THE PREPARATION AND CHARACTERISATION OF IRON AND VANADIUM OXIDE MONOLAYER
CATALYSTS ON TiO_2 AND ZrO_2

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SUMMARY
    Iron oxide and vanadium oxide monolayer catalysts have been made by reacting
toluene solutions of the corresponding acetylacetonates with the surface OH
groups of TiO_2 or ZrO_2. The product of the reaction, acetylacetone, competes
with the acetonates for the adsorption sites. Of the four adsorption methods
attempted, continuous adsorption and high-temperature adsorption gave approx-
imately complete monolayers; the latter is the more promising method as it is
more rapid and consumes fewer chemicals.
    TPR and CO-oxidation measurements for the Fe_2O_3-TiO_2 samples show that the
monolayer is well-spread and that there is a significant interaction with the
support. The iron cannot be reduced beyond the FeII state, possibly due the
formation of a surface ilmenite. The Fe_2O_3 monolayers are less active for CO
oxidation than is bulk Fe_2O_3. Impregnation of TiO_2 by $Fe(NO_3)_3$ gives rise to
small crystallites of Fe_2O_3 which have higher activities for CO oxidation than
do the monolayer materials.

INTRODUCTION
    Oxidation catalysts containing transition metal oxides play an important role
in industrial processess. However, the choice of the catalyst for these pro-
cesses is mostly empirical [1-2] as correlations between the structure of such
catalysts and those properties which determine their activities and selectivit-
ies are not well established. In order to attempt to establish such correla-
tions, we have prepared and studied well-dispersed oxides supported on various
high-area oxidic materials using a general preparative method involving adsorp-
tion of $Me(AcAc)_n$ (AcAc = acetylacetone); as reported previously [3-4], this
method probably gives monolayer spreading. In particular, we have described the
preparation of catalysts containing Fe_2O_3 and V_2O_5 on various supports.
    Monolayer materials have the advantage that the active metal oxide is more
effectively used than if it is present as crystallites on the support, as is
often the case when wet or dry impregnation are used. Moreover, the mechanical
and thermal stabilities are also increased, larger surface areas (depending on
the support used) can be obtained and the influence of the support is at its
maximum. In previous publications, we have shown how the structure of the sup-
port in such catalysts influences their activity and selectivity for the oxida-
tion of methanol, toluene or o-xylene [5]. The preparation technique used can

have great influence on the spreading of the oxide on the support. We have now studied in greater detail the method of preparation of the monolayer materials, paying particular attention to the way in which the $Me(AcAc)_n$ complexes are reacted with surface hydroxyl groups. The aim is thus to study the factors that influence the adsorption of $Me(AcAc)_n$ on oxidic supports in the preparation of monolayer catalysts and to determine the differences between monolayer and bulk oxides. In the present paper, we report on the preparation of iron and vanadium oxide materials supported on titanium and zirconium oxides, on the use of temperature programmed reduction to characterise the catalysts and on the use of CO oxidation as a test reaction.

EXPERIMENTAL

Materials

Al_2O_3 ($80m^2g^{-1}$) and TiO_2 (68% anatase and 32% rutile; $50m^2g^{-1}$) were obtained from Degussa, ZrO_2 (monoclinic; $11.5m^2g^{-1}$) from Viking Chemicals, and $Fe(AcAc)_3$, $VO(AcAc)_2$ and toluene from Merck (Analytical Grade).

Methods

Four methods are used to prepare the supported oxidic catalysts.

(i) Continuous adsorption. A solution of $M(AcAc)_n$ in toluene is passed slowly (50 cm^3h^{-1}) through a bed of support particles. The adsorption is assumed to be complete when the concentrations at the outlet and inlet are the same.

(ii) Batch adsorption. A solution of $M(AcAc)_n$ in toluene is added to the support particles and the slurry is stirred or shaken for a period between 20 and 500 h.

(iii) Batch adsorption at high temperature. A solution of $M(AcAc)_n$ in of toluene is added to the support particles and is heated with stirring at 130^oC for a period between 1 and 3 h.

(iv) Wet impregnation. Water is slowly evaporated from a stirred slurry of the support particles suspended in an aqueous solution of $Fe(NO_3)_3$, the temperature being maintained at 95^oC (2 to 2.5 h).

After the preparation, the resultant catalyst material is dried for 1h at 100^oC and is then calcined in air for 2h at 450^oC.

