Comparison of the degradation of benzamide and acetic acid on different TiO_2 photocatalysts

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Abstract

The degradation of benzamide and acetic acid with different TiO_2 photocatalysts have been studied. These two pollutants differ from each other in their interaction with TiO_2 (acetic acid is partially adsorbed on TiO_2 whereas and benzamide is not). The results show that the degradation rate of benzamide, contrary to that of acetic acid, is not much affected by the specific area of the catalyst. © 2000 Published by Elsevier Science S.A.

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1. Introduction

Titanium dioxide (TiO_2) in powder form is a catalyst largely used in the field of detoxification of aqueous effluents [1]. Different types of TiO_2 are commercialized. They differ mainly in their preparation mode (e.g. hydrolysis of $TiCl_4$ or sulphate process) and so in their crystallographic structure (anatase or rutile in major cases), particle size and specific surface. Their activities are different but even with extensive studies [2,3], the effect of each of these physical properties are not clearly understood for all the pollutants. The use of powered form catalysts implies a filtration before rejecting clean water. So, in order to avoid the filtration stage, many works are nowadays based on supported catalysts [4–6]. Deposition is always followed by a thermal treatment so as to stabilize the TiO_2 film, and this treatment has an influence on physical properties of the oxide (e.g. specific surface or crystallographic structure).

As a first step, we have begun studying the degradation rate of the benzamide and the acetic acid with three different commercial TiO_2 before and after thermal treatments. These treatments (oxidative and reductive) permit to obtain different catalysts which are compared for degradation of two different pollutants in an aqueous phase. The benzamide and acetic acid were chosen because of their degradation have

being studied before [7–9]. Actually, some studies mention a preliminary adsorption step before acetic acid degradation, while no adsorption could be registrated in the case of benzamide. In order to compare the degradation of these two pollutants, we have chosen to work on three commercial TiO_2 and to perform different thermal treatments on this catalyst. Finally, we have tested 9 TiO_2 which are different by specific area, crystallographic structure and stoichiometry.

2. Experimental

Three photocatalysts (from Degusa (P25), Prolabo and Aldrich) were used. Each of these samples was subjected to a reductive treatment (to obtain redTiO_2) and an oxidative treatment (oxTiO_2). These two treatments were performed in a tubular oven at 900°C for the duration of 15 h, under oxygen for the oxidative treatment, and an Ar–H_2 mixture (2% of H_2 in volume) for the reductive treatment.

The specific surfaces were determined using N_2 physisorption at 77 K (BET model) with a sorptomatic 1900 apparatus. The crystallographic structures were obtained by X-ray diffraction in Debye–Scherrer mode. In the case of benzamide, the concentration measurements were made by high performance liquid chromatography (HPLC Waters 600 pump and 996 photodiode array detector, C-18 apolar column and methanol (10%) water (90%) mixture as mobile phase). Before injecting, the solutions were filtered through micropore filters (0.45 mm of diameter). In the case

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of acetic acid, the concentrations were measured classically by pH-metry.

The photocatalytic reactor has been already described elsewhere [10]. No buffer were used, and the pH is fixed by the catalyst content and the pollutant concentration (pH$\approx$3 in all cases). To obtain a fluid solution and to avoid the TiO$_2$ decantation, a 2.0 g l^{-1} catalyst concentration has been chosen. This value is a compromise between degradation rate and viscosity of solution. For degradation, 1.2 g of TiO$_2$ powder was suspended in 600 ml of aqueous solution of each pollutant. The initial benzamide concentration was 20 ppm and the acetic acid concentration was 100 ppm (ppm in mass).

3. Results and discussion

3.1. Properties of catalysts

Some characteristics of the catalysts are presented in Table 1.

The particle sizes are obtained from suppliers. Commercial samples (untreated) show differences in specific surface and crystallographic structure (anatase percentage for the untreated TiO$_2$ P25 comes from Tanaka et al. [11]). The thermal treatment effects the specific surface, crystallographic structure as well as stoichiometry degree of the catalyst. As expected, the specific surfaces degrade during treatments (either oxidative and reductive).

