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Photocatalytic degradation of AZO dyes by supported TiO_2 + UV in aqueous solution

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Abstract

The photocatalytic degradation performance of photocatalysts TiO_2 supported on 13-X, Na-Y, 4A zeolites with different loading content was evaluated using the photocatalytic oxidation of dyes direct fast scarlet 4BS and acid red 3B in aqueous medium. The results showed that the best reaction dosage of TiO_2–zeolite catalysts is about 2 g/l and the photocatalytic kinetics follows first order for all supported catalysts. The photocatalytic activity order of the three series catalysts is 13X type > Y type > 4A type. The physical state of titanium dioxide on the supports is evaluated by X-ray photoelectron spectra (XPS), powder X-ray diffraction (XRD), BET, and FTIR. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: TiO_2; Zeolite; Photocatalytic degradation; Dye

1. Introduction

Now the textile industry utilizes about 10 000 different dyes and pigments, and the worldwide annual production of these dyes is over 7×10^5 tons (Spadary et al., 1994). Among these dyes, azo dyes are by far the largest group of colorants. Over 50% of all the dyes used in the industry are azo dyes. Some of these dyes have documented health hazards (Nilsson et al., 1993).

The toxicity and mass production of dyes leads to the necessity of treatment. The major difficulty in treating textile wastewater containing dyes is the ineffectiveness of biological processes (Tang and An, 1995). While physical processes, such as coagulation and adsorption, merely transfer the pollutants from wastewater to other media and cause secondary pollution. So in recent years, due to the non-toxic, insoluble, inexpensive, and highly reactive nature of TiO_2 under UV irradiation, TiO_2 photocatalytic degradation technique has been used to oxidize wastewater containing dyes and has attracted much attention (Fox and Dulay, 1993). For example, Matthews investigated the photocatalytic oxidation of methylene blue, rhodamine B and methyl orange using supported TiO_2 on sand, and the results showed that TiO_2/UV process is effective in totally mineralizing these compounds (Matthews, 1991). Davis and Grainer used TiO_2/UV for the treatment of municipal wastewater containing dyes, and it was found that COD can be reduced while removing the color from the sewage (Davis and Gainer, 1994). Chen and Chou studied that in the process of photobleaching methyl orange, the dye can be decolorized after 40 min of reaction (Chen and Chou, 1993).

In the past, most of the studies related to such photoreaction have been carried out using suspensions of powdered TiO_2 in the polluted solution. However,

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from a practical view it may not be possible to use catalyst suspensions in slurry photoreactor because of the filtration problems linked to the small size of titanium oxide. This led to a large attempt to immobilize the catalysts on supports including ceramic (Sunada and Heller, 1998), fiber glass (Shifu et al., 1996), glass, quartz and stainless steel (Fennandez et al., 1995), activated carbon (Takeda et al., 1998) etc. However, these efforts have not produced materials which meet all demands of photocatalytic activity. Importantly the photocatalytic efficiency of immobilized TiO_2 is often lower than the suspended particles (Matthews, 1990). Attempts to find a suitable support for TiO_2 should take into account several factors. The most important factor is the adsorptive ability. TiO_2 has a polar surface and is not a good adsorbent for non-polar organic molecules. Preconcentration of substrates onto the surface where photons are adsorbed is a desirable feature for oxidation kinetics. So among various supports for TiO_2 photocatalyst, zeolite seems to be an attractive candidate for its less polar surface and large surface area (Torimoto et al., 1996). Xu and Langford (1995, 1997) have utilized zeolites as supports for TiO_2, and it was observed that for the degradation of acetophenone or 4-chlorophenol in aqueous medium, supported titania on a hydrophobic molecular sieve ZSM5 shows high photoactivity even at low Ti loading.

In this study, 13-X, Na-Y, 4A zeolites are selected as supports for TiO_2 with different loading content. Photoactivity of the catalysts is evaluated using the photocatalytic oxidation of dyes 4BS and 3B. The physical state of the titanium dioxide on the supports is evaluated by X-ray photoelectron spectra (XPS), powder X-ray diffraction (XRD), BET, and FTIR.