The test reaction used here, CO oxidation, is carried out in a continuous flow reactor with a fixed bed of 0,5g catalyst (particle size 0,3-0,6mm); a gas flow of $50mlmin^{-1}$ (1 atm., 20^oC) consisting of $1 - 1,5%$ CO, $1 - 1,5%$ O_2 and $97 - 98%$ He is used. The composition of the product gas mixture is measured by gas chromatography.

TPR (temperature programmed reduction) experiments are performed with an apparatus described elsewhere [6] using a heating rate of 16^oCmin^{-1} and a flow of $10mlmin^{-1}$ of 6% H_2 in Ar. The amount of catalyst used was chosen so that the

amount of vanadium or iron in the reactor in every experiment was about 1.5 mg.

Analysis of the Catalysts

Metal contents of the catalysts were determined by X-ray fluorescence; BET surface areas and X-ray powder diffraction patterns were obtained as described previously.

RESULTS AND DISCUSSION

Catalyst Preparation

Preliminary experiments showed that the $Fe(AcAc)_3$ could be brought onto a TiO_2 surface either from from the gas phase or from the liquid phase. Sublimation of $Fe(AcAc)_3$ onto the TiO_2 resulted in a catalyst which was visibly inhomogeneous, consisting of light and dark grains; analysis of these showed them to have Fe contents of 1.07 and 2.7 wt.% Fe respectively. This method was therefore not used further.

Adsorption of $Fe(AcAc)_3$ from toluene on TiO_2 was found to be a very slow process as can be seen from the results of Fig. 1. Only after some 20 h was

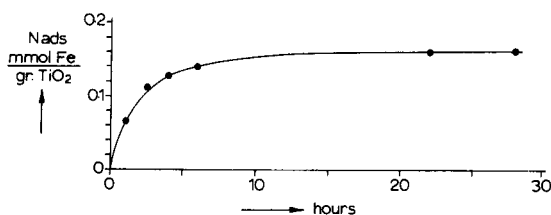Fig. 1. Dependence on time of the amount of $Fe(AcAc)_3$ adsorbed on TiO_2 at $20^{\circ}C$; C_o = 4 mmol 1^{-1}, volume toluene = 300 ml, 1 g TiO_2. (0.1mmol = 0.56 wt% Fe).

adsorption apparently almost complete. However, a series of experiments was carried out with adsorption times of 14 days and it was found that the extent of adsorption was now approximately 30% higher. Fig. 2 shows the dependence of the amount of Fe adsorbed on TiO_2 as a function of the concentration of the impregnating solution for adsorption times of 28 h and 14 days; in both cases, the influence of the concentration was found to be negligible above 1.5 mmol 1^{-1}. It is probable that the limiting uptakes shown in Figs. 1 and 2 correspond to approximately a monolayer of $Fe(AcAc)_3$ adsorbed on the TiO_2. If one takes the area occupied by one $Fe(AcAc)_3$ molecule to be 50 A^2 [7], a quantity of 0.16 mmole $Fe(AcAc)_3$ (0.9 wt% Fe) is calculated as the monolayer capacity of the TiO_2 (area 50 m^2g^{-1}) and this is the limiting value reached after 28 h adsorp- tion (Figs. 1 and 2). The level of adsorption achieved after 14 days must therefore correspond to the adsorption of more than a monolayer of $Fe(AcAc)_3$. From

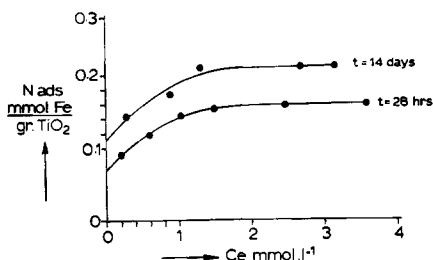Fig. 2. Dependence on concentration of the amount of Fe(AcAc)$_3$ adsorbed on TiO$_2$ for two different times at 20°C; volume of toluene = 300 ml, 1 g TiO$_2$.
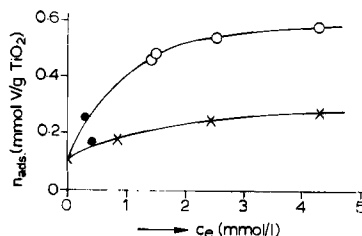
Fig. 3. Dependence on concentration of amount of VO(AcAc)$_2$ adsorbed at 20°C on TiO$_2$ for two different volumes and two different amounts of TiO$_2$; O 200ml, 2g TiO$_2$; O 200ml, 1g TiO$_2$; x 100ml; 2g TiO$_2$. (0.1 mmol V = 0.5 wt%V)

thermogravimetric experiments carried out after adsorption [3], it appears that the adsorbed Fe(AcAc)$_3$ looses AcAc-groups by adsorption with time.