Concerning the crystallographic structure, even if thermodynamically the rutile phase should dominate at high temperature [12], the results obtained for Prolabo can be explained by the size of the particles. The higher the size of particles, the slower kinetics of allotropic transformation. For big particles like Prolabo TiO$_2$, the treatment may not be sufficient to change the structure over the whole sample volume. No stoichiometric measurements have been made. Nevertheless, the colour of catalysts allows to differentiate the samples in two categories: stoichiometric (yellow colour) and below stoichiometry (blue shadow colour) [13]. The colour of the untreated samples is white. Below the stoichiometry, samples show oxygen vacancies which in surface, increase the number of hydroxylating sites [14]. For the same specific surface (as in so far it is possible to dispose of such a

sample), an under stoichiometric TiO$_2$ will show a better catalytic activity, since free radicals that may appear will be more numerous.

There are certainly a lot of other parameters, not studied here, which could influence the activity of catalysts (e.g. the process of preparation and the presence of elements like chloride or sulfates). But, our simplest approach permits even to do some interesting conclusions, perhaps concerning the catalyst films, which always present a poor specific surface.

3.2. Rate of degradation

Studies of benzamide degradation have already been published [8]. The degradation of benzamide follows a first-order kinetics, and in the first step leads to the formation of hydroxylated derivatives of benzamide. With a first-order kinetics, it is easy to calculate the reaction rate k (in min^{-1} units) as discussed for all the experiments.

For the acetic acid, kinetics are not as easily interpreted as for benzamide. The kinetic is of zero order in the first step and of the first order subsequently [14]. The degradation are monitored during the same time for all catalysts and since the degradation rates are quite different, the same model could not be used for all the samples. So, in order to compare, only the first points have been considered to calculate the constant with a zero order model (k is in ppm min^{-1}).

The kinetic constants for all samples are presented in Fig. 1.

Concerning the untreated catalysts, it appears that for benzamide the important parameter is the crystallographic structure. For the Prolabo and P25 untreated catalysts that both, partly or completely, present the anatase structure, the kinetic constants are comparable, in spite of difference of factor 4 against Prolabo on the specific surface (53 m^2 g^{-1} for the P25 and 12 m^2 g^{-1} for the Prolabo). This is confirmed by the weakness of the kinetic constant with the Aldrich catalyst whose specific surface is exactly half the one from Prolabo, although its crystallographic structure is pure rutile. The specific surface may however affect the rate but, here, the preponderant influence of the crystallographic structure masks this effect.

Table 1
Characteristics of catalysts

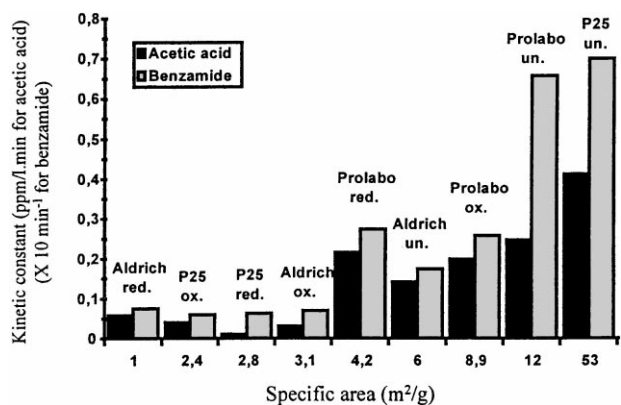|	Degussa (P25)			Prolabo			Aldrich		
	ox.[a]	Untreated	red.[b]	ox.	Untreated	red.	ox.	Untreated	red.
Structure	ru.[c]	an72%–ru28%	ru.	an.[d]	an.	an.	ru.	ru.	ru.
Colour	Yellow	White	Blue	Yellow	White	Blue	Yellow	White	Blue
Particle size (mm)	–	0.021	–	–	0.3	–	–	1	–
S_{BET} (m^2 g^{-1})	2.4	53	2.8	8.9	12	4.2	3.1	6	1.0

[a] Oxidized.
[b] Reduced.
[c] Rutile.
[d] Anatase.