2. Experimental

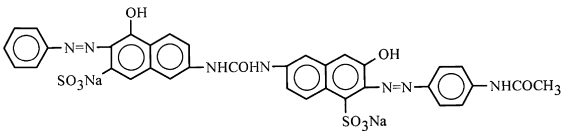
2.1. Materials

Supports used for TiO_2 loading were powder particles of 13-X type, Na-Y type and 4A type zeolites (provided by Nanjing Shuguang Chemical Plant). Two azo dyes (direct fast scarlet 4BS and acid red 3B) were market sale. The structure of dyes is shown in Fig. 1. Titanium tetraisopropoxide was obtained from Nanjing Shuguang Chemical Plant. All chemicals used in this experiment were analytical grade or chemical grade.

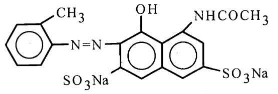
2.2. Preparation of supported TiO_2 photocatalysts

The TiO_2 sol was synthesized by the method called acid-catalyzed sol–gel formation (Anderson et al., 1988). The reactant composition was 20 ml 1M HNO_3, 7.4 ml titanium tetraisopropoxide. The hydrolysis reaction equation is

$$Ti(iso-OC_3H_7)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4C_3H_7OH.$$



Direct Fast Scarlet 4BS



Acid Red 3B

Fig. 1. The structure of two azo dyes in experiment.

The typical procedure was as follows: titanium tetraisopropoxide was added drop by drop to HNO_3 aqueous solution (Takeda et al., 1998), stirring at the same time, followed by agitation for 1.5 h to give a transparent TiO_2 sol, which contained 2.0 g TiO_2. The pH of the colloidal solution was adjusted to pH 2.5 with addition of 1M NaOH to prevent destruction of the zeolite supports by reaction with acid.

A certain amount of a support saturated with water for half an hour was mixed with a certain amount of TiO_2 sol, with stirring for 1 h, then followed by washing–centrifugation procedure to make the supernatant nearly neutral. The mixture was dried for 0.5 h at 120°C, calcined at 300°C for 2.5 h. Finally, the heated products were ground into fine powder, followed by screening to obtain < 0.225 mm powder. All the samples were stored in the dark to avoid preactivation by room light. Zeolites used for supports were 13-X, 4A and Na-Y type, respectively. For each of the three zeolites, five catalysts numbered 1, 2, 3, 4, 5 were made with different TiO_2 content (1.96%, 5.66%, 9.09%, 16.67%, 23.08%, respectively). And in order to compare the XRD spectra among catalysts with high TiO_2 loading and those with low TiO_2 loading, a catalyst with 50% TiO_2 content was also prepared. So there were 16 catalysts synthesized in this experiment. In this report, TiO_2% is reported as the amount of titanium oxide added into the support during synthesis. It was confirmed (Xu and Langford, 1995) that the measured content of TiO_2 is close to that calculated from synthesis.

2.3. Characterization of the supported catalysts

A D/MAX-RA rotating anode X-ray diffractometer (XRD, Rigaku, Japan) was used to record the powder XRD patterns. Diffraction patterns were taken over the 2θ range 5–50°. FTIR analyses were carried out on

VECTOR22 Fourier transform infrared spectrometer (FT-IR, Bruker, Germany). The samples were incorporated in KBr pellets for the measurements. Transmission electron microscopy was performed on JEM-200CX transmission electron microscope (TEM, JEOL, Japan). XPS were recorded with ESCALAB MK-II electron spectrometer (XPS, VG, U.K.). Calibration of the spectra was done at the C1s peak surface contamination at 284.6 eV. The BET specific surface area of the TiO_2 supported on 4A zeolites was determined by nitrogen adsorption at liquid nitrogen temperature on an ASAP 2000 Micromeritics Instrument Corporation (USA) surface area analyzer.