The same type of behaviour as described above was found (see Fig. 3) for the adsorption of VO(AcAc)$_2$ on the same TiO$_2$, it also being found that the extent of adsorption depends strongly on the total volume of the solution from which adsorption occurs; the amount adsorbed is much higher if a large volume of solution is used relative to the weight of TiO$_2$. We believe that this is a result of an increased desorption of AcAc groups (as acetyl acetone HAcAc [3]) when the volume of the solution is higher.

To show that the reaction product HAcAc competes with the metal complex for sites on the support surface, the results shown in Fig.4 for the adsorption of
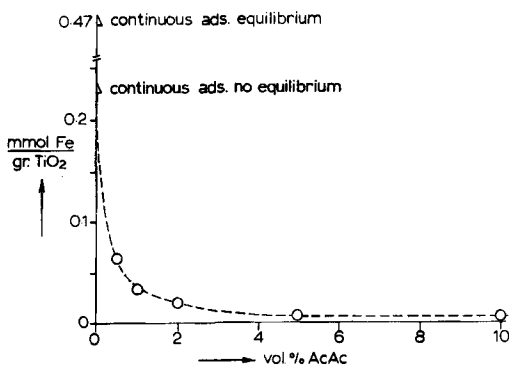

Fig. 4. Dependence on concentration of HAcAc of the amount of Fe(AcAc)3 adsorbed on TiO$_2$ at 20°C; volume of toluene = 100ml, 2g TiO$_2$.

$Fe(AcAc)_3$ on TiO_2 were obtained; different amounts of HAcAc were added to a $Fe(AcAc)_3$ adsorption solution in a constant volume (100 ml) of toluene to which a constant weight (2g) of TiO_2 was added.

In order to keep the concentration of the HAcAc formed during the adsorption as low as possible, continuous adsorption experiments were carried out by lead- ing a fresh solution of $Me(AcAc)_n$ over the support; this allows the product HAcAc to be removed together with the unused reactant. A typical example is given in Fig. 5, where the concentration of the effluent from the adsorption
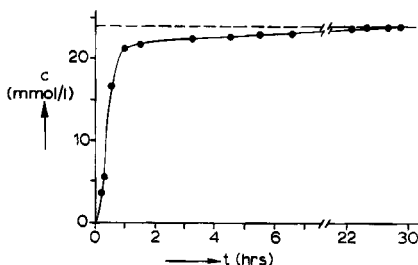

Fig. 5. Breakthrough curve for the continuous adsorption of $Fe(AcAc)3$ on TiO_2: results for a 2.1 wt% Fe catal- yst; C_o = 24mmol 1^{-1}, flow = 62 ml h^{-1}.

vessel is given as a function of time. In this case, the amount of Fe adsorbed on TiO_2 was found to be 2.1 wt%. The results for continuous adsorption experi- ments with both the iron and vanadium complexes on TiO_2 and ZrO_2 are summarised in Table 1 where they are compared with the results of comparable batch ad- sorption experiments for the TiO_2 support and for the V complex on ZrO_2; a limited number of these results were also given in reference [3]. Also included in the table are the percentages of the theoretical coverages achieved, these being based on figures of 2.8 wt% Fe or 2.5 wt% V for the maximum coverage calculated for a TiO_2 support with an area of $50m^2g^{-1}$ [3]; it should be noted that these theoretical monolayer coverages are based now on adsorbed oxide species, the assumption being that all the AcAc groups of the adsorbing complexes can be removed during the adsorption process. For the TiO_2 support, it is clear that a higher coverage is achieved in the continuous adsorption experiments than in the batch experiments. This appears not to be the case for the ZrO_2 support. A surface concentration of 2.64 wt% Fe (96% monolayer) can be reached on TiO_2 by the continuous adsorption method after adsorption times longer than 30 h.

In both batch and continuous adsorption experiments, it takes a long time to

TABLE 1

Comparison of batch and continuous adsorption of $Fe(AcAc)_3$ and $VO(AcAc)_2$ on TiO_2 (50 m^2g^{-1}) and ZrO_2 (11.5 m^2g^{-1}) at 20 °C.

