CATALYST ACTIVATION BY REDUCTION

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ABSTRACT

   After having strictly defined the concept of activation by reduc-
tion, the industrial procedures for the reduction of the catalysts for
high and low temperature CO conversion and for ammonia synthesis are
reported and the basic principles on which they are based are discus-
sed.

   Emphasis is given to the difficulty of obtaining laboratory-scale
data that can be easily connected with such industrial procedures.

   The experimental techniques used for basic and applied research on
catalyst reduction are briefly discussed, in particular thermogravi-
metry and temperature programmed reduction.

   Finally the now available knowledge about the reduction mechanisms
of the above-mentioned industrial catalysts is summarized.

1. THE CONCEPT OF ACTIVATION

   The manufacture of an industrial catalyst (refs.1-2) involves so-
me unit operations, which can be grouped into three main classes
(Chemical Preparation, Thermal Treatments and Forming). The class
"Thermal Treatments" includes three main unit operations: Drying,
Calcination and Activation. There is no universally accepted defini-
tion for these unit operations. For instance, there is some confusion
between drying and calcination: some people distinguish them only on
the basis of the temperature level, while others pay attention to
the purpose of the operation. Other misunderstandings may occur about
calcination and activation. In an attempt to reach a more uniform ter-
minology among catalysis specialists, we propose the following defi-
nitions.

   By drying we strictly mean a thermal treatment performed with the
aim of eliminating the absorbed water, though we admit that also the
hydration water may be partially or completely eliminated. Drying
can be performed in air or inert gas atmosphere or under vacuum at
temperatures usually not much higher than 100°C.

By calcination a thermal treatment carried out in an oxidizing
atmosphere should be strictly understood. However we prefer to mean
by calcination any thermal treatment carried out with the following
purposes: to decompose some compounds present in the catalyst, gene-
rally with evolution of gaseous products, and/or to allow solid state
reactions among different catalyst components to occur and/or to make
the catalyst sinter. The importance of calcination is straightforward,
as it can influence all the catalyst properties, especially porous
structure and mechanical strength.

Having so defined drying and calcination, it is possible to re-
strict the definition of activation to thermal treatments carried out
in the reactor itself, either industrial, pilot or laboratory scale,
usually in special gaseous atmospheres. Such treatments are required
only for some catalysts. As a further restriction we do not consider
a kind of activation the regeneration of poisoned catalysts, even if
it is carried out "in situ". Therefore the term "activation" is due
to fresh catalysts only.

2. ACTIVATION BY REDUCTION

It is a matter of fact that in most cases the activation consists
in a reduction by suitable gaseous reducing agents. This is needed
because it is very troublesome for the manufacturer to prepare cata-
lysts where the oxidation states of the metallic elements are lower
than those existing in air atmosphere. In the few cases where the
reduction is carried out by the manufacturer, a passivation procedu-
re is then needed to handle the catalyst in air and finally an acti-
vation by reduction, though shorter, must be performed.

The most important catalytic processes, from an industrial point
of view, involving catalyst activation by reduction, are summarized
in Table 1.

TABLE 1

Some catalytic processes involving catalyst activation by reduction

Catalytic process	Catalyst reduction *
Steam reforming of hydrocarbons	$NiO \longrightarrow Ni$
High temperature CO conversion	$Fe_2O_3 \longrightarrow Fe_3O_4$
Low temperature CO conversion	$CuO \longrightarrow Cu$
Methanation	$NiO \longrightarrow Ni$
Ammonia synthesis	$Fe_3O_4 \longrightarrow Fe$

* Only the main compound to be reduced is reported here.

It should be stressed that such activation, though not performed
by the manufacturer, is in fact the final stage of catalyst preparation
and that its incorrect performance may have dramatic effects on cata-

lyst efficacy. To consider only one example, if exothermic reductions
are carried out at too high rates, the catalyst temperature may exceed
the maximum allowable, with consequent decrease of catalyst surface
area and/or undesirable solid state reactions. To avoid such dangers,
usually the manufacturer specifies the reduction procedure in detail,
having taken into account the characteristics of the plant. We will
give here some examples of these procedures, after having discussed
the principles on which they are based.

3. PROCEDURES FOR THE REDUCTION OF SOME INDUSTRIAL CATALYSTS

3.1 High temperature CO conversion catalyst

   Taking into account the chemical composition of various commercial
catalysts, the reactions that may occur during reduction in the conver-
ter are reported in Table 2, together with their standard enthalpy
values.

As it is necessary to avoid catalyst overheating during reduction
(otherwise a decrease of catalytic activity, due to sintering, and/or
of mechanical strength will result), the following general conclusions
can be drawn from Table 2 about the influence of catalyst composition

TABLE 2

Reactions occurring during reduction of high temperature CO conver-
sion catalysts.

Reaction	$\triangle$H at 25°C, Kcal/mole
2α-FeOOH $= \alpha$-Fe$_2$O$_3$ + H$_2$O	+ 9.3
2γ-FeOOH $= \gamma$-Fe$_2$O$_3$ + H$_2$O	+ 5.0
3α-Fe$_2$O$_3$ + H$_2$ = 2Fe$_3$O$_4$ + H$_2$O	− 2.3
3α-Fe$_2$O$_3$ + CO = 2Fe$_3$O$_4$ + CO$_2$	− 12.1
3γ-Fe2O3 + H$_2$ = 2Fe$_3$O$_4$ + H$_2$O	− 20.3
3γ-Fe2O3 + CO = 2Fe$_3$O$_4$ + H$_2$O	− 30.1
2CrO$_3$ + 3H$_2$ = Cr$_2$O$_3$ + 3H$_2$O	−163.6
2CrO$_3$ + 3CO = Cr$_2$O$_3$ + 3CO$_2$	−193.1

on the reduction process:

a) the content of CrO$_3$ should be as low as possible (in practice, a
   maximum content of 0.5% can be easily tolerated);

b) the presence of γ-Fe$_2$O$_3$, hence of γ-FeOOH, in high amounts should
   be avoided:

c) the presence of α-FeOOH (goethite) is very useful, due to its endo-
   thermic decomposition in a range of temperature where Fe$_2$O$_3$ reduc-
   tion has already started.