2.4. Photocatalytic activity measurement

Photodecomposition experiments were carried out on a merry-go-round photochemical reactor. The irradiation source was a 500 W medium pressure mercury lamp. The relative photocatalytic activity of various catalysts was evaluated by determination of loss of dye 4BS in aqueous medium. 7.0 ml 4BS or 3B (35 mg/l) was mixed with a certain amount of a catalyst in quartz tube (1.5 cm diameter, 10.0 cm length). The suspension was air-saturated before sealing, and oxygen was not deliberately purged into the reactor during experiment. Prior to illumination, the suspension was equilibrated for 1 h and then stirred for 5 min, so TiO_2 could be uniformly dispersed in solution. Then the tubes were put into the reaction chamber before the lamp and the rotator were turned on. The change of solution concentration in 1 h was used to evaluate the adsorbability of the photocatalysts in the dark. After reaction, the mixture was centrifuged to isolate the catalyst powder. The supernatant was used to analyze the concentration of dye.

Dyes were analyzed on UV–VIS 7520 spectrophotometer. The determination wavelengths were 500 nm for 4BS and 538 nm for 3B, which are the maximum absorption wavelengths. The determined absorption were converted to concentration through the standard curve method of dyes.

The simple regression analysis program in Statgraphics software (STSC Rockville MD, USA, 1987) was used in statistic analysis. Model adequacy was measured as correlation coefficient (r), and the significance level (p).

3. Results and discussion

3.1. Characterization of the TiO_2-zeolite photocatalysts

3.1.1. XRD analysis

The XRD spectra of supported TiO_2 are complicated by the X-ray of the supports. In XRD spectra of 13X-5, 4A-5 and 13X-1, 13X-3, 4A-2, 4A-4 (not listed here), the reflection at $dA = 3.52$ ($2\theta = 25.3°$), $dA = 3.25$, characteristic of anatase and rutile respectively, are not observed. This indicates that neither anatase nor rutile TiO_2 is formed in those catalysts. There may be amorphous TiO_2 formed in catalysts. However, from XRD spectrum of catalyst at high coverage of titanium (50%), it can be seen that there is anatase crystallite and a little rutile crystallite on the catalyst, and at the same time the larger peak width of XRD spectrum implies their very fine crystal size. For the catalysts with low coverage of titanium, the small amount of well-dispersed TiO_2 on the zeolites inhibits the mutual approach of fine TiO_2 particles, hence leads to the formation of amorphous titanium oxide. Peak packets were found for all the catalysts with low coverage of titanium, indicating the existence of non-crystalline substances. The intensity and area of peak packets increase with the increasing content of loaded titanium oxide, so the peak packets may be caused by amorphous titanium oxide. This observation confirmed the existence of non-crystalline TiO_2 supported on zeolites. In conclusion, oxide of titanium on zeolite surface is amorphous at low coverage, but approaches anatase crystal at high coverage.

3.1.2. TEM analysis

The TEM photograph of 50% TiO_2–4A zeolite shows that the size of titanium oxide particle is uniform, but their distribution on the surface of zeolite is not uniform. Through the change of the magnification times of TEM, the particle size of $\sim$5 nm can be obtained. The size is in accordance with its larger XRD peak width.

3.1.3. FTIR spectra

Andries and Sauer de Man Andries and Sauer (1996) reported that titanium is predicted to easily incorporate into tetrahedral site of siliceous zeolites. The primary effect of substituting titanium into a SiO_2 framework is a increase of the bond length from about 160 pm (Si–O) to 180 pm (Ti–O), leading to the shift of Si–O–Si vibration to lower frequency. Near 960 cm^{-1} can be assigned to Ti–O–Si antisymmetric stretching modes. In our experiment, the IR spectra of 10 catalysts in Table 2 and 13X, Y and 4A zeolites were detected. No band near 960 cm^{-1} is found for all 10 supported catalysts. So the substitution of Ti into tetrahedral Si sites during calcination process does not take place.