Fig. 1. Kinetic constants for all samples.

For the oxidative and reductive treatments the evolutions are similar. When the catalysts are treated, the specific surfaces are weak and in each case the effect of thermal treatment is to reduce the kinetic constants. The sample which presents the largest specific surface after treatment corresponds to the one for which degradation is the fastest. However, for the two other samples (P25 and Aldrich) presenting different specific surfaces, the kinetic constants are very close. Furthermore, no difference has been observed between oxidated Prolabo ($S=8.9\,m^2\,g^{-1}$) and reduced Prolabo ($S=4.2\,m^2\,g^{-1}$). These results show that the crystallographic structure is an important parameter for benzamide degradation. Only the Prolabo sample still presents a fraction of anatase structure after treatment and only this sample continues to show an important catalytic activity.

As far as the stoichiometry is concerned, results are more difficult to interpret. It appears that for the Prolabo and Aldrich samples, in spite of a weaker specific surface for reduced TiO_2, kinetic constants are similar than in the case of oxidated samples. This behaviour comes in the same way that an increase of active sites in surface. On the other hand, for P25, both the samples, reduced or oxidated, present a similar specific surface, but the oxidated sample is more active than the reduced one. Some more tests would be necessary to conclude more specifically.

The results obtained for acetic acid show a predominant influence of the specific surface. The P25 presents the best activity, it is followed by Prolabo and, finally by Aldrich. The crystallographic nature might have had an effect, but this cannot be observable in this case. In each case, the thermal treatments contribute to a drastic decrease of the catalytic activity. As we could note for the untreated catalysts, the catalytic activity varies mainly in accordance with the specific surface. However, like for benzamide, the results show the same activity for reduced Aldrich and oxidated Aldrich, and for reduced Prolabo and oxidated Prolabo, even if the oxidated samples present a higher specific surface than reduced ones.

The results which were obtained in the set of TiO_2, for the benzamide and acetic acid degradations, permit to precise the role of the specific surface and crystallographic struc-

ture of catalysts. In the low specific surface domain (below $10\,m^2\,g^{-1}$), the behaviour is the same for the two pollutants; the kinetic constant increases with the specific surface. In contrast, for higher values of specific surface, the kinetic constant of benzamide seems to be constant while for acetic acid, it always increases with specific surface. The Fig. 1 clearly shows that the kinetic constant of benzamide is the same for untreated Prolabo and P25 in spite of a great difference in specific surface. These evolutions perfectly resume the above discussion. Moreover, for benzamide and acetic acid, and with Prolabo and Aldrich thermal treated samples, the activity of reduced catalysts are of the same order than the oxidated ones, even if these later present an higher specific surface. These results are in good agreement with the higher reactivity of reduced TiO_2 which present in surface some oxygen vacancies.

4. Conclusion

Having prepared different samples of titanium dioxide which differ in specific surface and crystallographic structure, we show the effect of these two parameters on the activity of the catalyst for the degradation of pollutants in an aqueous solution. For a pollutant such as benzamide, which does not adsorb on the catalyst, the specific surface does not seem to play a predominant role for the kinetic constant (in this case the kinetics of degradation is of first order). On the contrary, for acetic acid, which adsorbs on the catalyst, the specific surface plays a major role (in this case the kinetics of degradation is complex). These results are very promising as far as the supported catalysts are concerned. Indeed, it is difficult to get films of catalysts which present a large specific surface. Well, it appears that for benzamide at least, and maybe for a larger group of pollutants, the crystallographic structure has a preponderant effect for the degradation. So, since it is possible to control the crystallographic structure of the catalyst, even on films, we can hope to prepare stabilized catalysts, that is to say catalysts for which the filtration stage is no more necessary and which, in spite of a poor specific surface present a correct catalytic activity for a family of specific pollutants. To conclude, the influence of the stoichiometry has not really been demonstrated. Only two samples of three are more active when they are reduced. Tests are in progress in order to clear this problem up.

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