumion is less probable since
the metaloxide samples had been outgassed at a tempera-
ture as high as $500^\circ C$. We therefore are of the opinion
that the reaction of 1-butene with the O_2^- ion involves
the formation of an allylradical.The following equation
can be drawn up:

$$CH_2 = CH - CH_2 - CH_3 + 2O_2^- \leftrightarrows \begin{array}{cc} CH_2 \text{---} CH \text{---} CH-CH_3 & + \ H \\ \downarrow & \downarrow \\ O_2^- & O_2^- . \end{array}$$

This explanation suffers however from the known fact
that the surface density of O_2^- is very low and that as
a consequence the chances for the reaction to occur are
almost negligible. One might therefore consider as an
alternative solution the formation of a proton and a
negative allylic ion. The former could react with O^{2-}
to give OH^- while $C_4H_7^-$ would then interact with O_2^-.
However, the product of this reaction possesses an odd
number of electrons and should be detectable in prin-
ciple by EPR-measurements. It is not clear why this is
not the case. A possible explanation is that the ground
state of the radical ion formed is degenerate which
could preclude its observation. In fact so far C_4H_7-ra-

dicals have never been detected by EPR-methods although their existence is undoubted. At any rate the formation of the allylic species is necessary anyhow to explain the double bond isomerisation.We therefore believe that there is a good point to make for the actual presence of the peroxidic derivative.

The decomposition of the allyl peroxide might at higher temperature lead to the formation of free radicals that diffuse into the gasphase and initiate the homogeneous oxidation of the olefin thus explaining the total combustion observed. The problem now is whether the concentration of the O_2^- ions at the reaction temperature is high enough to account for the total combustion. The problem is the more pressing since we observed that the O_2^- EPR signal disappears if the sample is heated at temperatures higher than $160^\circ C$ and a pressure of about 10^{-2} Torr (see figure 28). Normally the signal intensity f, is proportional to $\frac{1}{T}$ but the actual decrease measured is much more pronounced. Therefore we have to assume that there is a dissociation of the O_2^- from the surface. As a measure for the amount of O_2^- present at the surface, C, we can accept the product of the signal intensity, f, and the absolute temperature, T.

$$C \simeq f \times T$$

Let us suppose that there are a certain number of sites at the surface that can adsorb oxygen as O_2^- ions. We shall assume that the adsorption is of a simple Langmuir type. The fraction of the surface covered is then given by:

$$\Theta_T = \frac{P}{P + P_{o_T}} = \frac{C}{C\backsim} \qquad (1)$$

in which: P = the actual oxygen pressure

P_o = the O_2 pressure necessary to cover half the available sites
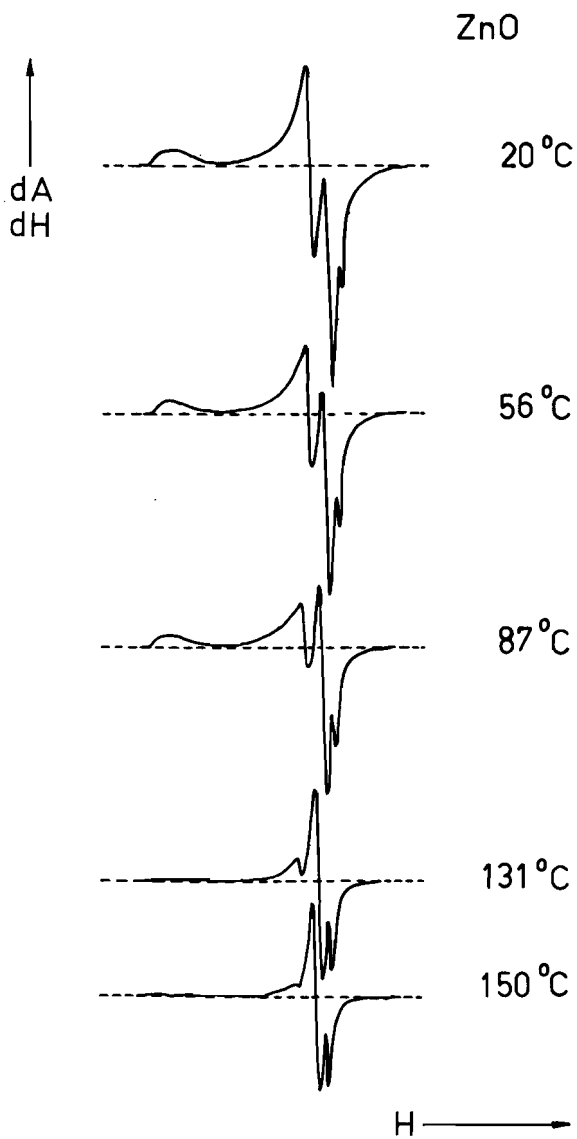
figure 28   EPR spectra of O_2^- and O^- present at the
            surface of ZnO as obtained at different tem-
            peratures.   **63**

