

ROOM TEMPERATURE PHOTOCATALYTIC OXIDATION OF LIQUID CYCLOHEXANE INTO CYCLOHEXANONE OVER NEAT AND MODIFIED TiO_2

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Received 6 April 1989; accepted 22 May 1989

Photocatalysis, photooxidation of cyclohexane, titanium oxide photocatalyst

The oxidation of liquid cyclohexane by O_2 over UV-illuminated TiO_2 at room temperature has been studied in a static slurry reactor. From the effects of the mass of catalyst, the temperature, the radiant flux, the concentration of C_6H_{12} (using acetonitrile as a solvent), it is concluded that the reaction is photocatalytic. Using mainly the 365 nm-ray of a mercury-lamp, an initial quantum yield of 0.1 is found for pure cyclohexane and radiant fluxes $< \text{ca. } 5 \text{ mW cm}^{-2}$ ($6 \times 10^{15} \text{ photons s}^{-1} \text{ cm}^{-2}$). A high selectivity to cyclohexanone is observed (83%), the other products being cyclohexanol (5%) and CO_2 (12%). The low amount of cyclohexanol is explained by the higher rate of oxidation of this alcohol compared to that of cyclohexane. Smaller oxidation rates are observed when TiO_2 is loaded with 0.5 to 10 wt%Pt and the cyclohexanone/cyclohexanol ratio decreases to ca. 4. Finally, the C_6H_{12} oxidation has been employed as a test reaction to confirm the detrimental effect of the doping with several tri or pentavalent cations upon the photocatalytic activity of TiO_2 .

1. Introduction

The photocatalytic oxidation of many organic molecules, including saturated hydrocarbons, by optically-excited semiconductor oxides is thermodynamically allowed in the presence of oxygen at room temperature. Selectivities different from those obtained by other oxidation means have been reported [1,3], showing the potential of the method for syntheses in the cases where the expected product is obtained with an acceptable quantum yield. Concerning saturated hydrocarbons, earlier detailed studies have dealt with the oxidation of linear and branched $\text{C}_2\text{--C}_8$ alkanes in gas phase [4]. The selectivity to carbonyl compounds with quantum yields of ca. 0.1 was remarkable; however several aldehydes and ketones were sometimes produced from the same alkane depending on its structure. No equivalent investigation for neat-liquid alkanes has been published

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as yet. Also, information on the photocatalytic oxidation of cycloalkanes is scarce. A brief report pointed out the oxidation of neat-liquid cyclohexane to cyclohexanone and carbon dioxide on several semiconductor oxides, with or without deposited Pt [5]. The organic product from adamantane was also the ketone corresponding to the oxidation of a secondary carbon atom [5]. Conversion of cyclohexane to CO_2 and minute traces of cyclohexanol upon illumination of an aqueous hydrocarbon emulsion containing platinized anatase for 24 hours has also been indicated [6]; total oxidation is expected in the presence of an excess of water because of the formation of OH° radicals and this can be of great interest for water decontamination [7]. Finally, the photocatalytic oxidation of gaseous cyclohexane over V_2O_5 [8], Ta_2O_5 [8] and MoO_3 [8,9] supported on SiO_2 has been studied. At 333 K in a tubular flow-photoreactor, CO_2 was by far the main product; cyclohexanone [8,9], propanal [9] and ethanal [9] represented only traces.

This paper presents an in-depth study of the photocatalytic oxidation over TiO_2 of cyclohexane, chosen as the model compound of cycloalkanes. The effect of platinum deposited on TiO_2 has also been examined. Finally, this oxidation was used as a test reaction to show the influence of homogeneous doping of titania.

2. Experimental

Most experiments were carried out with Degussa P-25 TiO_2 (mainly anatase, specific area $50 \text{ m}^2 \text{ g}^{-1}$, nonporous). This sample was found very active compared with other TiO_2 specimens in previous studies. Cyclohexane (Fluka, puriss) was employed as received.

The static photoreactor was a cylindrical flask of ca. 90 ml with a bottom optical window of ca. 4 cm in diameter transmitting wavelengths $> 300 \text{ nm}$. It was connected to a rotatory pump or to gas chromatographs. A volume of 10 cm^3 of cyclohexane was used. Illumination was provided by a Philips HPK 125 W high pressure mercury-lamp. A 2.2 cm thick circulating-water cell was placed in front of it to absorb the IR beams. The radiant flux entering the reactor was measured with a calibrated radiometer (United Technology, model 21 A). Unless otherwise indicated, it was equal to 46 mW cm^{-2} , i.e. $3.85 \times 10^{16} \text{ photons cm}^{-2} \text{ s}^{-1}$.