3.1.4. BET measurement

In general, the surface area of catalyst is the most important factor influencing the catalytic activity. Table 1 lists the BET surface area of catalysts 4A-2, 4A-4 and 4A-5.

Table 1
BET surface area of catalysts

Catalyst	4A-2	4A-4	4A-5
Surface area (m^2/g)	27.7983	91.0204	113.0251

The surface area increases with the increasing of TiO_2% in catalyst remarkably, implying the existence of TiO_2 with large surface area, which may be caused by their very fine particle confirmed in the XRD and TEM results.

3.1.5. XPS analysis

The determination results of XPS analysis are given in Table 2. The XPS analysis mainly reflects the component composition and chemical elementary state of the surface and the inferior surface of samples. For all the three series catalysts, the Ti% detected increases with the increasing of titanium oxide content in the catalysts. For catalysts with low TiO_2 content, TiO_2 concentrations in the surface of catalysts are much higher than the calculated TiO_2 dosages in catalyst preparation, indicating most of TiO_2 concentrating on the surface of zeolites. It is obvious that among the three series catalysts, the order of surface TiO_2 concentration is Y type catalysts >4A type >13X type.

The binding energies of Ti (2p) of all catalyst are basically equal to that of pure TiO_2, which indicates that Ti elements for all catalysts have the same chemical environment and chemical state, and similar to the chemical state in pure TiO_2. There is no obvious shoulder peak found for O (1s) peaks of all catalysts, implying no complicated oxygen species existing on the surface of catalysts. Probably due to the proximity of binding energy of the lattice oxygen O^{2-} of TiO_2 to that of zeolite, they merge into one peak. May be for the existence of zeolite lattice oxygen, the O (1s) binding energies of all the supported TiO_2 are lower than that of pure TiO_2. Since no binding energy difference >0.5 eV was observed, it could be approximately deduced that for the same series catalysts, no oxygen species changes with the increasing of Ti content in catalysts.

The similar phenomenon was found for Si (2p), Al (2p) and Na (1s). The binding energy order is Y type >13-X type >4A type. It is interesting that the order of surface Si/Al ratio, Y type >13-X type >4A, is similar to that of the binding energy order. This fact suggested that the composition of zeolites may influence the surface state of catalysts.

3.2. Effect of catalyst dosage

4BS degradation at varying 4A-2, 4A-4, 4A-5 catalysts dosages in the range 0.2–4.0 g/l are done in our experiment. Fig. 2 shows the 4BS degradation effect at different catalyst concentration. It can be seen that with the increasing of catalyst dosage, the decolor rate increases due to the increase of active sites. At the dosage

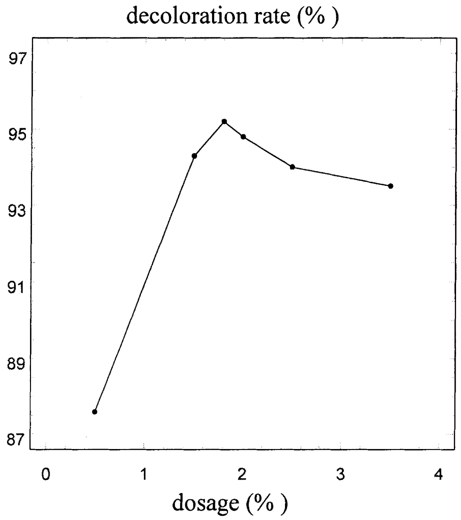


Fig. 2. The decoloration rate of 4BS at different 4A-4 catalyst dosages.