We assume that:

$$P_{O_T} = k \exp. \left(- \frac{\Delta H_{ads}}{RT}\right) \qquad (2)$$

We further assume that the surface is fully covered at $20^\circ C$ at a pressure of 10^{-2} Torr.

Substitution of (1) in equation (2) leads to:

$$\log \left(\frac{1}{C} - \frac{1}{C\sim}\right) = - 0.44 \frac{\Delta H_{ads}}{RT} + A \qquad (3)$$

The experimental results are replotted in figure 29 according to equation (3).

figure 29   Relation between the amount adsorbed $\overline{O_2}$ and the temperature.

Least squares interpolation gives equation (4)

$$\log \left(\frac{1}{C} - \frac{1}{C\nu}\right) = 8.28 - \frac{2000}{T} \qquad (4)$$

For $T = 700^{\circ}K$ which is the approximate reactiontempera-
ture of the oxidation reaction proper and an oxygen
pressure of 10^{-2} Torr we astimate:

$$\frac{C}{C\nu} \approx 0.0014$$

Actually the oxygen pressure in the catalytic experi-
ments is of the order of 100 Torr and if the coverage
is supposed to be linear in P the degree of coverage
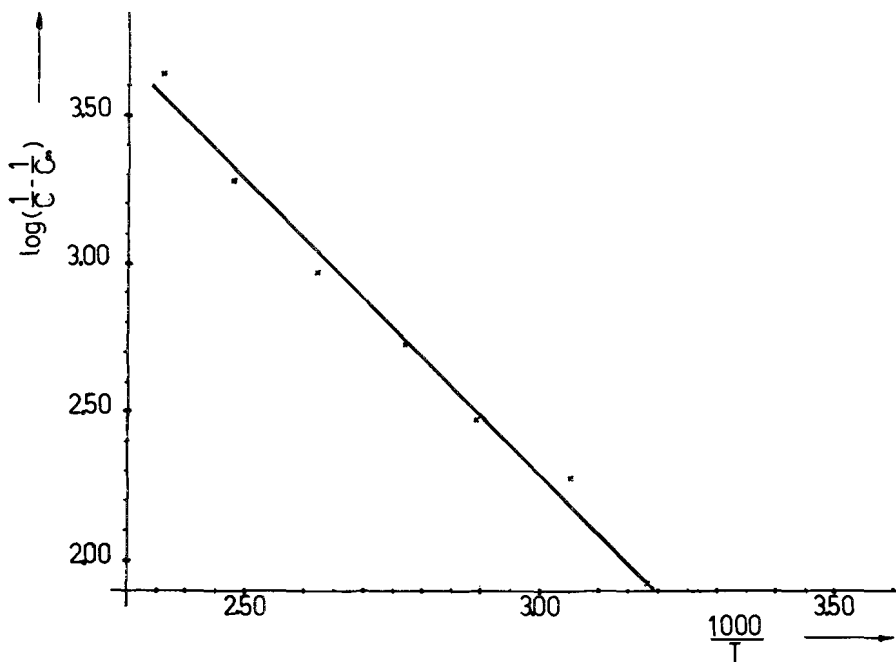calculated is 14 i.e. there must be an appreciable con-
centration of O_2^- at the reactionconditions.
Admittedly this is a crude calculation and further ex-
periments should be performed on signalstrength at
higher temperatures and pressures. However the impres-
sion has been gained that the O_2^- radical ion remains a
possible intermediate even at the high temperatures en-
countered in catalytic oxidation.