Carbon dioxide was analyzed by the use of a catharometer gas-chromatograph (Intersmat, model IGC20MB), equipped with a column of Porapak Q (80–100 mesh, $3 \text{ m} \times 1/4''$). Cyclohexane, cyclohexanol and cyclohexanone, were analyzed with a flame ionization gas-chromatograph (Intersmat, model IGC102EL) using a column of Carbowax 1500 (20% on Chromosorb W.HMDS, 60–80 mesh, $3 \text{ m} \times 1/8''$).

3. Results and discussion

1. INFLUENCE OF VARIOUS PARAMETERS UNDER CONSTANT RADIANT FLUX

The main product of the photocatalytic oxidation of cyclohexane is cyclohexanone, whereas cyclohexanol amounts to a few percents only. Therefore, in this section, the studies of the effects of various parameters will refer to the formation of cyclohexanone.

1.1. INFLUENCE OF THE MASS OF CATALYST

For the same volume of pure cyclohexane ($V = 10 \text{ cm}^3$), the mass m of suspended TiO_2 was varied between 0 and 70 mg (fig. 1). The activity increased with m up to a plateau obtained for $m = 55 \text{ mg}$. This corresponded to full absorption of light by the solid. All the experiments reported in the following paragraphs were carried out with 70 mg TiO_2 .

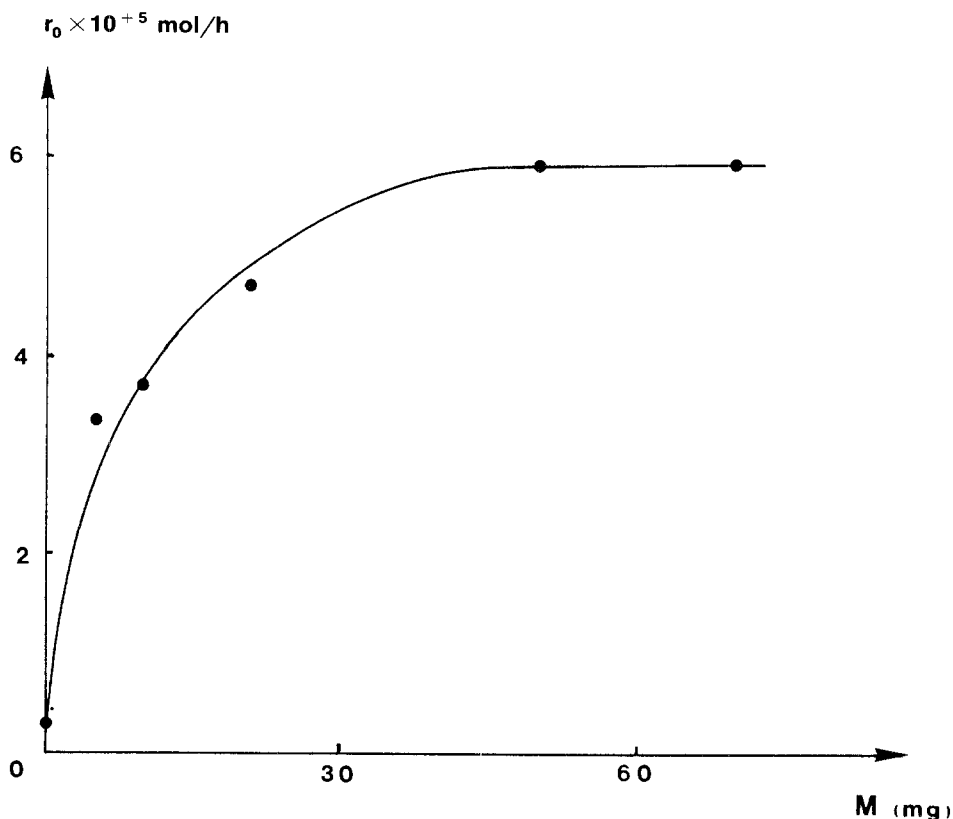


Fig. 1. Influence of the mass of catalyst on the initial rate of formation of cyclohexanone.

In the absence of TiO_2 , the amount of cyclohexanone was about 125 times smaller than over 70 mg of TiO_2 . Photochemical oxidation can therefore be neglected.

