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VARIATION IN THE THERMIONIC WORK FUNCTION OF SEMICONDUCTOR POWDERS EXPOSED TO ELECTROMAGNETIC RADIATION

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of the Photo-oxydation Mechanism of Paraffins.

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SUMMARY

The study of the variation of thermoelectronic work
function potential of TiO_2 in the presence of isobutane
shows that this gas is not adsorbed on this solid, nor in
the presence nor in the absence of ultraviolet radiation.
These results, as well as those obtained in a previous
work, lead to the mechanism of the photo-oxidation of iso-
butane at room temperature, in which excited atomic oxygen
is the active species.

INTRODUCTION

In order to pin down the photo-oxidation mechanism of paraffins
at ambient temperature in the presence of titanium dioxide (anatase)
and ultraviolet radiation [1], the nature of the interactions between
isobutane and the surface of the anatase is examined. The results
concerning isobutane, on the one hand, and oxygen on the other [2,3,4],
enable us to formulate a reactive mechanism of heterogeneous photo-
catalysis oxidation of paraffins.

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*Numbers in margin refer to foreign pagination.

EXPERIMENTAL RESULTS AND DISCUSSION

1. Effect of Isobutane on the Thermionic Potential of TiO$_2$.

To study the effect of isobutane on the surface properties of TiO$_2$, three experiments have been performed during which the Au - TiO$_2$ contact potential has been measured as a function of time, in the absence and in the presence of irradiation:

Experiment A.

The sample of anatase (67m^2/g) is "standardized" [1] and placed in darkness. An isobutane pressure of 2 torr is established in the measurement cell: ϕ remains constant. Then the solid is irradiated with ultraviolet light: ϕ keeps the same value.

Experiment B.

The standardized sample is placed in the presence of 2 torr of oxygen, in the absence of radiation. After ϕ stabilizes at the end of one hour (oxygen adsorption mainly in the form O-), the gas phase is evacuated (vacuum of 10^{-6} torr). ϕ decreases slightly (change in the dipple layer) [4] and stabilizes. An isobutane pressure of 2 torr is then established in the reactive chamber: ϕ remains constant.

Experiment C.

The standardized sample was placed in the presence of 2 torrs of oxygen in darkness (adsorption of O-) then irradiated by UV in order to photosorb O$_2$- also until we reach adsorption equilibrium [2]. One hour after irradiation is stopped, the gas phase is evacuated (10^{-6} torr), which leads to a slight decrease in ϕ, which then becomes constant. As the sample is then exposed to an isobutane pressure of 2 torr, ϕ remains constant.

These three experiments enable us to conclude first of all that in darkness there is no chemical adsorption of isobutane at the

2

surface of TiO_2, whether it should be "clean" or covered by one or more layers of adsorbed oxygen (O_2- and $O-$).

Similarly, practically no isobutane is physisorbed, or at least the Van der Walls type interaction forces between the TiO_2 surface and isobutane are extremely weak, since they are not detectable by measuring the contact potential (physical adsorption normally leads to a change in ϕ equal to at least several tens of millivolts, which is easily measurable given that the minimum detectable contact potential is a few millivolts).

In addition, experiment A enables us to verify, on the one hand, that the TiO_2 surface is indeed "clean" in the standard state; that is, that there is no oxygen adsorbed on the surface. In effect, if this were not so, isobutane, by oxidizing under UV irradiation, would lead to a change in ϕ, in contrast with what is observed experimentally. On the other hand, this experiment shows that it is not lattice oxygen at the surface which oxidizes isobutane under irradiation, for the same reason as explained above (assuming the opposite, ϕ should change.
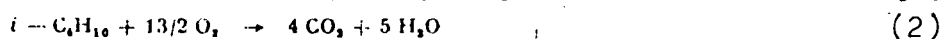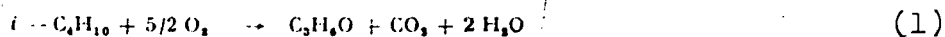
2. Mechanism of Initiating the Photo-oxidation of Isobutane.

With the help of experiments carried out, on the one hand, with isobutane and, on the other hand, under ultraviolet irradiation [2], we have tried to explain the photo-oxidation mechanism of isobutane in the presence of anatase.

This reaction, examined in detail in another work [5], arrived at the main conclusions reviewed below.

Isobutane is oxidized into acetone, carbon dioxide and water at ambient temperature in the presence of TiO_2 (anatase or rutile) exposed to ultraviolet radiation, according to the following reactions:

$$i - C_4H_{10} + 5/2\ O_2 \rightarrow C_3H_6O + CO_2 + 2\ H_2O \tag{1}$$
$$i - C_4H_{10} + 13/2\ O_2 \rightarrow 4\ CO_2 + 5\ H_2O \tag{2}$$

3

Reaction (1) leads to a gradual oxidation while reaction (2) leads to a total oxidation of the isobutane. However, reaction (1) predominates (between 65 and 100%, depending on the partial pressures of oxygen and the hydrocarbon).