When this manuscript was completed we became acquainted
with the paper of Horiguchi, Setaka, Sancier, and Kwan
(23). Their results concerned with ZnO are closely
similar to ours. Also the interpretation is very
similar, which is not surprising since Kwan was the
first to propose the presence of O^- besides O_2^- at the
ZnO surface. A point of interest mentioned by Kwan is
the oxygen pressure as function of the temperature at
which the sample is heated. We see then that there in-
deed is a dissociation of O_2 from the surface which is
in accordance with our assumption underlying the tem-
perature dependence of the EPR signals.

SUMMARY

The present investigation deals with the formation of various oxygencompounds at the surface of three metal-oxides, $TiO_2(A)$, ZnO and SnO_2 if these oxides after a slight reduction are brought into contact with oxygen at roomtemperature. The behaviour of these oxides when used as a catalyst for the oxidation of olefins suggest that at the surface besides oxideions also an activated form of oxygen is formed. The choice of EPR spectrometry as a method of investigation is explained in chapter II in which also the principles of this method are given.

The experimental results for titaniumdioxide (anatase) are discussed in chapter III. A slight reduction of this oxide leads to the formation of Ti^{3+}- and F-centres and to an increased electrical conductivity. Ti^{3+}- and F-centres as well as the conductivity disappear after contact with oxygen gas at $20°C$. From the EPR spectra we can conclude to two paramagnetical oxygencompounds being formed at the surface. One of these compounds disappears if 1-butene is added at roomtemperature. The use of N_2O or NO instead of O_2 leads to a similar result with respect to the disappearence of the Ti^{3+}- and F-centra and the electrical conductivity.

From the EPR spectrum it is clear however that in this case only one paramagnetical compound is formed that does not disappear if 1-butene is added. On that ground we assume that reaction with oxygen leads to the paramagnetical compounds O_2^- and O^- from which only O_2^- is

reactive with respect to 1-butene while a reaction with N_2O or NO produces only O^-.

The chapters IV and V deal with the results of the measurements with ZnO and SnO_2. At the surface of these oxides also O_2^- and O^- are formed after reoxidation with O_2 and only O^- if N_2O or NO are used.

Quantitative measurements with ZnO indicate that at the reaction with oxygen only about 1.25% of the reacting oxygen is transformed in one of the paramagnetical ions O_2^- or O^- the remainder being bonded either as O_2^{2-} or O^{2-}.

The differences between the O_2^- EPR signals at the different metaloxides are discussed in chapter VI. These differences can be explained by an electrical interacttion of the Ti^{4+}, Zn^{2+} and Sn^{4+} ions with the chemisorbed O_2^- ions. In this chapter we also suggest a mechanism for the strong oxidizing action of the O_2^- ion.

SAMENVATTING

In dit proefschrift worden de resultaten beschreven van een onderzoek naar de vorming van verschillende zuurstof verbindingen aan het oppervlak van de drie metaaloxiden $TiO_2(A)$, ZnO en SnO_2, indien deze oxiden na een zwakke reductie bij kamertemperatuur met zuurstof in contact worden gebracht.

In het eerste hoofdstuk wordt uiteengezet dat het afwijkende gedrag van deze oxiden bij het gebruik als katalysator voor de oxidatie van olefinen doet vermoeden dat er aan het oppervlak naast oxide ionen ook een geactiveerde vorm van zuurstof wordt gevormd.
De keuze van de EPR spectrometrie als onderzoek methode wordt toegelicht in hoofdstuk II waarin ook de principes van deze methode worden besproken.