From the same Table it is also possible to conclude that the reduction
of this catalyst should be carried out more by H$_2$ than by CO.

   However, about the composition of the reducing gas, there is another

important argument to be taken into account, namely the possibility of
Fe_3O_4 reduction to Fe (this should be carefully avoided, as metallic
Fe catalyzes the highly exothermic reaction of methanation). To elimi-
nate such risk, a sufficient amount of steam must be added to the redu-
cing gas to have a H_2O/H_2 ratio higher than the equilibrium one at the
working temperature (for instance $(H_2O/H_2)_{eq} = 0.09$ at 400°C). Steam
has also the function of balancing the higher reducing power of CO
with respect to H_2 for Fe_3O_4 (this is a second reason for having a low
CO content in the reducing gas).

In addition to the above considerations, based on thermodynamic da-
ta, the reduction procedures recommended by catalyst manufactures rely
also on other factors, like operating restraints typical of the plant
and ease of operation. In practice, they strongly depend on the reduc-
tion conditions of the reforming catalysts. We will report here the
main stages of the reduction procedure of the Montedison MHTC catalyst
in a shift converter following a modern steam reformer.

After having purged the converter with nitrogen, the catalyst is
heated firstly in nitrogen stream up to 150°C, then in superheated
steam up to 300°C (both these feeds come from the reformer). The reduc-
tion starts at this temperature when a H_2-steam mixture comes from the
reformer and continues with process gas $(H_2-CO-CO_2-N_2)$, always con-
taining much steam, up to 350°C (steam has also the function of in-
creasing heat transfer). If during reduction sudden increases of tem-
perature occur, it is necessary to lower the process gas content, or,
exceptionally, to stop it completely until the temperature decreases
below the recommended limit (500°C can be tolerated for short periods).
However, with proper operation the maximum temperature is unlikely to
exceed 400°C, with benefit for catalyst performances.

Other reduction procedures involve the use of wet process gas star-
ting at lower temperatures. This may cause steam condensation in the
catalyst bed, with possible damage for mechanical strength.

3.2 Low-temperature CO conversion catalyst

The reactions that may occur during reduction in the converter are
reported in Table 3, together with their standard enthalpy values
(the main components of commercial catalysts are CuO and ZnO, together
with some amount of amorphous alumina).

(refs. 3-4). In fact, this solid state reaction has a negative ΔG
value that can compensate, especially at low Zn concentrations, the
positive ΔG of ZnO reduction.

The low-temperature CO conversion catalyst requires very careful
reduction to give its best performances. Therefore the reduction pro-

TABLE 3

Possible reactions during reduction of low-temperature CO conversion

catalyst

Reaction	ΔH at 25°C, Kcal/mole
$CuO + H_2 = Cu + H_2O$	- 20.7
$CuO + CO = Cu + CO_2$	- 30.6
$ZnO + H_2 = Zn + H_2O$	+ 25.4
$ZnO + CO = Zn + CO_2$	+ 15.5

The reduction of ZnO should not occur ($\Delta G = + 19.2$ kcal/mole at 200°C);

however, attention has been drawn to the possible formation of brass

cedure does not appreciably depend on the characteristics of the plant,

contrary to that of the high temperature conversion catalyst. In fact,

it is performed independently of the start-up of both reforming and

high temperature shift converters. We will report here the main fea-

tures of the reduction procedures recommended by some manufacturers.

After having purged the catalyst free from air with an inert gas

(nitrogen or natural gas), the temperature is raised, always in inert

gas stream (space velocity 500-1000 h^{-1}) to 70-120°C. Then hydrogen

is gradually added up to 0.3-0.5 mole % and later the temperature is

slowly increased up to 180°C. At this temperature the hydrogen content

is raised to 1.5-2 mole % in 3-5 hours. The temperature is slowly in-

creased up to 200-220°C and finally the hydrogen content is raised to

about 10 mole%.

All manufacturers stress that it is necessary to decrease the hydro-

gen feed or even to stop it completely at any time, should any sudden

increase of catalyst temperature occur. It may be useful to remark that

the use of steam, to obtain a better temperature control, is not recom-

mended, because it seems to have a negative influence on catalytic activity.

3.3 Ammonia synthesis catalyst

The main reaction occurring during the reduction of the ammonia

synthesis catalyst is

$$Fe_3O_4 + 4H_2 = 3Fe + 4H_2O \qquad \Delta H = + 35.8 \text{ Kcal}$$
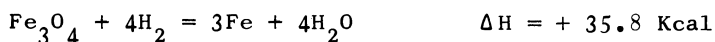
Small enthalpy differences, due to the presence of foreign cations

(Al, Mg, Ca) in the magnetite lattice and of small amounts of other

iron oxides in the catalysts (α-Fe$_2$O$_3$, FeO, ferrites), can be neglec-

ted, as a first approximation.

Owing to its endothermicity, this reduction is performed in the

plants following rather different guidelines with respect to the two

CO conversion catalysts. A powerful electric heater is needed to

startup the reduction and to sustain it almost till its end. To de-

crease power consumption, the reduction is usually performed with

synthesis gas (H_2-N_2 3:1), not with pure H_2, to take advantage of
the exothermicity of ammonia synthesis. After the synthesis reaction
has started, a careful temperature control is obviously needed.

The most important factor that influences the final catalytic pro-
perties is the water concentration in the gas in contact, during the
reduction process, with the already reduced catalyst. In fact, owing
to the high reactivity of iron surface towards oxygenated compounds,
repeated oxidation-reduction reactions occur in water-containing
hydrogen atmosphere with consequent recrystallization and growing of
iron crystallites. To minimize such phenomena, the following operating
criteria are adopted, when compatible with plant's characteristics:

- low reduction rate
- high space velocity
- low pressure
- effective drying of feed gas
- small catalyst granules

In any case, the measurement of the water content of the exit gases
has to be done, as catalyst manufacturers usually specify the maximum
value allowed. As an example, we will report here the main directions
for the reduction of the Montedison MSFN catalyst in a multibed con-
verter.