Table 2
Surface composition analysis and binding energies of catalysts from XPS

Catalyst	Weight TiO_2% in catalyst	Atomic Ti%	Weight TiO_2%	Atomic Si/Al	B.E. (eV)			
					Ti(2p)	O(1s)	Si(2p)	Al(2p)
TiO_2	–	–	–	–	458.8	533.9	–	–
13X-1	1.96	1.97	5.71	1.70	458.7	531.7	102.2	74.3
13X-3	9.09	3.09	12.18	1.82	458.8	532.2	102.8	74.7
13X-5	23.08	3.68	14.78	1.87	458.8	531.7	102.4	74.4
Y-1	1.96	3.55	10.39	3.65	458.7	532.3	102.8	74.6
Y-2	5.66	5.90	16.94	2.75	458.7	532.4	102.8	74.9
Y-3	9.09	6.29	18.37	3.16	458.9	532.5	102.9	74.6
4A-2	5.66	3.29	9.84	1.48	458.5	531.3	101.8	74.0
4A-4	16.67	5.01	14.56	1.15	458.9	531.7	102.0	74.3
4A-5	23.08	4.87	14.27	1.03	458.8	531.8	102.1	74.3

of 1.5–2.0 g/l, the decolor rates achieve the maximum. Then with the increasing of dosage, the decolor rates decrease. This phenomenon may be due to the light scattering and reduction in light penetration through the solution, caused by the lightproof suspended catalyst. For 4A-2, 4A-4, 4A-5 catalysts, the dosage producing the maximum effect changes from 2.0–1.5 g/l, which is due to the TiO_2 different content in catalysts. To keep the enough TiO_2 in reaction, the catalyst containing less TiO_2 needs more dosage. So 2.0 g/l was selected as the catalyst dosage for the photocatalytic activity study of all 15 catalysts in our experiment.

3.3. Photocatalytic kinetics of TiO_2-zeolite catalysts

In general, it has been accepted (Serpone and Pelizzetti, 1989) that adsorption is considered critical in the heterogeneous photocatalytic oxidation process. The langmuier–Hinshelwood model was used to describe the kinetics of dyes (Turchi and Ollis, 1990). However, dark adsorption experiments in our study showed that there is no detectable adsorption of 4BS on catalysts even after equilibration several days. So the effect of dye adsorption factor on photocatalytic activity is very limited. It can be deduced that 4BS adsorption may not be the most important determinative factor for 4BS photocatalytic degradation activity of catalysts in our study. The maximum diameter of 4BS molecule is approximately >1 nm due to the naphthalene ring with the large substituents of $–SO_3Na$ and –NHCONH–. The reported aperture sizes of 13X, Y and 4A type zeolites are all <1 nm. The big 4BS dye molecules cannot enter the massive inner surface of zeolites. So most of the adsorptive ability of zeolites cannot be utilized. The dye molecules can only be adsorbed on the outer surface of zeolites and TiO_2. At the same time, the steric inhibition of large dye molecules inhibits the approach of other dye molecules to the surface of catalysts. So no obvious dye adsorption phenomenon can be observed.

Self-photolysis 4BS dye experiment was performed at the same time. And no self-photolysis has been observed. The apparent decoloration of the solutions of 4BS dye in the presence of catalysts was seen after 25 min irradiation for all 15 photocatalysts, indicating the loss of their chromophoric groups. The above observations suggested that the photocatalytic activities of all 15 catalysts are remarkable, and photocatalytic degradation of dyes by these catalysts under UV light is possible.

The decoloration of the dye solution showed that the destruction of the dyes occurred. Azo dyes are characterized by nitrogen to nitrogen double bonds (–N=N–). They contain at least one and up to four azo groups usually attached to two radicals of which at least one but usually both are aromatic groups. The color of azo dyes is determined by the azo bonds and their associated chromophores and auxochromes (Reutergardh and Iangphasuk, 1997). Azo bonds are the most active bonds in azo dye molecules, which are liable to be oxidized by positive hole or hydroxyl radical or reduced by electron in the conduction band (Ganesh et al., 1994). The reactions of azo bonds lead to the decoloration of dyes. 4BS dye contains two azo groups, and the decoloration of dye 4BS showed that the azo bonds of dye molecule are destroyed. The 34% decrease of absorption at 310 nm was observed for 4BS dye after photodegradation in the presence of 4A-1 catalyst. This indicates that photocatalytic degradation not only destroys the conjugate system (including –N=N–), but also partly destroys the benzene and naphthalene rings in molecules.