Hoofdstuk III geeft de experimentele resultaten met titaniumdioxide (anataas). Zwakke reductie hiervan geeft aanleiding tot de vorming van Ti^{3+}- en F-centra en tevens tot het optreden van elektrische geleiding. Bij een reactie met zuurstof bij $20^{\circ}C$ verdwijnen zowel deze Ti^{3+}- en F-centra als de geleiding. Getuige de EPR spectra worden hierbij aan het oppervlak twee paramagnetische zuurstofverbindingen gevormd.Een van deze verbindingen verdwijnt indien bij kamertemperatuur 1-buteen wordt toegevoegd. Het gebruik van N_2O of NO in plaats van O_2 heeft hetzelfde resultaat ten opzichte van de verdwijning van de Ti^{3+}- en F-centra en de elektrische geleiding. Uit het EPR spectrum blijkt dat hierbij echter maar één paramagnetische verbinding

wordt gevormd, welke niet verdwijnt na toevoegen van 1-buteen.

Op grond hiervan wordt aangenomen dat bij de reactie met zuurstof de paramagnetische zuurstof verbindingen O_2^- en O^- worden gevormd waarvan O_2^- reactief is t.o.v. 1-buteen, en dat bij de reactie met N_2O of NO O^- wordt gevormd. De hoofdstukken IV en V geven de resultaten van het onderzoek met ZnO en SnO_2. Ook hierbij wordt bij reoxidatie met zuurstof aan het oppervlak O_2^- en O^- gevormd en met N_2O of NO alleen O^-.

Kwantitatieve metingen met ZnO geven aan dat bij de reactie met zuurstof slechts ca. 1,25% van de reagerende zuurstof wordt omgezet in de paramagnetische ionen O_2^- of O^- en dat de rest wordt gebonden als O_2^{2-} of O^{2-}.

In hoofdstuk VI tenslotte wordt ingegaan op de verschillen tussen de O_2^- EPR signalen bij de verschillende metaaloxiden. Deze verschillen worden verklaard door de elektrische interactie van de Ti^{4+}-, Zn^{2+} en Sn^{4+} ionen met de gechemisorbeerde O_2^- ionen. Tevens wordt in dit hoofdstuk een mechanisme gesuggereerd voor de sterk oxiderende werking.

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LEVENSBERICHT

Op aanbeveling van de Senaat van de Technische Hoge-
school volgen hier enkele persoonlijke gegevens.

Ik werd op 31 januari 1935 geboren te Eindhoven waar ik
ook het lager en middelbaar onderwijs volgde. In 1952
behaalde ik het diploma H.B.S.^{B} aan het St. Joris Col-
lege, waarna ik de lessen volgde aan de H.T.S. Eind-
hoven. In 1955 behaalde ik aan deze school het diploma
H.T.S. Chemie. Na een onderbreking voor het vervullen
van de militaire dienstplicht trad ik in 1957 in dienst
van de N.V. Organon te Oss. Hier was ik gedurende een
jaar werkzaam op het microbiologisch laboratorium. In
1958 werd ik als technisch ambtenaar aangesteld bij de
Technische Hogeschool Eindhoven. Hier was ik werkzaam
bij de groep Anorganische Chemie tot 1961 onder leiding
van Prof. Ir. J.G. Hoogland en daarna onder leiding van
Prof. Dr. G.C.A. Schuit. Hiervoor door het bestuur van
de Technische Hogeschool in de gelegenheid gesteld
volgde ik ook het onderwijs aan dit instituut dat in
1964 werd afgesloten met het behalen van het ingenieurs
diploma in de scheikundige technologie. Het afstudeer-
onderwerp was: "Elektron-Paramagnetische-Resonantie van
Overgangsmetaal complexen".
Daarna aanvaarde ik de benoeming tot wetenschappelijk
medewerker bij de groep Anorganische Chemie van de
Technische Hogeschool Eindhoven. Tot 1966 was ik hier
instructeur op het anorganisch preparatief practicum
waarna ik de leiding kreeg over de researchgroep

Heterogene Katalyse. In deze periode verrichte ik het
in dit proefschrift beschreven onderzoek.
Op 1 mei 1968 trad ik in dienst bij de Koninklijke Zwa-
velzuurfabrieken v/h Ketjen N.V. te Amsterdam als hoofd
van het Anorganisch Research Laboratorium.