After having purged the converter free from air, the catalyst tem-
perature is slowly increased by means of the heater in a stream of
synthesis gas at 70-100 Atm. The temperature of the first bed is in-
creased over 300°C, while those of the other beds are kept below this
value. When the catalyst in the first bed has started its reduction,
the operating conditions (mainly synthesis gas space velocity and
heat supply) are controlled in such a way as to have a water content
between 2000 and 3000 ppm in the exit gas. As an additional restraint,
the bed temperature should not exceed 480°C. When the first bed cata-
lyst is almost completely reduced (80-90%), the other beds are reduced
in turn in the same way. At the end of the reduction stage the heater
is taken out of service and the pressure is slowly increased until
the normal working value is reached. During this operation the reduc-
tion of the residual unreduced magnetite slowly occurs.

3.4 Relation with applied laboratory-scale research
From the above-reported description of the reduction procedures of
some industrial catalysts, it is clear that it is very difficult, if
not impossible, to strictly define the operating conditions at the
catalyst level. To justify this statement, let us summarize the main
features of the reduction of the above-mentioned catalysts.

In the more complex case (high temperature CO conversion) three dif-

ferent chemical processes (without considering the physical ones)
are simultaneously involved:

- hydroxide decomposition
- oxide reduction
- CO conversion

In the intermediate case (ammonia synthesis) we have simultaneously:

- oxide reduction
- ammonia synthesis

Even in the simpler case (low temperature CO conversion), where only
reduction takes place, the reduction is performed with both tempera-
ture and hydrogen partial pressure variable over a wide range.
In fact, the reductions of the industrial catalysts are often performed
under conditions varying very irregularly, with the aim ensuring
that temperature and/or water concentration in the bed are under con-
trol. An additional complication is given by the use of high pressures.

The difficulties of reproducing on a laboratory scale such complex
processes and of obtaining meaningful data have caused a marked lack
of applied research on this subject. What is usually done is the com-
parison of the catalysts in the same experimental conditions, obviously
chosen in such a way as to obtain results that can be easily inter-
preted. Now we will briefly discuss the experimental techniques used
for these investigations.

4. EXPERIMENTAL TECHNIQUES FOR RESEARCH ON CATALYST REDUCTION

4.1 Thermogravimetry (TG)

As catalyst reduction involves usually oxygen abstraction, apart from
other simultaneous decomposition processes, like dehydration, thermo-
gravimetry is the most suitable technique, and the most widely used
indeed, to get information useful both in applied and basic research.

The modern commercial thermogravimetric balances have eliminated
most of the experimental difficulties commonly encountered by re-
searchers until about 20 years ago. Ease of use and high sensitivity
(up to 10^{-7} g) make now feasible investigations previously very dif-
ficult. However one must be completely aware of the many experimental
variables that may strongly influence the results obtainable with
a thermogravimetric balance. Such experimental variables can be sum-
marized as follows:

- geometry of the balance
- shape of the pan
- mass and shape of the sample
- flow rate of the reducing gas (pure or mixed
  with inert gas)

 – rate of temperature increase

 – way of reaching constant temperature (for
   isothermal runs).

It may be seen that only variables connected with the actual exper-
iment have been considered, while other important factors can be detec-
ted in the previous history of the sample. Obviously, we do not intend
to deeply discuss here such thermogravimetric problems; however, some
typical results will be reported later.

We would recall here some difficulties connected with the possibil-
ity of using thermogravimetry in conditions simulating the actual
reduction of some industrial catalysts, namely that commercial thermo-
gravimetric balances are usually not qualified for work under pressure
and/or with high water concentrations in the reducing gas.

Very often it is necessary to obtain additional information about
the processes occurring during catalyst reduction; this goal can be
reached by physical methods of analysis of the gases leaving the thermo-
balance. Connections of thermobalances with quadrupole mass spectro-
meters, gas chromatographs, infrared spectrometers, etc. have been
already effected (ref. 5). They are strongly recommended when proces-
ses different from reduction and from dehydration may simultaneously
occur.

We will limit our discussion to the collection of thermogravimetric
data, which can be obtained by either dynamic heating or isothermal
method. In the case of catalyst reduction studies, the former is usu-
ally employed for fast characterization of the reduction process,
mainly on a comparative basis. Mathematical methods of data treatment
have been developped for the dynamic heating method (ref. 6); all these
are based on the equation

$$\frac{d\alpha}{dT} = \frac{Z}{q} e^{-E/RT} (1-\alpha)^n$$

where α = degree of transformation, T = temperature (°K), Z = frequency
factor, q = rate of temperature increase, E = activation energy,
n = reaction order.

However, the physical meaning of the kinetic parameters obtained
by such treatments of the experimental data is very uncertain, so that
it is probably preferable to rely on the data immediately available
from the thermogram, namely starting reduction temperature (T_S),
maximum reduction rate (R_m) and its corresponding temperature (T_m).
The best data can be obtained if the differential thermogravimetric
(DTG) curve is also available, as in most modern instruments. We
stress that, if a correct comparison among different catalyst samples

is to be done, the previously mentioned experimental factors must be kept strictly constant.

The isothermal method is more frequently used for basic studies on reduction mechanisms. The experimental result consists in a curve of degree of transformation versus time at constant temperature. The experimental curve must be fitted to a theoretical one obtained on the basis of reasonable hypotheses concerning the reduction mechanism.

Various models are presently available for the mathematical treatment of isothermal thermogravimetric data (ref. 7). Though they are valid for any gas-solid reaction occurring with loss or increase of weight, we will briefly discuss them only in the aspects concerning oxide reduction. All these models assume that the nucleation process, namely the initial formation of germs of the metallic or reduced oxide phase, is very fast with respect to the progress of the reduction, so that the presence of an induction period cannot be explained.