Support	Weight /g	Me(acac)$_n$	CO /mmol1^{-1}	Time /h	volume /ml	%Me	%monolayer
TiO_2	1.0	Fe	11.10	70	200	1.55	55
TiO_2	2.0	Fe	24.00	31*	cont$^+$	2.64	94
TiO_2	2.0	V	9.08	72	100	1.22	49
TiO_2	5.1	V	4.40	11	cont$^+$	2.47	96
ZrO_2	2.5	Fe	24.40	1**	cont$^+$	0.38	59
ZrO_2	1.0	V	6.04	70	160	0.37	64
ZrO_2	1.9	V	3.73	24	cont$^+$	0.37	64

* Presented in reference [3] erroneously with adsorption time 1 h.
** Already presented in reference [3]; given here for completness.
\+ Continuous adsorption; flow 50-60 ml h^{-1}.

TABLE 2

High temperature adsorption (130°C) of $Fe(AcAc)_3$ on TiO_2 (50 m^2g^{-1}).

Adsorption method	Concentration /gl^{-1}	Fe /%wt	S_{BET} /m^2g^{-1}	k_{500} /$10^{-8}msec^{-1}$	k_{500} /$10^{-8}m^3g^{-1}sec^{-1}$
Batch*	2.75	1.11	45	–	–
Batch	2.75	1.61	45	–	–
Batch	8.25	2.35	42	1.5	63
Continuous**	7.5	2.85	43	1.3	56
Batch two***	7.3	4.4	39	1.2	47
Batch three***	7.3	5.5	32	1.6	51
3B+C$^+$	7.5	6.35	35	1.2	35

* Volume = 80ml; T = 130°C; time = 1-3h.
** T = 80°C; time = 15h; flow = 15ml h^{-1}.
*** Repeated adsorption (either two or three times) after calcination of the catalyst for 2h at 450°C.
\+ Batch adsorption conditions (three adsorptions) as above, then one continuous adsorption at 80°C for 10 h; flow = 15ml h^{-1}.

reach almost the theoretical monolayer coverages. In order to try to reduce the adsorption time, high temperature adsorption at 110 – 130°C was tried using both methods on TiO_2 (area = 50 m^2g^{-1}) for both $VO(AcAc)_2$ and $Fe(AcAc)_3$; the results for the Fe complex are shown in Table 2. In both cases, monolayer or near-monolayer coverages were achieved within 3 h. Short adsorption times at low concentrations (2.75 g l^{-1} is 1.07 mmol.l^{-1}) of $Fe(acac)_3$ yielded sub-monolayer catalysts, while higher adsorption times at higher concentrations (8.25 g l^{-1} is 32.23 mmol.l^{-1}) yielded reproducibly 2.35 wt% Fe on TiO_2 (average of three measurements), i.e. 84% of the theoretical monolayer. Continuous adsorption at 80 °C for 15 hours yielded 102 % of the theoretical monolayer. By successive adsorption experiments each after calcination at 450 °C for two hours, the higher amounts given in Table 2 were obtained. From these results, it is clear that an extra amount is adsorbed after calcination but that this is much less than the first amount adsorbed, apparently because less $Fe(AcAc)_3$ can be adsorbed on Fe_2O_3 than on the fresh support. At the higher percentages, the BET surface area also decreases, an observation which was not made for mono-layer or submonolayer catalysts. No Fe_2O_3 diffraction lines could be detected for any of the catalysts examined.

Catalyst Characterisation

TPR measurements showed a striking difference between catalysts with 2.85 wt% Fe or higher compared with those of a lower Fe content, as is shown in the results of Fig. 6; at and above 2.85 wt% Fe, a second reduction peak is found, its magnitude increasing with the percentage iron. The temperature of reduction corresponding to the first peak also increases with Fe content (from 360 to 400 °C)
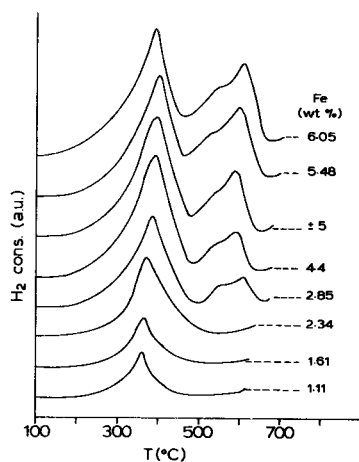

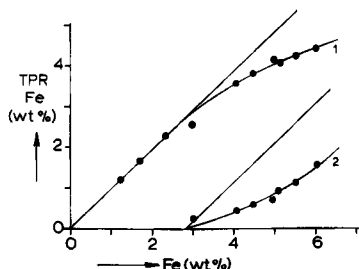Fig. 6. TPR profiles for Fe_2O_3 on TiO_2 for different wt% Fe.