1.2. INFLUENCE OF THE CONCENTRATION OF CYCLOHEXANE

Acetonitrile was used as a solvent, because it is stable under photocatalytic conditions [10]. The variations of the initial rate of formation of cyclohexanone, the main product, as a function of the initial concentration up to the maximum solubility of cyclohexane (1 M), are presented in fig. 2A.

The curve obtained has the shape of a Langmuir-Hinshelwood isotherm $r_0 = kKC_0/(1 + KC_0)$ where k is the rate constant which depends on the conditions and K is the adsorption constant of cyclohexane on TiO_2 from acetonitrile. The correspondance between the curve of fig. 2A and the Langmuir isotherm was confirmed by the linear transform $r_0^{-1} = f(C_0^{-1})$ (fig. 2B) from which it comes:

$$k = 9.1 \times 10^{-5} \text{ mol h}^{-1}, K = 4.3 \text{ l mol}^{-1}.$$

This implies a non-dissociative adsorption of cyclohexane on titania in agreement with previous results obtained with saturated hydrocarbons [11].

A conversion of 50% was obtained after illuminating a 0.1 M suspension for 23 h.

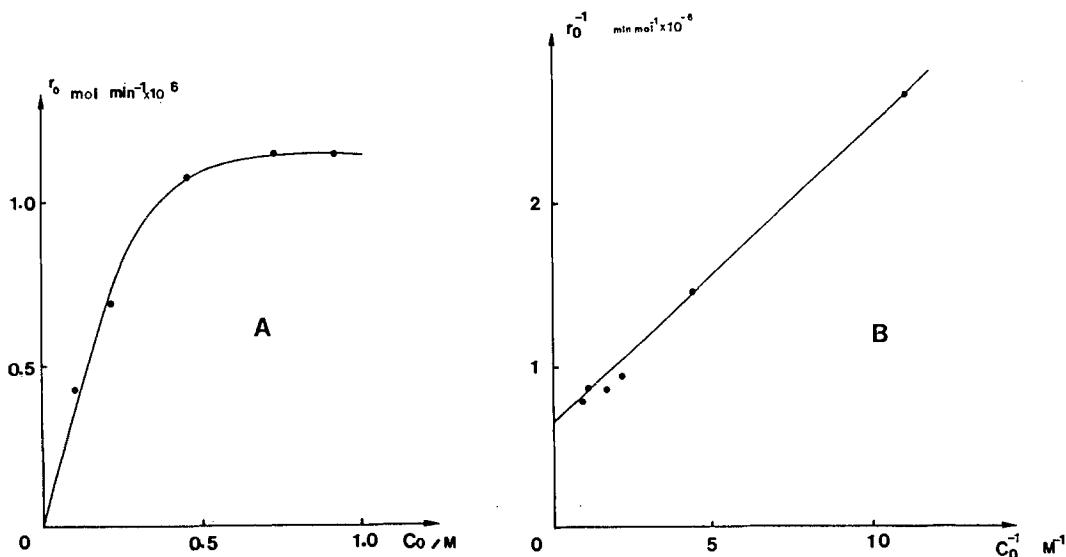


Fig. 2. (A) Influence of the initial concentration C_0 on the initial rate r_0 of formation of cyclohexanone. (B) Linear transform of curve (A).

1.3. INFLUENCE OF TEMPERATURE

The temperature was varied from 283 to 353 K by using a jacketed photoreactor connected to a Huber HS40 cryostat. The initial reaction rate was maximum at about 328 K (fig. 3A). The corresponding Arrhenius diagram (fig. 3B) can be interpreted as follows. In the medium temperature region (295–328 K), the reaction is purely photocatalytic because the apparent activation energy E_a is close to zero as expected for a process that is photoactivated and not thermally activated. At low temperature (< 295 K), the limiting step becomes the desorption of the main product and it appears in the expression of E_a a positive term