The simplest model, therefore more frequently used, is the unreacted shrinking core model. It assumes that the sample particle is completely non-porous, that the reduction occurs at the sharp interface between already reduced and unreduced solid and that in the particle, of simple geometric shape, there are no temperature gradients. In this very favourable case one can distinguish between reductions controlled by reaction at the phase boundary or by ash diffusion (however a shift from one controlling step to another usually occurs when temperature is changed, with possible existence of a wide range of intermediate states).

If the catalyst particles are porous and internal diffusion is very fast with respect to reduction, the homogeneous model should be applied, where reduction is visualized as occurring throughout the solid phase. However the mathematical treatment is very complex, so that some simplifications have been introduced. In the best known simplified model the particle is considered like an aggregate of small spheres, each of which is reduced according to the unreacted shrinking core model.

In the cases where the particle is porous and the reduction is fast with respect to ash diffusion, a modification of the unreacted shrinking core model has been developped, assuming that the reaction zone has a finite thickness.

For all these models more complex cases have been considered, assuming, for instance, irregular shape of the particle, temperature gradients inside and outside the particle, various reaction orders, particle contraction or expansion during reduction, various adsorption mechanisms of the reducing gas, more than one reducing agent, influ-

ence of particle size distribution, formation of cracks during reduc-
tion, etc.

The increasing complexity of the data treatment typical of these
more sophisticated models may sometimes discourage the catalysis
researcher; furthermore, he is aware that the conditions for the
validity of the various theoretical models are often very far from
the actual reduction procedures used for the industrial catalysts
(for instance, the frequently occurring retarding effect of water
is not taken into account). However, this seems to be the main road
along which one can hope to reach, soon or later, a comprehensive
picture of the complex phenomena occurring during the reduction of
industrial catalysts, with consequent benefit for the rational opti-
mization of this process.

4.2 Temperature programmed reduction (TPR)

This technique has been recently developed by Shell researchers
(ref. 8). The principle, on which TPR is based, can be summarized
as follows. If a hydrogen-inert gas (except helium) mixture (H_2
usually about 5%) is allowed to pass, successively, over the first
detector of a thermal conductivity cell, through the catalyst sample
placed in a furnace connected to a linear temperature programmer,
through an absorption trap able to collect any gaseous product of
catalyst reduction, finally over the second detector of the T.C.
cell, and the sample temperature is linearly increased, when hydrogen
will be consumed owing to catalyst reduction, the T.C. cell will be
unbalanced and a signal, proportional to the difference of hydrogen
concentration between inlet and outlet of the sample, will be received
by the recorder. If the gas flow is constant, such difference is
proportional to the rate of hydrogen consumption, namely to the rate
of catalyst reduction.

In practice, the TPR profile is quite similar to that arising
from DTG, but with the great advantages that the effect of any other
reaction simultaneous with reduction is eliminated and that, as the
reducing gas passes through the sample, not over, like in thermogra-
vimetry, the elimination of external diffusion effects is much easier.
Moreover the sensitivity of TPR measurements is often higher than
that of thermogravimetric measurements and, last but not least, the
required equipment is relatively inexpensive.

On the other hand, some difficulties may arise if accurate quan-
titative measurements are needed, as the calibration procedures are
still open to objections (according to Shell researchers an accuracy
of ± 10% can be reached). Moreover, like thermogravimetry, runs at
high pressures and high water concentrations are hardly feasible.

As TPR is a relatively recent technique, the influence of the various operating variables on the TPR data is still to be investigated. When a deeper knowledge of the capabilities of this technique will be available, it will surely represent a powerful tool to obtain information on catalyst reduction mechanisms.

4.3 Other techniques

While at present thermogravimetry and temperature programmed reduction are undoubtedly the most widely used techniques in research on catalyst reduction, in special cases the techniques hereafter mentioned may find application.

Differential thermal analysis (DTA). This well-known technique may give qualitative information in addition to the thermogravimetric data, if one can take advantage of the modern instruments simultaneously monitoring both thermogravimetric and DTA curves (however, when precise DTA data are required, the use of an indipendent DTA equipment is recommended). In fact, when complex simultaneous phenomena occur during catalyst reduction, the comparison of thermogravimetric and DTA curves may help to give an insight into the whole process.

DTA could be useful also to detect the total thermal effect of the reduction process in industrial conditions, however, as in the case of thermogravimetry, only appropriately built equipment can withstand high pressures.

Magnetic measurements. When the non reduced and/or the reduced phases include ferromagnetic or ferrimagnetic materials (Fe, Co, Ni, Fe_3O_4, etc.), one can take advantage of the possibility of measuring the saturation magnetization as a function of time to follow the reduction process with high sensitivity. However this technique has been scarcely used.

Mössbauer spectroscopy. The use of this powerful technique in catalyst reduction is practically confined to iron-containing catalysts. The main advantage of Mössbauer spectroscopy with respect to thermogravimetry and TPR is that it allows one to distinguish simultaneous reduction processes due to different oxides. On the other hand, as the recording of each Mössbauer spectrum takes some hours, it is necessary to cool the sample for the measurement, so that the reduction process is discontinuous.

5. REDUCTION MECHANISMS OF SOME INDUSTRIAL CATALYSTS

The title of this chapter is probably too ambitious, as, owing to the previously mentioned inadequate knowledge on catalyst reduction

carried out in industrial conditions, only the information coming
from basic research, carried out very often on single catalyst compo-
nents and in easy experimental conditions, is available at present.
Yet some interesting conclusions can be drawn from such basic knowl-
edge. In addition, we will report hereafter the results of reduction
characterization of some industrial catalysts.