Fig. 7. Dependence of the H_2 consumption during TPR for the data of Fig.7.

while maximum of the second peak remains almost constant. The area of the first peak increases linearly with Fe content, as shown in Fig. 7, until the iron content is 2.5 wt% Fe, i.e. approximately the monolayer coverage for this TiO_2 sample (area 50 m^2g^{-1}). Beyond the monolayer coverage, the size of the first peak increases less rapidly and the area of the second peak begins simultaneously to increase. The amounts of hydrogen consumed in the reduction process agree with the amount of iron in the catalyst only if we assume that the well-spread Fe_2O_3 giving the first peak is reduced only to FeO while the Fe_2O_3 giving rise to the second peak is reduced fully to Fe; the lack of complete reduction in the first stage is probably caused by a strong interaction between TiO_2 and the FeO formed on reduction. We therefore suggest that there are two Fe_2O_3 phases present in the calcined catalyst, the oxidic species corresponding to the monolayer and a second phase perhaps consisting of micro-crystallites. The TPR profiles of the reduction of samples of bulk Fe_2O_3 prepared from $Fe(AcAc)_3$ and $Fe(NO_3)_3$ are shown in Fig. 8; these show a small peak at 385-395°C and a split peak with maxima at 600 - 605°C and 654 or 718 °C respectively. From the consumption of H_2 per gram of Fe_2O_3, it is calculated that the first peak
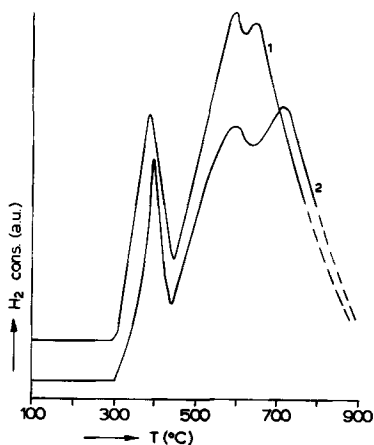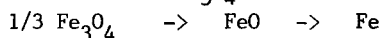

Fig. 8. TPR profiles for unsupported Fe_2O_3 prepared from $Fe(AcAc)_3$ and $Fe(NO_3)_3$.

accounts for the reduction of Fe_2O_3 to Fe_3O_4 and the second and the third peaks for the reduction of Fe_3O_4 to Fe, possibly in the two steps:

$$1/3 \ Fe_3O_4 \quad -> \quad FeO \quad -> \quad Fe$$

Thus, if the second peak in the TPR profile of catalysts with more than a monolayer (Fig. 6) corresponds with the reduction from Fe_3O_4 to Fe, than part of the first peak for these samples should belong to the reduction of Fe_2O_3 to Fe_3O_4. This is not, however, consistent with iron percentages determined by X-ray fluorescence. We shall return to this problem in a later section.

CO Oxidation Experiments

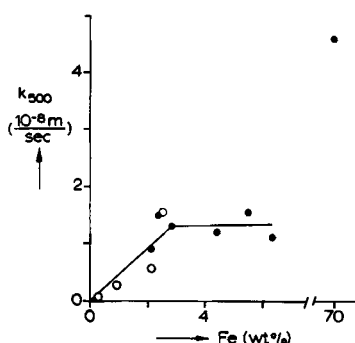CO oxidation experiments with these catalysts given in Fig. 9 are consistent

Fig. 9. Dependence on wt% Fe of the rate constant for CO oxidation at 500K.

with the TPR results. Up to 2.8 wt% Fe, there is an lineair increase in activity (Give in legend: part of the results marked O are from our earlier publication (3)). But at higher percentages, the activity stays constant as long as the lower total surface area is taken into account; if this is not done, then the activity decreases slightly. The activity per m^2 of unsupported Fe_2O_3 is much higher than that of the monolayer catalysts. It would thus appear that TiO_2 has a negative influence on the activity of the monolayers of Fe_2O_3 in CO oxidation and one would expect that Fe_2O_3 crystals (i.e. more than a monolayer) on TiO_2 would be less influenced. The catalysts shown in Table 3 were therefore prepared

TABLE 3
Results for CO oxidation for Fe_2O_3/TiO_2 catalysts prepared by impregnation of TiO_2 with $Fe(NO_3)_3$.