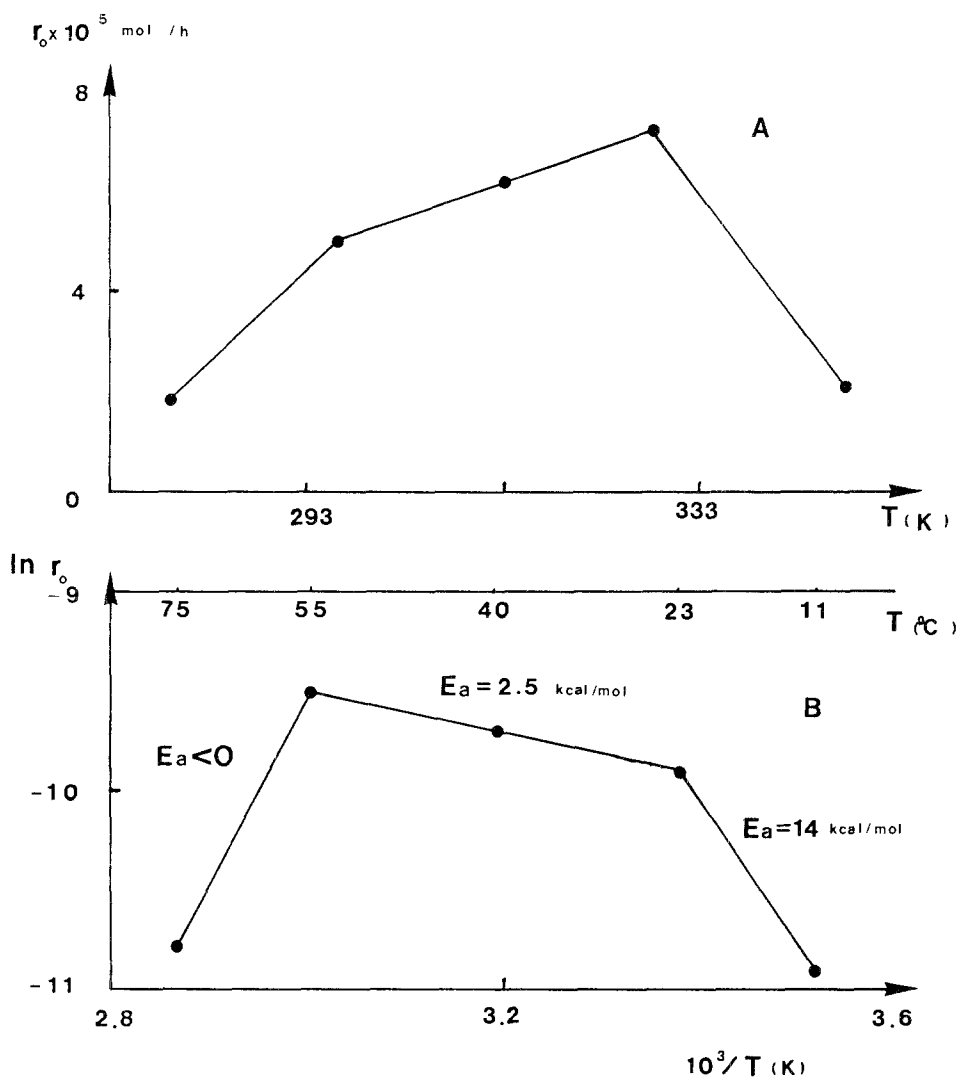


Fig. 3. (A) Influence of the temperature on the initial reaction rate of formation of cyclohexanone. (B) Arrhenius diagram corresponding to (A).

which contains the heat of adsorption Q_p of cyclohexane: $E_a = E_t + \alpha Q_p$, where E_t is the true activation energy in the absence of thermally activated steps ($E_t = 0$) and α a coefficient comprised between 0 and 1. By contrast, at temperature > 328 K, the limiting step becomes the adsorption of the reactant (the temperature is closer to its boiling point) and E_a includes the heat of adsorption Q_A of cyclohexane ($E_a = E_t - \alpha Q_A$).

1.4. INFLUENCE OF THE CONCENTRATION OF DISSOLVED OXYGEN

The effect of the concentration of dissolved oxygen has not been studied systematically. However, pure oxygen or air has been used, TiO_2 being maintained in suspension either by gas bubbling or by magnetic stirring. Almost no difference was found. Consequently, in most of the experiments, the reaction was carried out with ambient air in a photoreactor that was closed to prevent evaporation.

2. INFLUENCE OF THE RADIANT FLUX. QUANTUM YIELD

The radiant flux Φ was varied by the use of calibrated metallic grids which provide attenuations independent of the wavelength. The nonattenuated polychromatic radiant flux Φ_0 received by the suspension was equal to 46 mW cm^{-2} . It corresponded to a flux of efficient photons equal to $3.85 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$. Figure 4 shows the relative photocatalytic activities as a function of Φ/Φ_0 . For $\Phi/\Phi_0 < \text{ca. } 0.6$, the photocatalytic activity increases linearly with Φ , whereas above this value, it tends to vary as $(\Phi/\Phi_0)^{1/2}$. The linear variations with Φ imply that the majority of photoproduced charges do not recombine. At higher radiant flux, the rate of generation of electrons and holes becomes greater than the reaction rate. Consequently the recombination of electrons and holes dominates, which provides a square root variation of the reaction rate vs Φ as demonstrated in ref. [12].