5.1 <u>High temperature CO conversion catalyst</u>

    As we have previously seen in Chapter 3.1, the activation of this
catalyst involves mainly the reductions of γ-Fe_2O_3 and α-Fe_2O_3 to
Fe_3O_4. The mechanisms of these reductions have been studied in Mon-
tedison some years ago (ref. 9). Isothermal thermogravimetric runs
were performed in the temperature range 250-350°C in pure H_2 and
H_2-He mixtures. Samples were in the form of fine powders, so that the
influence of ash diffusion was minimized (according to ref. 10 it
begins above 8000 Å particle size). Qualitative and quantitative
analyses of the crystal phases in samples taken at various degrees
of reduction were carried out by X-ray diffraction.

    As concerns the reduction of γ-Fe_2O_3, it occurs through the solid
solution $Fe_{3-x}O_4$ $(0 \leqslant x \leqslant \frac{1}{3})$ without phase change. The kinetic equation
is of the type $\ln(1-\alpha) = -Kt$, with an activation energy of 29 Kcal/mole.
Two simultaneous reduction mechanisms are involved:
a) Fe^{2+} ions formed on the surface migrate through the lattice to
   occupy vacant octahedral sites;
b) electron trasfer from Fe^{2+} ions on the surface to Fe^{3+} ions in
   the bulk, therefore regenerating Fe^{3+} ions on the surface and
   allowing the reduction to continue.

    More important for our purposes is the reduction of α-Fe_2O_3, which
is usually the main component of the high temperature CO conversion
catalysts. It occurs with different mechanisms, depending on the
amount of lattice disorder present in the sample. In highly-disordered
samples α-Fe_2O_3 is firstly completely reduced to Fe_3O_4, which is
later reduced to Fe. For ordered samples (natural or treated at high
temperature) the reductions of α-Fe_2O_3 to Fe_3O_4 and of Fe_3O_4 to Fe
simultaneously occur. In both cases at the beginning of the reduction
an outer shell of Fe_3O_4 is formed, with a degree of disorder similar
to that of the parent α-Fe_2O_3 phase. As the reduction of α-Fe_2O_3
proceeds through the migration of Fe^{2+} ions and electrons from the
outer surface to the Fe_2O_3-Fe_3O_4 interface and as this migration is
easier in the case of disordered lattice, in well-ordered samples
the reduction of the outer spinel phase begins when a large amount
of α-Fe_2O_3 is still to be reduced. In the case of the high temperature

CO conversion catalysts the lattice disorder is obviously high (the surface area is of the order of 100 m^2/g), so that the risk of Fe formation is minimized.

Information about the influence of water vapour on the reduction of α-Fe$_2$O$_3$ to Fe$_3$O$_4$, though very important for industrial reductions, is scanty. According to a recent paper (ref. 11), the reduction rate is lowered by water vapour for Mg- and Li-doped α-Fe$_2$O$_3$, while for pure α-Fe$_2$O$_3$ it is firstly decreased, then increased. On this subject research work concerning the high temperature CO conversion catalyst is clearly needed.

Now we will discuss some results obtained during our investigations on the reduction behavior of the Montedison MHTC catalyst. In Table 4 we report some TPR data concerning laboratory preparations of the high temperature CO conversion catalyst, as function of both Cr$_2$O$_3$ concentration and method of preparation.

The method of preparation of all the samples reported in Table 4 is based on precipitation from FeSO$_4$ and Na$_2$CO$_3$ aqueous solutions, while chromium is added as Cr^{VI}. The following main conclusions can be drawn from Table 4 (samples A-B-C):

TABLE 4

TPR data of high temperature CO conversion catalysts (laboratory preparations).

Sample	Cr$_2$O$_3$ (%)	Shoulder temp.(°C)	α-Fe$_2$O$_3$ red.		Fe$_3$O$_4$ red.
			T_s (°C)	T_m (°C)	T_s (°C)
A	–	–	195	335	342
B	7.5	264	196	338	374
C	7.5	270	197	325	373
D	7.5	–	221	350	433

The definitions of T_s and T_m have been given in chapter 4.1

a) the presence of Cr in the catalyst has practically no influence on the reduction of α-Fe$_2$O$_3$ to Fe$_3$O$_4$, while the reduction of Fe$_3$O$_4$ to Fe is slightly hindered (samples A and B have been prepared by the same method);

b) as the shoulder on the α-Fe$_2$O$_3$ reduction peak is present only in Cr-containing samples, it has been attributed to the reduction of Cr^{VI} to Cr^{III} (this has been confirmed by chemical analysis, that gives a Cr^{VI} concentration of 0.5-1% in samples B and C).

Moreover, the data obtained for sample D show that it is possible, through special methods of catalyst preparation, not only to eliminate the harmful presence of Cr^{VI}, but also to obtain such a good distribution of Cr^{III} in the Fe oxides as to delay both α-Fe$_2$O$_3$ and

Fe_3O_4 reductions, the latter by about 90°C. It is expected that a better distribution of Cr^{III} in the catalyst should appreciably improve its life.

Some data concerning the reduction behavior of the Montedison industrial catalyst MHTC are reported in Table 5.
The good agreement of TPR and TG data is firstly to be noticed (compare T_m α-Fe_2O_3 red. and T_s Fe_3O_4 red. of runs 1 and 2). The attribution of the α-FeOOH decomposition peak comes immediately from comparison of run 1 with run 2 and of runs 2-3 with run 4. The determination of T_s α-Fe_2O_3 red. in TG runs was not possible owing to overlapping with the α-FeOOH decomposition peak (see the TPR value of T_s α-Fe_2O_3 red. and the TG values of T_m α-FeOOH dec.). The in-

TABLE 5

Reduction data of the Montedison catalyst MHTC (size 0.2-0.3 mm)

Run	Technique	Gas	α-FeOOH dec.		α-Fe_2O_3 red.		Fe_3O_4 red.	
			T_s (°C)	T_m (°C)	T_s (°C)	T_m (°C)	T_s (°C)	T_m (°C)
1	TPR	H_2 5% N_2 95%			195	325	370	
2	TG	H_2 5% N_2 95%	125	235		330	380	640
3	TG	H_2	125	225		290	315	385
4	TG	H_2	130	225				

The rate of temperature increase was 2°C/min for all the runs.
The definitions of T_s and T_m have been given in chapter 4.1.

fluence of H_2 concentration on the reduction of α-Fe_2O_3 to Fe_3O_4 and especially on the reduction of Fe_3O_4 to Fe is quite evident (the same phenomenon was reported in ref. 9). From the relatively low values of T_s Fe_3O_4 red. it is clear the need of excess water vapour during industrial reductions, where catalyst temperature may well exceed 400°C.