Through statistic correlation analyses, it was found that the kinetics of photocatalytic degradation for 15 catalysts all follows first order kinetics. Table 3 gives linear regression equations for all 15 catalysts.

Table 3
Linear regression equation of 4BS photodegradation using different catalyst

Catalyst	Weight TiO_2% in catalyst	Regression equation	r_1	P_1
13X-1	1.96	$\ln C = 3.086 - 0.1411t$	−0.972	0.00115
13X-2	5.66	$\ln C = 3.219 - 0.1240t$	−0.976	0.00064
13X-3	9.09	$\ln C = 3.047 - 0.1151t$	−0.958	0.00259
13X-4	16.67	$\ln C = 3.573 - 0.1148t$	−0.999	0.00003
13X-5	23.08	$\ln C = 3.512 - 0.1055t$	−0.999	0.00007
Y-1	1.96	$\ln C = 3.090 - 0.09763t$	−0.948	0.0404
Y-2	5.66	$\ln C = 3.067 - 0.1190t$	−0.961	0.00222
Y-3	9.09	$\ln C = 3.589 - 0.09009t$	−0.994	0.00059
Y-4	16.67	$\ln C = 3.481 - 0.1005t$	−0.998	0.00001
Y-5	23.08	$\ln C = 3.426 - 0.1130t$	−0.996	0.00003
4A-1	1.96	$\ln C = 3.091 - 0.04948t$	−0.838	0.03726
4A-2	5.66	$\ln C = 3.053 - 0.05019t$	−0.821	0.04525
4A-3	9.09	$\ln C = 3.096 - 0.07923t$	−0.926	0.00808
4A-4	16.67	$\ln C = 3.643 - 0.1238t$	−0.989	0.00145
4A-5	23.08	$\ln C = 3.461 - 0.1130t$	−0.981	0.0052

The similar statistic correlation analyses was also done for photocatalytic degradation process of acid red 3B by 13X-1 catalyst. The obtained first linear regression equation is as follows:

$$\ln C = 3.470 - 0.1320t \quad r = -0.9894 \quad P = 0.00017.$$

The obvious decoloration was observed after 25 min reaction. So the prepared catalyst in our experiment can also be used to degrade other dyes. From the fact that the rate constant of 4BS is larger than that of acid red 3B, it can be concluded that 4BS is easier to be oxidized than 3B.

The change curves of k values of 3 series catalysts with the TiO_2 content in catalysts are given in Fig. 3. 13X type shows the highest photocatalytic activity, Y type has higher catalytic activity than 4A type. The aqueous suspension of 13X, Y and 4A zeolites (2 g/l) give pH of 9.55, 9.21 and 10.1, respectively. All the reaction systems are under alkaline condition. At high pH level, hydroxyl radicals are considered as the predominant oxidation species for the increase of hydroxyl ions, which induces more hydroxyl radical formation. 4BS (sodium salt) is totally dissociated in aqueous media. Due to the amphoteric character of TiO_2, either a positive or negative charge can develop on its surface. As pH exceeds the pH_{ZPC} of TiO_2 (6.8) (Kormann et al., 1991), adsorption is reduced because of the dissociated 4BS (sulfonate anion) and the negatively charged TiO_2 surface, with a resulting loss of photoreactivity. This point can be confirmed by the above dark adsorption experiment result that adsorption is not significant in this system. As we all know, the surface area and aperture size of 13X zeolite are higher than those of Y which are in turn larger than those of 4A type (Da Lian Chemical and Physical Research Institute, 1978). The higher surface area and bigger aperture size of zeolite favors the adsorption of more water molecules, hydroxyl ions and dye molecules, thus leading to higher photoreactivity. The Si/Al ratio is another influencing factor. Higher Si/Al ratio means lower polarity of zeolite. Alumina acts as Lewis acidic center, which can stabilize reactive intermediates (Xu and Langford, 1997), adsorb the reactant anions. Maybe the generated hydroxyl radicals can be stabilized in the rigid framework of the zeolites, hence electron-hole recombination is prevented, which favors the increase of reaction rate. Overall, the synthesis action of the above factors (such as pH, surface area, Si/Al) determines the photoreactivity order of 13X, 4A, Y type catalysts.