Differential quantum yield: It is considered as a dynamic characteristics of the system and is defined as the ratio of the reaction rate to the photon flux which was calculated from the intensities of the rays of the UV lamp given by the supplier, the transmittances of the filter we used and of the optical window of the photoreactor, the absorbance of TiO_2 (both measured with a UV spectrophotometer) and the radiant flux received by the catalytic bed in suspension and measured with a radiometer. To obtain a better accuracy, we employed a Corning 7.60 filter whose maximum transmittance is close to the most intense ray of the mercury lamp at 365 nm. As a result, the other rays at 313 and 334 nm did not contribute much (less than 13%) to the excitation of TiO_2 . Under these conditions, a quantum yield of 0.1 was derived for Φ corresponding to the linear part of the plot of fig. 4.

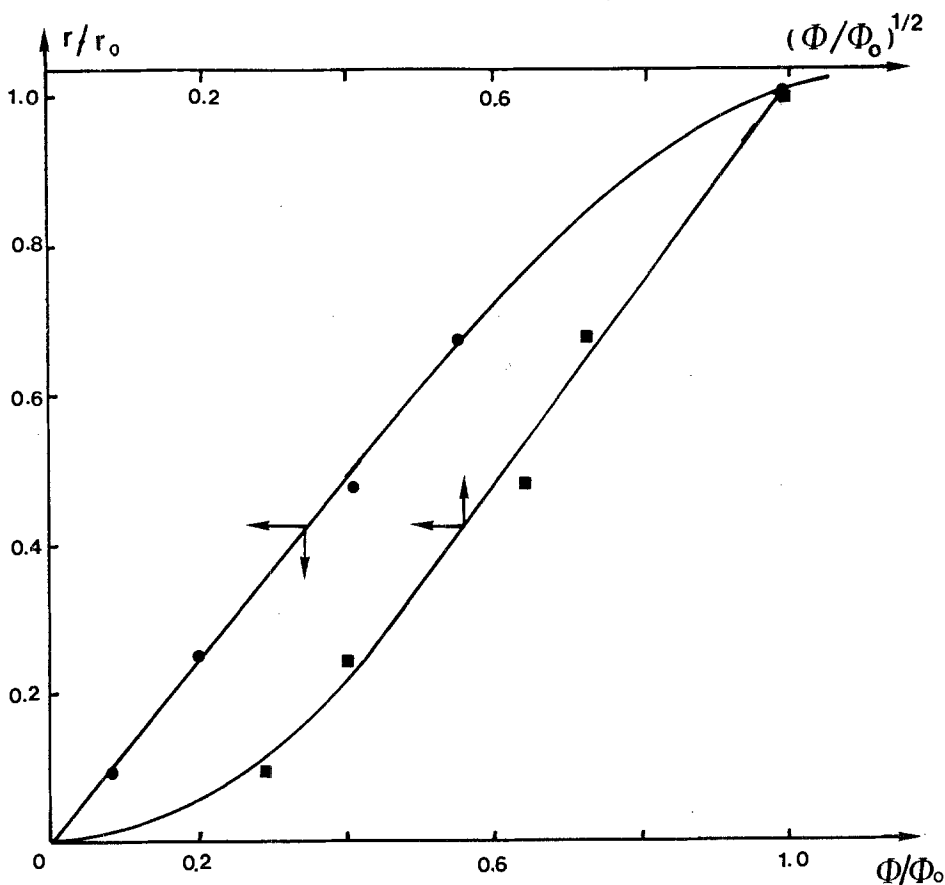


Fig. 4. Influence of the relative light flux (Φ/Φ_0) on the catalytic formation of cyclohexanone. The subscript 0 refers to a nonattenuated beam.

From the effects of the mass of TiO_2 , the concentration of C_6H_{12} , the temperature and the radiant flux, as well as from the number of converted molecules much higher than the number of surface group available, it is concluded that the oxidation of cyclohexane is photocatalytic.