Finally, we will notice the strictly similar reduction behavior of laboratory and industrial high temperature CO conversion catalysts, when prepared by same method (compare sample B of Table 4 with run 1 of Table 5). The only difference is that no shoulder due to the presence of Cr^{VI} was detected in the industrial catalyst.

5.2 Low temperature CO conversion catalyst

As it was shown in chapter 3.2, the activation of this catalyst involves the reduction of CuO to Cu. CuO and ZnO are practically the only crystalline phases detected in the commercial Cu-Zn-Al oxide catalysts. However, in some of them the presence of small amounts of the following crystalline compounds can be detected by X-ray diffraction: γ-alumina, zinc or copper aluminate, basic zinc

carbonate, basic copper carbonate (the presence of the two last compounds is clearly due to low calcination temperature).

The reduction degree of ZnO at temperatures below 230°C should be negligible; in fact, the formation of brass reported in ref. 3 occurs in appreciable amount at temperatures higher than 250°C, while at lower temperatures it requires a very long time. Therefore during catalyst activation, unless the catalyst is incautiously overheated, the reduction of ZnO can be neglected.

The reduction of pure CuO has been studied by many Authors; Bond (ref. 29) and Schoepp (ref. 30) seem to have performed the most comprehensive thermogravimetric investigations. The method of preparation was found to have a strong influence on the reduction behavior. The reduction kinetics were satisfactorily interpreted in terms of both instantaneous and constant-rate nucleations (ref. 31).

Though the basic knowledge concerning the reduction of pure CuO may be an useful starting-point, we clearly need information about the reduction of CuO dispersed over a ZnO-Al_2O_3 mixed carrier. This kind of information is almost completely lacking. We are aware only of a Bulgarian DTA study (ref. 32) on the reduction of two commercial catalysts not containing alumina (CuO-ZnO and CuO-ZnO-Cr_2O_3). The starting reduction temperatures were, respectively, 130°C and 150°C with hydrogen concentration 2.6% and heating rate 6°C/min. The CuO reduction was found to occur in two stages: firstly to Cu_2O, then to Cu. However, from our TG and TPR experiments we never obtained any evidence of a two-stages reduction process.

We are investigating the influence of various factors concerning catalyst composition and preparation procedure on the reduction behavior. Some preliminary results are reported in Table 8.

TABLE 8

TPR data of pure and supported CuO catalysts.

Sample	Chemical composition	T_s (°C)	T_m (°C)
S	CuO	180	250
LTC 4	CuO	110	198
LTC 6	CuO-ZnO	140	200
LTC 1	CuO-ZnO-Al_2O_3	157	202

The definitions of T_s and T_m have been given in chapter 4.1

While sample S has been prepared by thermal decomposition of $Cu_2(OH)_2CO_3$, the preparation of sample LTC 4 has been performed

with the procedure used for the Montedison catalyst. It may be noticed that the strong influence of the preparation method on the reduction behavior of CuO, already reported by Bond (ref. 29), has been confirmed. By comparison of the TPR data of the samples of the LTC series, all prepared with the same procedure, it is possible to conclude that the retarding effect of ZnO addition concerns only the nucleation of metallic Cu. A further retarding effect on Cu nucleation is given by the addition of Al_2O_3.

The reduction behavior of industrial catalysts is also under investigation in our laboratories. Some preliminary results are reported in Table 9.

TABLE 9

TPR data of some low temperature CO conversion catalysts.

Catalyst	$T_s(°C)$	$T_m(°C)$
Montedison	158	218
A	127	177
B	105	158
C	129	195

The definitions of T_s and T_m have been given in chapter 4.1.

Appreciable differences exist among the values of T_s and T_m of the examined catalysts. Obviously, as the preparation method of catalysts A, B and C is not known, we cannot draw any conclusion from the above-reported data, which only suggest the need of further studies. However, we were successful in preparing a catalyst of lower reducibility; we think that this feature should make easier the temperature control during industrial reduction.

5.3 Ammonia synthesis catalyst

As we have seen in chapter 3.3, the activation of this catalyst occurs by the endothermic reduction of Fe_3O_4 to Fe, which proceeds without intermediate phases (FeO is not stable below 570°C).

As the catalyst (promoted fused magnetite) is practically non-porous, the unreacted shrinking core model could be used to handle the isothermal thermogravimetric data. Unfortunately the catalyst particle shape is very irregular, while the model is strictly valid only for spherical particles of uniform size; a mathematical treatment for various spherical particle size distributions is however available (ref. 12).

The classical unreacted shrinking core model has been applied to the reduction of a commercial ammonia synthesis catalyst by some Polish researchers (ref. 13). Cube-shaped catalysts particles were used. It was found that the reduction process proceeds in the inter-

mediate region between chemical reaction and ash diffusion controls.
However, the temperature range investigated (450-550°C) is at the
upper limit of the usual reduction temperatures of the ammonia syn-
thesis catalysts (some of them begin to reduce below 350°C). The
same Polish group (ref. 14) developped a mathematical model for the
constant-rate reduction performed at temperatures slowly increasing.
Though the starting temperature chosen is rather high (400°C) and
the total reduction time too short (15 hours), and though the inter-
actions among neighbouring particles were not considered, this work
represents the first attempt towards the mathematical modeling of
catalyst reduction in industrial conditions.