STELLINGEN

I   De door IYENGAR, CODELL en TURKEVICH gegeven ver-
klaring voor de verbreding van het EPR signaal van
O_2^- bij overmaat O_2 is in strijd met hetgeen wordt
waargenomen bij metingen bij verlaagde temperatu-
ren.

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II   De interpretatie van de EPR spectra van Mn^{2+} in
vooraf uitgewisselde X-zeolieten door BARRY en LAY
is zeer twijfelachtig.

    T.I. BARRŸ, L.A.LAY, J.Phys.Chem.Solids 27 1821
    (1966)

III   De reactievergelijking voor de vorming van kalium-
tetraperoxochromaat (V) zoals die door RIESENFELD,
WOHLERS en KUTSCH wordt gegeven en waarnaar in
recente publicaties nog wordt verwezen is onjuist

    $2 \ CrO_3 + 6 \ KOH + 7 \ H_2O_2 \rightarrow 2 \ K_3CrO_8 + 10 \ H_2O$
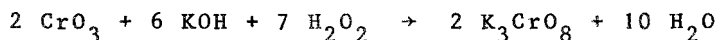
    E.H. RIESENFELD, H.E. WOHLERS, W.A. KUTSCH,
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                nische Chemie Stuttgart 1962 II 1216.

IV   Met behulp van het bandmodel is men niet in staat een adequate beschrijving te geven van de reacties die verlopen aan het oppervlak van een halfgeleider.

      A.H. BOONSTRA, Proefschrift Eindhoven 1967.

V   De resultaten welke in test units worden verkregen bij de vergelijking van amorfe silica-alumina kraakkatalysatoren met katalysatoren op basis van synthetische zeolieten geven een veel te gunstig beeld van de eigenschappen van de zeolietkatalysatoren ten opzichte van de resultaten die in commerciële installaties worden bereikt.

      R.W. BAKER, J.J. BLAZEK, P.K. MAHER,
      F.G. CIAPETTA, R.E. EVANS,
      The oil and gas journal May, 4 1964 p. 78
   D.H. STORMONT,
      The oil and gas journal April 1, 1968 p.104

VI   Voor de bepaling van de activiteit van mangaandioxide voor het gebruik in Leclanché cellen is de chemische methode met een ammoniakale hydrazinesulfaat oplossing zoals die door DROTSCHMANN wordt gegeven minder geschikt.

      C. DROTSCHMANN, Batterien 14 77 (1960)
      C. DROTSCHMANN, Batterien 20 887 (1966)

VII   De resultaten die SEARS vindt bij de bepaling van het specifieke oppervlak van colloïdaal silika door titratie met een natriumhydroxide oplossing kunnen worden verklaard door aan te nemen dat de zuurconstante van de reactie

$$\equiv SiOH \; \rightleftarrows \; \equiv SiO^- + H^+$$
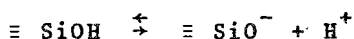
overeenkomt met de constante van de eerste disso-
ciatiestap van het ortho-kiezelzuur.

G.W.SEARS Jr., Analytical Chemistry 28 1981
(1956)

VIII De conclusies die RICHARDSON trekt,uit de metingen
van de magnetische susceptibiliteit van kobalt-
molybdeenoxide katalysatoren, voor en na reductie,
over de verschillende componenten waaruit deze
katalysatoren zijn opgebouwd zijn aan twijfel on-
derhevig.

J.T. RICHARDSON, Ind. and Eng.Chem.Fundamentals
3 154 (1964)

IX Het verdient aanbeveling het onderricht in de vak-
ken natuur- en scheikunde in de klassen van het HAVO
en het VWO door een docent(e) te laten verzorgen.

.

Eindhoven, 1 oktober 1968   J.H.C. van Hooff