3. SELECTIVITY

The analysis by gas chromatography under the conditions indicated in the experimental section revealed only 3 products: cyclohexanol (5%), cyclohexanone (83%) and carbon dioxide (12%). This selectivity pattern was independent of the reaction time up to 6 h, the radiant flux and the temperature in the ranges indicated above. This is understandable because of the great differences in the selectivities to cyclohexanone and to the two other products detected and of the

low conversion attained: for a reaction time of 3 h, the conversion of liquid cyclohexane was equal to 0.3%. Under the same conditions, the oxidation rate of cyclohexanol was found ca. 1.3 times greater than that of cyclohexane. This implies that the oxidation of cyclohexanol is not the rate-limiting step and is consistent with the low selectivity in cyclohexanol.

4. MODIFICATIONS OF TITANIA

4.1. INFLUENCE OF PLATINUM CONTENT

Since a beneficial role of platinum deposited on titania had been mentioned for the photocatalytic oxidation of organic compounds in the presence of O_2 [5,6] a study of the oxidation of cyclohexane over a series of Pt/TiO₂ photocatalysts was undertaken.

The Pt/TiO₂ photocatalysts were prepared by impregnation with H_2PtCl_6 and reduction in H_2 at 693 K of Degussa P-25 TiO₂. Their Pt content varied from 0.5 to 10 wt%. The mean diameter of the metal crystallites was ca. 2 nm, nearly independently of the content [13].

Figure 5 shows that the initial formation rate of cyclohexanone decreases as a function of the platinum weight percentage according to a hyperbolic-type curve. The photoconductance of TiO₂ measured under vacuum was found to depend similarly upon the Pt content, which was interpreted by a transfer of electrons from the semiconductor to the metal particles [14]. This transfer was corroborated by photoacoustic spectra in a nitrogen-water vapor atmosphere [15]. Also, the quantity of oxygen photoadsorbed on TiO₂ as negatively charged species was decreased for increasing Pt contents [16]; in other words, in an oxygen atmosphere, the transfer of electrons from TiO₂ to Pt still occurs. Figure 6 indicates that the initial rate of cyclohexanone formation roughly correlates with the amounts of oxygen photoadsorbed under the conditions of ref. [16] for similar Pt/TiO₂ samples. The amounts of photoadsorbed oxygen reflect the numbers of electrons that are available on illuminated TiO₂ in addition to those present in the dark (n-type semiconductor). Any photocatalytic reaction implies an equal consumption of photoproduced electrons and holes. In the present case, the surface Pt atoms are likely saturated by oxygen in the dark forming Pt-O bonds, so that electrons trapped in Pt particles cannot be captured by additional adsorption of oxygen. Electrical neutrality requires these electrons to recombine with holes; in other words, Pt particles behave as recombination centers. The minimum Pt content starting from which the effect becomes appreciable can depend on the type of sample and the oxidizable molecule [18].

From photoconductivity measurements, it was deduced that two types of oxygen species, O^- and O_2^- , control the electronic equilibrium between oxygen and UV-illuminated TiO₂. In the case of 5 wt% Pt/TiO₂, this equilibrium is

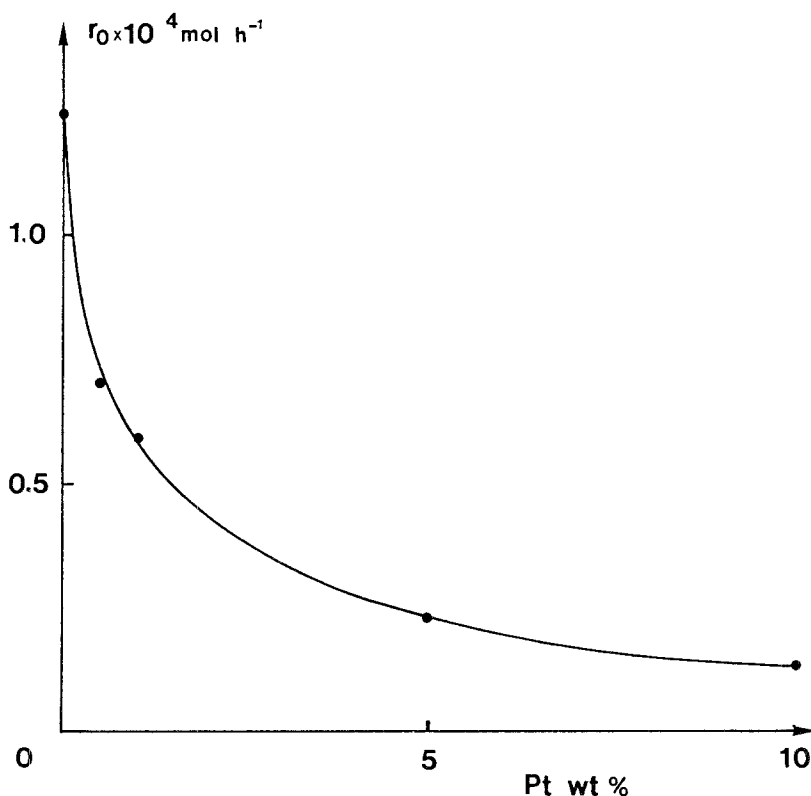
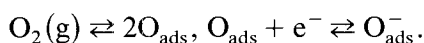