The oxidation reactions take place only if the energy of the radiation used is greater than or equal to the width of the band gap of TiO_2 (3.5 eV). It has been verified that the curve that gives the UV absorption of TiO_2 as a function of wavelength can be superposed on the curve expressing the catalytic activity of TiO_2 as a function of wavelength. This last result indicates clearly that the presence (due to irradiation) of free holes at the surface of TiO_2 is necessary for reactions (1) and (2) to take place, since these holes are created by the photons of energy greater than or equal to width of the band gap of TiO_2 in the solid lattice.

The positive holes present on the surface can, in principle, react either with the isobutane or with a form of oxygen at the surface.

The first possibility (reaction with isobutane) is to be excluded. In effect, as has been shown, isobutane is not adsorbed in the absence of irradiation on TiO_2 in the standard state [1] nor on TiO_2 covered with adsorbed oxygen. Now for the holes to be able to react with the isobutane molecules, they have to be adsorbed prior to irradiation, which is not the case. This reasoning is confirmed by experiment A (ϕ does not change under irradiation), which also shows that the electrons freed by irradiation (just like the holes) do not react with the isobutane. On the other hand, isobutane cannot be adsorbed through any action of the holes on any oxygen form previously chemisorbed, for the following reason. In the absence of adsorbed oxygen (experiment A), the probability of an isobutane molecule trapping a hole is negligible (ϕ does not change while isobutane is introduced onto TiO_2 in the absence or in the presence of irradiation). The presence of chemisorbed oxygen introduces trapping centers for the holes, which further decreases the probability of holes being trapped by isobutane, which had already been negligible for clean TiO_2.

Since the holes do not interact with isobutane, they must necessarily react with one form of oxygen on the surface. Since this form is not lattice oxygen, as experiment A shows, it consequently is one form of adsorbed oxygen; that is, $O-$ or O_2-.

Furthermore, it has been shown [2] that the holes produced by ultraviolet radiation and reacting at the surface, are, in practice, trapped only by the $O-$ form, from the beginning of irradiation and for at least several tens of additional minutes (that is, while the concentration of photoadsorbed O_2- is negligible compared with the concentration of $O-$). Since the oxidation products from reaction (1) and (2) are detected by chromatography practically from the beginning of irradiation [6], the reaction is already taking place while the holes are trapped only by $O-$. This enables us to conclude that the holes active in starting the photocatalysis reactions are those which react with the $O-$ species.

Therefore, the following simultaneous stages take place.

First the oxygen is adsorbed chemically in the absence of radiation, mainly in the dissociated form (after physical adsorption) [2]:

$$O_{2(g)} \rightleftharpoons O_{2(ads)} \tag{3}$$
$$O_{2(ads)} + 2e^- \rightarrow 2\,O^-_{(ads)} \tag{4}$$

The creation of free electrons in holes by the absorption of photons in the titanium dioxide lattice can be written symbolically as:

$$h\nu \rightarrow \oplus + e^- \tag{5}$$

Part of the holes is trapped by the $O^-_{(ads)}$ species, in the reaction:

$$O^-(ads) + \oplus \rightarrow O^*(ads) \tag{6}$$

where the $O^*_{(ads)}$ form is an excited adsorbed atomic species, which can evolve according to reactions (7),(7') and (8):

$$O^*(ads) \rightarrow O^*(g) \tag{7}$$
$$2\,O^*(g) \rightarrow O_2(g) \tag{7'}$$
$$O^*(ads) + e^- \rightarrow O^-(ads) \tag{8}$$

5

In other words, in the absence of isobutane, the $O^*_{(ads)}$ form can be described (equation 7), then recombined in part to give $O_{2(g)}$, or even resorbed per reaction (8) which is the inverse of reaction (6). The set of reactions (6) and (7) leads to a decrease in ϕ under ultra-violet light in the presence of oxygen, due to photodeionization and photodesorption of $O^-_{(ads)}$. Under irradiation, there is therefore a constant concentration of the $O^*_{(ads)}$ and the $O^*_{(g)}$ species.

Finally, part of the electrons generated by radiation is trapped [2] in the reaction.

$$O_1 + e^- \rightarrow O_1^-. \tag{9}$$

CONCLUSION

We can therefore conclude that to initiate photo-oxidation the isobutane molecules should be attacked by entering into contact either with $O^*_{(ads)}$ or with free O^*, the forms of excited atomic oxygen which are very active (see, for example, [7] and [8]). /1027

However, it is also possible that, after the attack on the iso-butane molecules by atomic oxygen, certain fragments of the molecules (free radicals) react partly with the other form of adsorbed oxygen, O_2^-, even though it is not involved in the mechanism of initiating photo-oxidation, and it is totally inert with respect to isobutane in darkness (experiment C and reference [1]).

Finally, a recent study [6] of photo-oxidation of linear and ramified paraffins, ranging from ethane to octane, seems to show in-directly that the active species of oxygen is a dissociated species, thus confirming the conclusions of this work.

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