Fe %wt	S_{BET} m^2g^{-1}	k_{500} $10^{-8}msec^{-1}$	k_{500} $10^{-8}m^3g^{-1}sec^{-1}$
6.5	44	4.1	180
6.7	45	4.4	200
9.1	43	9.6	410
12.3	38	11.6	440
20.5	42	14.5	610
Fe_2O_3	10	4.6	47

by impregnation of TiO_2 in $Fe(NO_3)_3$ followed by calcination. X-ray diffraction showed the presence of lines due to small crystals of Fe_2O_3. The activity in CO oxidation for catalysts with high percentages of these small crystals is larger than for pure Fe_2O_3. This argument also holds if the comparism is made per unit of surface area.

Model for the Catalysts

This work shows that it is possible to prepare well spread oxides on TiO_2 or ZrO_2 by both batch and continuous adsorption of $Fe(AcAc)_3$ or $VO(AcAc)_2$. Earlier measurements [3] demonstrated that other oxides such as Al_2O_3 or CeO_2 can also be used as supports. The product of the reaction of the metal complex with the surface, acetylacetone (HAcAc) competes with the complex for the available adsorption sites (Fig. 4) and even at low concentrations inhibits the further adsorption of $Me(AcAc)_n$. As a consequence, use of a continuous adsorption method gives rise to the most complete monolayer material, but the method has the draw-back that it is very time- and chemical-consuming. High temperature adsorption appears to favour the adsorption of the $Me(AcAc)_n$ and gives rise in a rather short time to monolayer or near monolayer coverages. All these results are consistent with the mechanism proposed earlier [3,4] for the adsorption of acetylacetonates on TiO_2. According to Boehm [8,9], there are two hydroxyle groups per TiO_2 entity at the surface of Degussa P-25 and we suggest that these can react with two AcAc groups, binding the acetylacetonate to the surface:

$$Ti \overset{OH}{\underset{OH}{\diagdown}} + Fe(acac)_3 \rightarrow Ti \overset{O}{\underset{O}{\diagdown}} Fe(acac) + 2\ Hacac$$
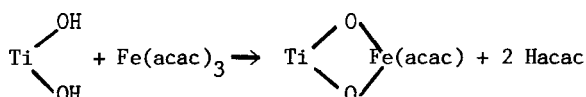
The process produces two molecules of HAcAc which can apparently also adsorb on TiO_2, inhibiting further adsorption of $Me(AcAc)_n$. How the acetylacetone is bonded to the TiO_2 surface is not yet clear; it may possibly occur by a coordinative bond, thereby forming a surface titanium oxy-acetylacetonate.

The TPR results (Figs. 6 and 7) strongly suggest that until the theoretical monolayer is reached, an iron oxide structure exists on the TiO_2 surface which is different from bulk Fe_2O_3. This structure can be reduced at lower temperatures than can bulk (i.e. unsupported) Fe_2O_3 but it can be reduced no further than FeO and this occurs in one step. This contrasts with the two-step reduction of bulk Fe_2O_3 which occurs via Fe_3O_4. A similar difference in behaviour was found for V_2O_5 on TiO_2 and unsupported V_2O_5 [5,6,10], the reduction of the supported V_2O_5 stopping at V_2O_3; this was explained by suggesting that there exists a strong interaction between V_2O_3 and TiO_2 which prevents further reduction [5]. Such a strong interaction is also possible in the case of Fe_2O_3

on TiO_2; the formation of $FeTiO_3$ (ilmenite) could take place on reduction [11].
If such a well-defined structure formed, this would explain the lower reduction
temperature observed and the fact that it is impossible to achieve further
reduction of the associated Fe^{2+}; the surface ilmenite is unlikely to be reduced
at these temperatures. FeO is unstable below 570 ^{o}C if unsupported, so it should
easily be reduced [12]. It has been shown for other supports such as Al_2O_3
[13], MgO [14], or SiO_2 [15] that part of the Fe_2O_3 cannot be reduced beyond the
Fe^{2+} state.