Fig. 5. Influence of the percentage of deposited platinum on the initial rate of formation of cyclohexanone.

controlled by O^- species since the photoconductance varies as $P_{O_2}^{-1/2}$ (fig. 7):



This is consistent with an electron transfer from the support to the metal that causes dissociated oxygen, which has a higher electroaffinity than molecular oxygen, to play the essential role in the equilibrium over TiO_2 partially depleted from free electrons. Previous conclusions indicating that O_{ads}^- is determinant in

Table 1

Influence of the platinum content of TiO_2 on the selectivity to mild oxidation products

Pt (wt%)	% cyclohexanol	% cyclohexanone
0	5.5	94.5
0.5	19	81
1	20	80
5	24	76
10	22	78

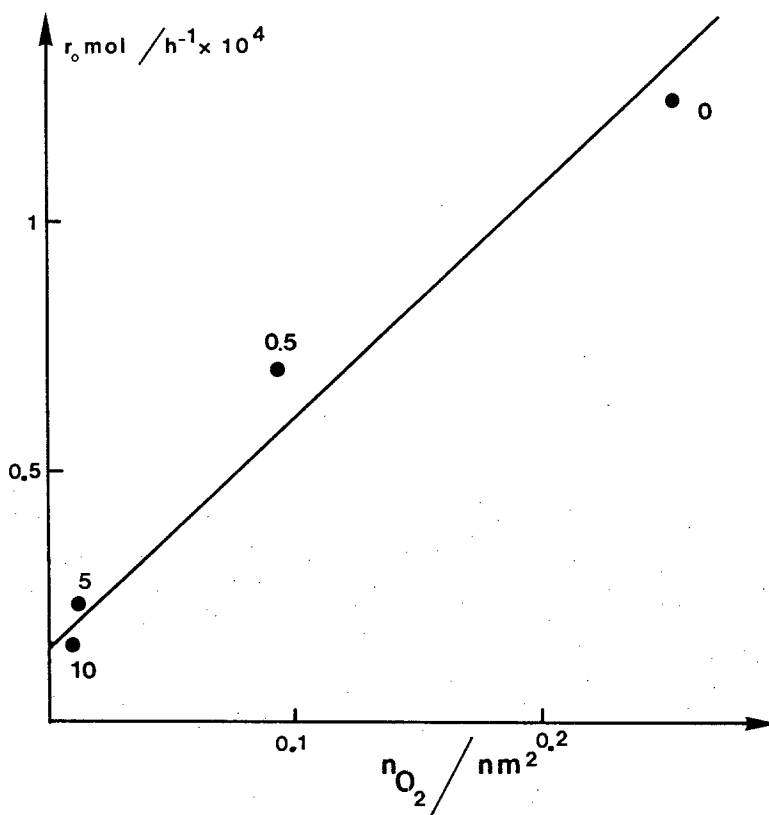


Fig. 6. Variations in the initial rate of formation of cyclohexanone over various Pt/TiO₂ samples as a function of the amount of photoadsorbed oxygen. Pt contents (wt%) as indicated.

the initial oxidation step, (here, the oxidation of cyclohexane to cyclohexanol) are substantiated.

On the other hand, the cyclohexanone/cyclohexanol ratio was diminished in the presence of deposited Pt (table 1). This change in selectivity cannot exclusively be attributed to smaller activities, since reduced radiant fluxes caused no variation in the case of TiO₂ (vide supra). Furthermore, table 1 indicates that the selectivity was not modified much for Pt contents increasing from 0.5 to 5 wt%, despite a decrease in activity by a factor of almost three (fig. 5). Other results are needed to explain these selectivity variations.