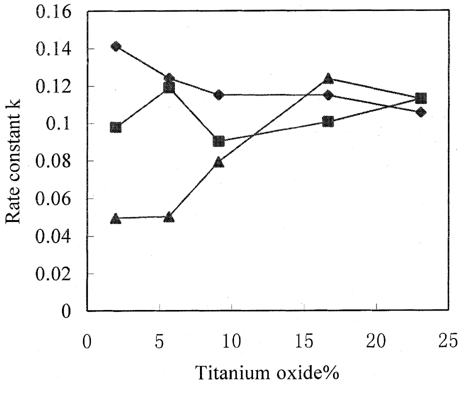


Fig. 3. k values vs. TiO_2% of three types supported catalysts ◆ 13X type catalysts ■ Y type catalysts ▲ 4A type catalysts.

The similar change trend is observed for the three series catalysts. The rate constants do not increase linearly with the increasing of TiO_2 content, and they all achieve the highest rate constants at the low or medium TiO_2%. This may be caused by two competition processes: more TiO_2 loaded favours the generation of more holes, more hydroxyl radicals, thus results in higher reaction rate; too much TiO_2 occupying too much capacity of zeolites, will decrease the adsorption of hydroxyl ions, reactant ions, and the stabilization of hydroxyl radicals due to their negatively charged surface, hence leading to the decrease of reaction rate. The loaded titanium oxide concentrations producing the highest photoreactivity are different for the three types of catalysts. 13X type reaches the highest reaction rate at the lower TiO_2% than Y type that is in turn lower than 4A type. The order is contrary to the reaction rate order of the three series catalysts. It is understandable that catalysts with lower photocatalytic activity may need more TiO_2% to reach higher reaction rate.

4. Conclusions

1. Under this experimental condition, for catalysts with low TiO_2 content, most of the titanium oxide supported on zeolites concentrates on the surface of catalysts. At low coverage, they exhibit amorphous morphology. However, at sufficiently high coverage, discrete crystals, mainly anatase, form on zeolites. The very fine particles of dimension near 5nm, which have large surface area, grow on the supports. The Si–O bonds of zeolites are not disturbed by the linkage to Ti. So no chemical bonding takes place between zeolites and TiO_2.
2. The best reaction dosage of TiO_2–zeolite catalysts is about 2 g/l.
3. The photocatalytic kinetics follows first order for 15 supported catalysts.
4. The photocatalytic activity order of the three series catalysts is 13X type >Y type >4A type. The photoreactivy does not increase linearly with increasing TiO_2%.

5. Suggestion

If the TiO_2–zeolite photocatalysts synthesized in our study can be used to degrade the wastewater or waste gas with much smaller molecular size than dyes in our experiment, the large surface area of the photocatalysts will be fully utilized and then the photocatalysts may show greater photoactivity.

References

Anderson, M.A., Gieselman, M.J., Xu, Q., 1988. Titania and aluminia ceramics membranes. J. Membr. Sci. 39, 243–258.

Chen, L.C., Chou, T.C., 1993. Photobleaching of methyl orange in titanium dioxide suspended in aqueous solution. J. Mol. Catal. 85, 201–214.

Da Lian Chemical and Physical Research Institute, 1978. Zeolite Molecular Sieve, Science, Moscow.