However, it is our opinion that the basic knowledge of the reduc-
tion mechanisms of promoted magnetites is still too incomplete to
allow a sound development of the applied research. With this concept
in mind, we have carried out some investigations with the aim of
clarifying the basic phenomena occurring during magnetite reduction.
The problem was attacked through an isothermal thermogravimetric
study (ref. 15) of pure magnetite reduction in the low-temperature
range (220-330°C) that should allow both to minimize the influence
of ash diffusion and to work with the low water concentrations re-
quired in industrial reductions. The experiments were carried out
by means of a sensitive electrobalance; powdered magnetite with
particle size in the range 0.5-3 μm was used (according to ref. 16
the influence of ash diffusion should be negligible with particle
size below 200 μm).

It was found that the reduction rate decreases with the increa-
sing of sample mass in the range 0-30 mg; it also decreases when
water vapour (1500 vpm) is added to the reducing gas (pure hydrogen).
This behavior can be explained in terms of interparticle diffusion
phenomena. In fact, as in TG experimental conditions there is no
hydrogen flow through the powder, a water concentration gradient
may easily arise between the interior of the sample and the hydrogen
stream. In other words, the magnetite heap tends to react as a whole
grain from the outer layers towards the interior. This is confirmed
by the presence of many unreacted particles in samples reduced up
to 65%. However, this interparticle diffusion should be considered
more properly, as suggested in ref. 17, a surface diffusion consi-
sting, owing to the high reactivity of finely divided iron towards
oxygenated compounds, of repeated oxidation by water-reduction by
hydrogen steps. This is also in accordance with the relatively high
value of the activation energy (14.5 kcal/mole). It may be observed
that the situation occurring in these experiments (interaction of

reduced particles with water vapour coming from the neighbours)
reminds what occurs, on a larger scale, during reduction in indu-
strial conditions, where, however, also ash diffusion is to be taken
into account. Unfortunately no mathematical model is available, as
yet, to describe such a complex behavior.

It was also found that an induction period is always present if
dry hydrogen is used and that it disappears if water vapour is added.
As mixing of magnetite with Pt black has no influence on the induc-
tion period, the rate-determining step in the initial stage of the
reduction should not be the formation of metallic germs, but rather
the hydroxylation of the oxide surface. Surface hydroxyls should
indeed make easier the migration of dissociated hydrogen (ref. 18).

The substitution of Fe^{3+} with Al^{3+} ions in magnetite decreases
the reduction rate and makes the induction period to disappear
(ref. 19). The latter fact could be related to a higher amount of
hydroxyls connected to Al, the former to the formation, during re-
duction, of $FeAl_2O_4$ groups, unreducible in our experimental condi-
tions, that could decrease the advancing of the reacting interface.
In fact, it was demonstrated that $FeAl_2O_4$ groups included in the
lattice of -Fe occur in the reduced samples (ref. 20).

We have also carried out isothermal thermogravimetric runs to
measure the reduction rate of some commercial catalysts on samples
of different particle size (1-5 μm and 0.3-0.4 mm). The influence
of sample mass on the reduction rate was much lower in the case of
0.3-0.4 mm samples. It means that for these samples interparticle
diffusion is negligible with respect to the intraparticle one. The
induction period, like in the Al-containing magnetites, is not pre-
sent. Values of the reduction rate $K_{0.5}$ (slope of the reduction cur-
ve at 50% conversion) of some commercial catalysts (particle size
0.3-0.4 mm) are reported in Table 6.

TABLE 6

Reduction rate of some commercial catalysts for ammonia synthesis.

Catalyst	$K_{0.5} \cdot 10^3$ (min^{-1})	Experimental conditions	
MSFN	1.63	Temperature	345°C
A	0.68	Sample mass	20 mg
B	1.40	Reducing gas	pure H_2
C	3.15		

It may be seen that appreciable differences exist among the examined
catalysts, though the chemical composition is practically the same.
This fact shows the importance of the preparation method, whose
details obviously are not disclosed by manufacturers, with respect

to the reduction process. From a practical point of view, a very
low reducibility makes easier the control of water concentration in
the bed, but may prolong too much the reduction period, while the
opposite holds if the reducibility is very high.

For a better characterization of the reduction behavior of com-
mercial catalysts for ammonia synthesis, we have also carried out
dynamic heating thermogravimetric reduction runs. The results obtained
are reported in Table 7. There are some catalysts (MSFN, F, H) that
begin to be reduced, in our experimental conditions, at about 350°C,
while for others (D, E, G) the starting reduction temperature is
about 380°C. In the DTG profiles of the former group a shoulder cen-
tered at about 420°C is present, which is completely absent in those
of the latter. As in catalysts MSFN, F and H a small amount of FeO

TABLE 7

TG reduction data of some commercial catalysts for ammonia synthesis.

Catalyst	T_s (°C)	T_m (°C)	$R_m \cdot 10^3$ (min^{-1})
MSFN	345	590	9.9
D	385	575	12.3
E	375	570	13.8
F	345	580	9.5
G	380	595	9.9
H	355	600	9.8

Experimental conditions: Rate of temperature increase 5°C/min
                         Reducing gas   pure H_2
The definitions of T_s, T_m and R_m have been given in chapter 4.1.

is present (estimated 1-5% from X-ray diffraction powder pattern)
and as FeO is usually reduced at temperatures lower than Fe_3O_4, the
lower T_s values of catalysts MSFN, F and H can be explained. This
is confirmed by the results obtained by other Authors (ref. 21),
who studied the reduction of FeO-containing ammonia synthesis cata-
lysts by Mössbauer spectroscopy. These Authors found also different
reduction mechanisms depending on FeO content (4% and 27%).

If the R_m values reported in Table 7 are considered, it may be
noticed that the catalysts D and E are more easily reducible than
the others (the same holds for catalyst C in Table 6). We have found
that in the less easily reducible catalysts FeO and $CaFe_3O_5$ are
present (these two compounds are always present together, as shown
also in ref. 22), while in catalysts C, D and E two unidentified
crystal phases (probably complex ferrites) have been detected. The
same two phases have been found in a catalyst prepared in our labo-
ratory by very fast cooling of fused promoted magnetite. This is a
clear indication of the influence that the method of preparation
may have on the reduction behavior of ammonia synthesis catalysts.