The TPR profiles for samples with iron contents above 2.85 wt% are more
complex, there now being an additional pair of poorly-resolved peaks (Fig. 6).
It can be deduced that a second Fe^{3+} phase, different from that discussed in the
last paragraph, had been formed (see Fig. 7) and that this probably comprises of
Fe_2O_3 crystallites which are too small to be detected by XRD but which can be
reduced to metallic Fe in one or two steps. A comparison of the data of Fig. 6
with those of Fig. 8 for the reduction of a-Fe_2O_3 prepared by decomposition of
$Fe(AcAc)_3$ or $Fe(NO_3)_3$ shows that there is an extra peak for the bulk oxide at a
temperature of about 390°C, probably corresponding to the reduction from Fe_2O_3
to Fe_3O_4. We cannot fully exclude the possibility that this process also occurs
for the crystallites present in the supported catalysts, as it would occur at
the same temperature as the peak attributed to the reduction of the monolayer;
however, calculations based on the hydrogen consumption and catalyst composition
lead us to believe that this is not so. If such a process does occur, the
resultant will still be small in comparison to the first reductions peaks of
Fig. 6: the area will be approximately an eighth of the total of the higher-
temperature peaks if the reduction occurs first from Fe_2O_3 to Fe_3O_4 and
subsequently to Fe.

Fig. 7 shows the behaviour of these peaks as a function of Fe content. If all
the iron beyond a monolayer is present as Fe_2O_3-like crystallites, line (1)
would be expected to rise to a steady value and then stop. This is clearly not
the case. We therefore conclude that a second layer of Fe^{3+} species builds up
gradually on top of the monolayer in addition to the additional Fe_2O_3 crystal-
lites formed and that, as with the monolayer and because of the interaction with
the support, this additional layer can only be reduced to Fe^{2+}; as the thickness
of the layer builds up, the interaction with the support decreases slightly, as
evidenced by the movement of the lowest reduction peak to higher temperatures.
It should be noted that this model was used in the construction of Fig. 7 from
the data of Fig. 6: no other possible model was found to fit the data.

The CO oxidation results (Fig. 9) are, within experimental uncertainty, in
good agreement with this model. Until the theoretical monolayer of Fe_3O_3 on TiO_2
has been achieved, there is a linear increase of activity with wt% Fe. At higher
Fe contents, the activity per unit surface area is more or less constant. The

activity of a-Fe_2O_3 itself is much higher. Catalysts prepared by impregnation of TiO_2 with $Fe(NO_3)_3$ also show a higher activity than the monolayer materials and also than pure Fe_2O_3 (Table 4). The relatively bad performence of the monolayer catalysts in CO oxidation must be connected with the fact that it can only be reduced to FeO and the fact that a relatively inactive surface ilmenite structure may be formed.

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DISCUSSION

G. CENTI : You indicate a parallel behaviour between V- and Fe-Ti monolayer catalysts. On V-Ti oxide, the V interacting with TiO_2 surface was suggested to be present in a different coordination situation (tetrahedral vs. octahedral). Have you any evidence (for example Mössbauer data) that a similar situation may be present also on $Fe-TiO_2$ samples?

J.G. van OMMEN : Our results with Fe_2O_3 monolayer catalysts indicate that the first layer of Fe_2O_3 is in strong interaction with the TiO_2, in the same way as we proposed with Bond for V_2O_5 monolayers. This is possibly connected with a different coordination situation. However, the difference in coordination was suggested for low coverages of V_2O_5 on Al_2O_3; on TiO_2, the situation could be different. From Mössbauer spectroscopy, we only have evidence that the Fe_2O_3 present in the monolayer is very well dispersed even after a long measurement time of about one week; no splitting of the iron signal has occurred.

L. HEINRICH : The Degussa P25 is a very active type of TiO_2. The interactions between this TiO_2 and the iron and vanadium oxides should be observed by IR measurements : the characteristic IR absorption of the components will be disturbed or disappear. Did you observe an upper temperature limit, where the monolayer changes to agglomerates of iron or vanadium oxide? This effect must be observed by the appearance of typical IR bands of the support and catalytic components.

J.G. van OMMEN : For the Fe_2O_3 monolayer, we did not observe an upper temperature limit of stability because we did not heat it higher than 500°C. Until this temperature, the monolayer is stable. For a V_2O_5 monolayer on TiO_2 it was found that V_2O_5 dissolves as V^{IV} into the TiO_2 lattice at temperatures above 550°C. From IR measurements, we have until now no proof that either V_2O_5 or Fe_2O_3 on TiO_2 is different from bulk V_2O_5 or Fe_2O_3; because of the deep colour of these samples, IR spectra are very difficult to measure. We can however observe that the OH groups of TiO_2 disappear if a monolayer of Fe_2O_3 or V_2O_5 is adsorbed on this support.