Davis, R.J., Gainer, J.L., 1994. Photocatalytic decolorization of waste water dyes. Wat. Environ. Res. 66, 50–53.

de Man Andries, J.M., Sauer, J., 1996. Coordination, structure, and vibrational spectra of titanium in silicate and zeolites in comparison with related molecules An ab initio study. J. Phys. Chem. 100, 5025–5034.

Fennandez, Lassaletta, G., Jimenez, V.M., Justo, A., 1995. Preparation and characterization of TiO_2 photocatalysts supported on various rigid supports (glass, quartz and stainless steel). Comparative studies of photocatalytic activity in water purification. Appl. Catal. B: Environ. 7, 49–63.

Fox, M.A., Dulay, M.T., 1993. Heterogeneous photocatalysis. Chem. Rev. 93, 341–357.

Ganesh, R., Boardman, G.D., Michelssen, D., 1994. Fate of azo dyes in sludges. Wat. Res. 28, 1367–1376.

Kormann, C., Bahnemann, D., Hoffman, M.R., 1991. Photolysis of chloroform and other organic molecules in aqueous TiO_2 suspensions. Environ. Sci. Technol. 25, 494–500.

Matthews, R.W., 1990. Purification of water with near-UV illuminated suspensions of titanium dioxide. Wat. Res. 24, 653–660.

Matthews, R.W., 1991. Photooxidative degradation of coloured organic in water using supported catalysts on TiO_2 sand. Wat. Res. 25, 1169–1179.

Nilsson, R., Nordlinder, R., Wass, U., 1993. Asthma, Rhinitis, and Dermatitis in workers exposed to reactive dyes. British J. Ind. Medi. 50, 65–70.

Reutergardh, L.B., Iangphasuk, M., 1997. Photocatalytic decolourization of reactive azo dye: a comparison between TiO_2 and CdS photocatalysis. Chemosphere 35, 585–596.

Serpone, N., Pelizzetti, E. (Eds.), 1989. Photocatalysis: Fundamentals and Applications. Wiley, New York.

Shifu, C., 1996. Photocatalytic degradation of organic pesticide containing phosphorus by TiO_2 supported on fiber glass. Environ. Sci. 17, 33–35.

Spadary, J.T., Isebelle, L., Renganathan, V., 1994. Hydroxyl radical mediated degradation of azo dyes: evidence for benzene generation. Environ. Sci. Technol. 28, 1389–1393.

Sunada, F., Heller, A., 1998. Effects of water, salt water, and silicone overcoating of the TiO_2 photocatalyst on the rates and products of photocatalytic oxidation of liquid 3-octanol and 3-octanone. Environ. Sci. Technol. 32, 282–286.

Takeda, N., Iwata, N., Torimoto, T., Yoneyama, H., 1998. Influence of carbon black as an adsorbent used in photocatalyst films on photodegradation behaviors of propyzamide. J. Catal. 177, 240–246.

Tang, W.Z., An, H., 1995. UV/TiO_2 photocatalytic oxidation of commercial dyes in aqueous solutions. Chemosphere 31, 4157–4170.

Torimoto, T., Ito, S., Kuwabata, S., Yoneyama, H., 1996. Effects of adsorbents used as supports for titanium dioxide loading on photocatalytic degradation of propyzamide. Environ. Sci. Technol. 30, 1275–1280.

Turchi, C.S., Ollis, D.F., 1990. Photocatalytic degradation of organic water contaminants: mechanisms involving hydroxyl radical attack. J. Catal. 122, 178–192.

Xu, Y.M., Langford, C.H., 1995. Enhanced photoactivity of a titanium (IV) oxide supported on ZSM5 and zeolite A at low coverage. J. Phys. Chem. 99, 11501–11507.

Xu, Y.M., Langford, C.H., 1997. Photoactivity of titanium dioxide supported on MCM41 zeolite X, and zeolite Y. J. Phys. Chem. B 101, 3115–3121.