4.2. INFLUENCE OF ION DOPING

In previous studies, substitutional doping of TiO₂ by Cr³⁺ cations was shown to decrease the photocatalytic activity with regard to that of pure TiO₂ in a variety of oxidations in different media, and this was attributed to the role of Cr³⁺

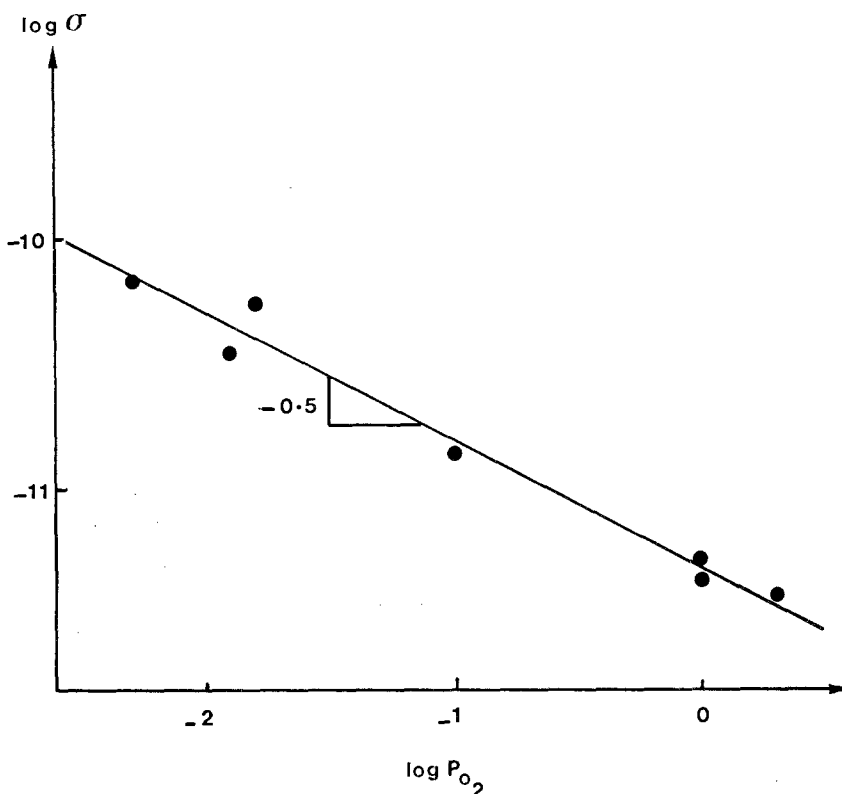


Fig. 7. log-log plot of the variations in the electrical photoconductance (in ohm^{-1}) of 5 wt% Pt/TiO₂ as a function of the oxygen pressure (in Torr).

cations as recombination centers. In the course of the present study, to generalize this conclusion, anatase samples doped with three other cations were employed.

Nonporous samples of titania containing the percentages indicated in table 2 of Ga³⁺, Cr³⁺, Sb⁵⁺ and V⁵⁺ were prepared by the flame reactor method [19]: a vaporized solution of the appropriate salt in TiCl₄ was injected in an oxyhydric flame where homodispersed particles of doped anatase were generated. Their

Table 2

Photocatalytic activity in cyclohexanone formation of titania doped with tri- and pentavalent ions.

Samples	dopant content (at. %)	Surface area (m^2g^{-1})	Initial reaction rate ($\mu\text{mol h}^{-1}$)	Relative activity (doped/pure TiO ₂)
TiO ₂	0	50	124	1
Ga ³⁺ -TiO ₂	0.74	50	30	0.24
Cr ³⁺ -TiO ₂	0.86	60	6	0.048
Sb ⁵⁺ -TiO ₂	0.84	55	36	0.29
V ⁵⁺ -TiO ₂	2	77	15	0.12

specific areas (table 2) were close to that of Degussa P-25 taken as a reference; this enables one to minimize possible effects of different textures.

The results (table 2) show that these dopings with trivalent or pentavalent heterocations are detrimental to the photocatalytic activity. The effect is the most pronounced in the case of Cr^{3+} ions. These tri or pentavalent ions create acceptor or donor centers respectively that attract charge carriers of the opposite sign with an efficiency depending on their nature and concentration, and thereby behave as recombination centers.

As platinum deposition, ion doping decreases the cyclohexanone/cyclohexanol ratio, although cyclohexanone remains by far the main product.

Acknowledgement

We thank Mr. J. Disdier for the photoconductivity measurements.

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