R.I. BICKLEY : Did you prepare your catalysts in the absence of daylight, or artificial light, since it is well known that organometallic reagents can easily be photocatalytically degraded at room temperature?

J.G. van OMMEN : We were aware of the photocatalytic degradation of $Fe(AcAc)_3$ in toluene solution, especially for the long measurement times; the samples were therefore stored in the dark and a reference solution of $Fe(AcAc)_3$ was also measured to check that such degradation did not occur in our case.

L. GUCZI : As far as the reducibility is concerned, it is known from the literature that, at low concentration, the iron fills up the coordinatively unsaturated sites and thus one cannot reduce it beyond Fe^{2+}. This is in line with the TPR experiments. My question is how stable is the disordered iron oxide layer ? Is there any evidence, e.g. XRD, for the stability of the non-crystalline layer during CO oxidation ?

J.G. van OMMEN : As far as stability of the monolayer of Fe_2O_3 is concerned, we can only state that there is no decrease in activity during CO oxidation for at least one week after calcination at 450°C for 2 hours. Further calcination at 450°C for 17 hours did not decrease the activity of the catalyst.

M.J. LEDOUX : We have found, on alumina, that the important points to obtain
a monolayer (checked by EXAFS, see paper F6) were :
1/ Control of the OH concentration on the support before impregnation;
2/ Washing of the catalyst before calcination to extract the non-reacted
   AcAc complex;
3/ Impregnation at 120°C in order to displace the equilibrium by the
   evaporation of HAcAc (boiling point 118°C).
Did you make the same observations ?

J.G. van OMMEN : We observed the same phenomena as you mention. However, our
high temperature adsorption was performed at 110°C; the increased adsorption
of the AcAc complex can also be caused by differences in adsorption between
the complex and HAcAc at this temperature, giving rise to displacement of
HAcAc by the complex. The boiling point of HAcAc is 139°C (at 746 mm Hg).
So, it could be that its evaporation also plays an important role, as you
suggested.

F. CAVANI : Have you experimental evidences, beyond the theoretical ones,
based on geometrical considerations, about the formation of a complete
monolayer of iron oxide over the TiO_2 ? Do you think the "monolayer" is
constituted by isolated unities of iron oxide, or are these in some way ineracting with one another to form a uniform bidimensional structure ?

J.G. van OMMEN : We only have indirect evidence to support our suggestion : no
XRD pattern or Laser Raman spectrum of Fe_2O_3; the BET surface area remains the
same after adsorption, and the amount adsorbed during continuous adsorption
stops at the theoretical amount. From the results presented in the paper, it
can be seen that Fe_2O_3 formed up until the theoretical monolayer percentage
is reduced at a lower temperature than that above the monolayer and the
monolayer and submonolayer material can only be reduced to FeO. We think that
the Fe_2O_3 monolayer forms a bidimensional structure on top of TiO_2 in a way
similar to that presented in our publication with Bond over V_2O_5 monolayers.

J.B. MOFFAT : You presented indirect evidence for the existence of a monolayer.
Do you have any direct evidence ? What experiments are you contemplating to
generate such direct evidence ?

J.G. van OMMEN : We have no other evidence as that mentioned above for a well-
spread Fe_2O_3 monolayer on TiO_2. We can possibly generate more direct evidence
from EXAFS or ESCA measurements.

E.V.W. GRITZ : 1/ The support has a strong influence on the success of Fe
monolayer formation according to our own research. But is there evidence that
the Fe monolayer survives the catalytic reaction ? Did you characterize your
spent catalyst with TPR ?
2/ You presented a model of active Fe surface formation for TiO_2-support.
High metal loading on ZrO_2 was not possible according to your experimental
data. Is your model of monolayer formation only limited to the TiO_2-support ?

J.G. van OMMEN : 1/ We did not characterize our spent catalyst with TPR but
as answered in relation to the question on the acitivty of the catalyst in CO
oxidation, the catalyst did not change its activity during CO oxidation, nor
at the start of the measurement nor after seven days of CO oxidation.
2/ We think that our model is not limited to TiO_2; monolayers can also be
obtained on Al_2O_3, for instance,. We do not know why the loading on ZrO_2 is
not as good as on TiO_2. It is possibly caused by a lower surface coverage of
OH groups. The formation of the monolayer of Fe_2O_3 on TiO_2 is caused by the
surface reaction of $Fe(AcAc)_3$ with the available OH groups. If, for instance,
TiO_2 is dehydrated and lost part of its OH groups, less $Fe(AcAc)_3$ can be
adsorbed.