The final degree of reduction has been reported (ref. 23) to be
a crucial point for the activity of ammonia synthesis catalysts.
For promoted catalysts the iron specific activity always increases
with the reduction degree, but, due to the possible occurring of
sintering phenomena, the catalytic activity may reach a maximum va-
lue, then decrease. For a better understanding of this problem, a
discussion of the structure of the reduced catalyst is certainly
useful. According to our (refs. 20 and 24) and Hosemann and coworkers
(refs. 25-26) results, in alumina-containing reduced catalysts
$FeAl_2O_4$ groups are endotactically built into the α-Fe lattice (one
$FeAl_2O_4$ group takes the place of seven Fe atoms), causing paracry-
stalline distortions. Other Authors (ref. 27) suggest that Al_2O_3,
not $FeAl_2O_4$, is present in samples reduced over 400°C. However, the
X-ray diffraction lines of $FeAl_2O_4$ were clearly detected by us after
high temperature annealing in inert atmosphere of samples reduced
at 500°C. Moreover, the presence of Al_2O_3 groups was excluded on
the basis of SIMS experiments (ref. 28).

Another debated argument is the constitution of the $FeAl_2O_4$ groups
(are single groups or clusters, and in the latter case what is their
size ?). Hosemann has recently demonstrated (ref. 26) that the pre-
sence of paracrystallinity can be explained only if no more than two
$FeAl_2O_4$ groups are joined together. On the contrary, other Authors
(ref. 27), on the basis of Mössbauer spectroscopy data, stated that
the size of the inclusions in the α-Fe lattice, either $FeAl_2O_4$ or
Al_2O_3, should be at least 30 Å. We too suggested the presence of
small clusters of $FeAl_2O_4$ (ref. 20). However, if according to
Hosemann's data (ref. 26), we assume an average size of 15 Å for
each $(FeAl_2O_4)_2$ cluster, in the case of our alumina-promoted samples
about 250 clusters are included in each α-Fe crystallite. In this
circumstance it may be calculated that about 3% of the Fe atoms
are contacting the $(FeAl_2O_4)_2$ clusters, while the remaining 97% is
in the same structural configuration as in pure α-Fe. Such a small
percentage could not have a detectable influence on both Curie point
and Mössbauer parameters of α-Fe. Moreover, Hosemann questions (ref.
26) the parallelism between Fe-Al alloys and reduced alumina-promo-
ted Fe catalysts, on which other Authors (ref. 27) have based their
conclusions. If we take into account the structure of Al-containing
magnetites, where the Al^{3+} ions are randomly distributed in the spi-
nel lattice, and also the reduction mechanism (shell by shell from
the external surface towards the interior), for reduction tempera-
tures below 500°C it does not seem reasonable to assume that a group
like $FeAl_2O_4$ can easily diffuse in the α-Fe lattice to reach other

groups and form large clusters. This may be another argument in sup-
port of Hosemann's results.

The disorder introduced in the alumina-cointaining catalysts
through their reduction has also some relevancy with their catalytic
activity. In fact, we have found (ref. 24) that the specific activity
of iron increases in the presence of alumina, which is not therefore
a structural promoter only.

While the alumina-containing catalysts have been studied rather
deeply, this is not the case of the industrial catalysts, which con-
tain also K, Ca, Mg and Si oxides. Clausen et al. (ref. 21) found
evidence of some unreduced Fe compound in their Mössbauer spectra
of catalysts reduced at 550°C and suggested that it could involve
Ca. In fact, we have detected $CaFe_3O_5$ in some reduced commercial
catalysts. It is to be expected that interesting information could
be obtained on the mechanisms of the reduction process and its cor-
relations with catalytic activity if thorough studies were accom-
plished on magnetites promoted with the various oxides used in the
industrial practice.

CONCLUSIONS
After having discussed the industrial procedures for the reduction
of some commercial catalysts (high and low temperature CO conversion
and ammonia synthesis), the experimental techniques for laboratory-
scale investigations on the reduction process and the currently
available basic knowledge on the reduction mechanisms, we will sum-
marize here the present status of the problem.

The degree of knowledge of the reduction mechanisms of the above-
mentioned industrial catalysts should be defined insufficient. How-
ever, it is slightly better for the ammonia synthesis catalyst. As
concerns the reduction mechanisms of the pure main compounds (α-Fe_2O_3,
CuO, Fe_3O_4), the degree of knowledge is fairly good, however there
is wide space for improvement. For instance, more information on
the influence of the composition of the various reducing gas mixtures
used in the industrial practice on the reduction rate of these pure
compounds should be obtained.

For the complete knowledge of the reduction behavior of many com-
mercial catalysts much is still to be done. Information is lacking
about the influence of the other catalyst components on the reduc-
tion of the main compound (only the influence of Al_2O_3 on the reduc-
tion of Fe_3O_4 is fairly known). Also the influence of the gaseous
phase composition is not sufficiently known, except for the effect
of water vapour on the reduction of Fe_3O_4.

We have remarked the experimental difficulties that hamper the
collection of meaningful data about catalyst reduction. Most of the
published thermogravimetric data, though representing the main source
of information, should be considered with much caution, as not all
the experimental factors that may have a strong influence on the
obtained results were previously clearly recognized. Temperature-
programmed reduction seems to be a very promising technique, but it
requires deeper studies before a reliable evaluation of its capabi-
lities can be done. Many mathematical models are available to handle
the kinetic data concerning oxide reduction in gas—solid systems,
but their limitations, due to the need of avoiding mathematical dif-
ficulties, are still too many. However, some progress in this field
is to be expected in the near future.

In the general remarks on the previous Symposium on catalyst pre-
paration the editors of the proceedings noticed the almost complete
lack of reports about catalyst activation. The present paper prob-
ably explains some reasons of such a disappointing fact. It is to
be hoped that, starting with this Symposium, and still more in the
forthcoming ones, catalyst activation will receive increasing at-
tention in catalysis research.

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