Surface Acidity and Photocatalytic Activity of Nb_2O_5/TiO_2 Photocatalysts

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Samples of Nb_2O_5/TiO_2 mixed oxide powders were prepared by the incipient wetness method. The photocatalytic activities of TiO_2 based catalysts were evaluated by the degradation of 1,4-dichlorobenzene (DCB). The addition of Nb_2O_5 to TiO_2 greatly increased its photocatalytic activity and also increased the catalyst's surface acidity, as determined by the n-butylamine titration method. A correlation between the maximum photocatalytic activity and the number and strength of acid sites were observed. Consequently, the same structural feature that enhances the adsorption of n-butylamine appears to promote the catalytic activity. © 1995 Academic Press, Inc.

INTRODUCTION

It has been shown that the photocatalytic activity of titanium (IV) oxide is influenced by surface area, band gap, porosity, crystal structure (anatase and/or rutile), and density of surface hydroxyl groups (1–4). These will have an influence on the production of electron-hole pairs, the surface adsorption and desorption process, and the redox process. Recently, noble metals (Pd, Au, Ag, etc.) deposited on TiO_2 have been widely studied for the purpose of improving the photocatalytic activity of TiO_2 (5–9). Gerischer and co-workers (7, 10) have proposed that the rate of photooxidation of organic compounds is limited by the rate of electron transfer to oxygen. They have reported that the modification of the surface by noble metals increases the efficiency of electron transfer to oxygen and, hence, increases the efficiency of photoassisted oxidation.

In contrast to metal/TiO_2 photocatalysts, there have been few studies reported concerning the photocatalytic activity of metal oxide/TiO_2 catalysts. Several papers have reported (11, 12) on the use of chromium oxide and iron oxide as additives to TiO_2 in order to increase the rate of photooxidation of phenol. However, it has been shown (13) that the addition of these oxides was detrimental to the photooxidation process. In a recent study, it was found that the addition of WO_3 and MoO_3, respec-

tively, to TiO_2 greatly improved its photocatalytic activity toward the oxidation of 1,4-dichlorobenzene (14, 15). Both studies proposed that the similarity in band gaps between WO_3, MoO_3, and TiO_2 (Anatase: 3.2 eV; MoO_3: 3.0 eV; WO_3: 2.8 eV) (16), increased the photocatalytic activity of the system. This increased photoactivity was observed for the oxidation of both halogen- and oxygen-containing organic compounds.

It is also well known that surface hydroxyl groups play an important role themselves in the photocatalytic degradation of organic contaminants in water. They may provide anchoring sites for surface layers of other transition metal oxides and these newly created sites are even more efficient in the oxidation process. Electrochemical experiments have confirmed the importance of hydroxyl groups in promoting electron transfer from the conduction band of TiO_2 to chemisorbed oxygen molecules (17, 18). Morterra et al. (19, 20) studied the surface acidity of a TiO_2 anatase sample which had been prepared by the flame reactor method from pure $TiCl_4$ in much the same way as the commercial Degussa P25 is produced. They showed by the adsorption of pyridine and subsequent IR spectra that the surface acidity of anatase is mostly of the Lewis type.

Mixed metal oxides often generate additional acid sites over their individual end members because of an increase in the polarizability of the hydroxide groups present in the mixed oxides (21, 22). Hence, an alternative proposal involving surface hydroxyl groups and number and strength of acid sites in determining the efficiency of the photocatalyst for WO_3/TiO_2 and MoO_3/TiO_2 has been reported (23). A correlation between the maximum photocatalytic activity and the maximum surface acidity was observed (23). Recent investigators (24) have shown that Nb_2O_5/TiO_2 mixed oxides are acidic and active in the reduction of NO with NH_3 and isomerization of cyclopropane. It has been shown that for the Nb_2O_5/TiO_2 mixed system increasing the mole% of Nb_2O_5 loaded onto TiO_2 increased the acid strength (24). These stronger acid sites, produced on Nb_2O_5/TiO_2 as well as on other mixed

oxide systems, often contribute to increased catalytic activity and selectivity for various catalytic processes, such as the disproportionation of butene, and the isomerization of cyclopropane (24, 25).

In this investigation, the system Nb_2O_5/TiO_2 was studied in order to improve the photocatalytic activity of pure TiO_2. The surface acidity of the Nb_2O_5/TiO_2 system was also studied in order to gain a greater understanding of the physical nature of these photocatalysts. This is part of a systematic attempt to prepare mixed oxide/TiO_2 systems which can efficiently photodegrade chlorinated hydrocarbons. The study reported in this paper is the first which investigates members of the Nb_2O_5/TiO_2 system as catalysts for photooxidation of chlorinated hydrocarbons.

EXPERIMENTAL

Preparation of Nb_2O_5/TiO_2 polycrystalline samples. Members of the Nb_2O_5/TiO_2 system were prepared by the incipient wetness method. A solution of 10% w/v niobium isopropoxide in isopropanol (Johnson Matthey, N. 36572) was used as the source of Nb_2O_5 in this study. A fixed weight of TiO_2 (Degussa P25) was dispersed in solutions containing known amounts of niobium isopropoxide in order to prepare samples with varying concentrations of Nb_2O_5. Each solution was then stirred with a glass rod and the resulting mixure was placed under an infrared lamp in order to evaporate the isopropanol. The product was subsequently dried at 120°C for 16 hr and ground with a mortar and pestle. Finally, the product was calcined in an oxygen gas stream (100 ml/min) at 550°C for 1 hr. This was the minimum temperature required for complete decomposition of the niobium isopropoxide. A pure Nb_2O_5 powder sample was also made by drying 10% w/v niobium isopropoxide solution, followed by a heat treatment analogous to that described above.

Measurement of surface area. The surface area was measured by the single point BET method using a Flow Sorb (II) 2300 (Micromeritics Instrument Corp., Norcross, GA). The samples were degassed at 170°C for 2 hr and the adsorbate gas consisted of a mixture of 30% N_2/70% He.

Measurement of photocatalytic activity. The photocatalytic activities of various powder samples were evaluated by the degradation of 1,4-dichlorobenzene (DCB). A saturated DCB solution was prepared by adding an excess of DCB to distilled water and stirring for 8 hr. The solubility of DCB in water at room temperature is 76 ppm (26). The solution was capped and preserved in darkness. A standard stock solution containing 0.0015 wt.% of the ultrasonically dispersed oxide was prepared. Three milliliters of this solution was transferred to a silica cuvette and 0.2 ml of a saturated aqueous solution of DCB was added. A sample containing 0.2 ml of distilled water and 3 ml of the TiO_2 suspension was used as a blank for the absorption measurement. The sample was then irradiated with a 150 W xenon short-arc lamp whose output was passed through a Pyrex filter. The differential absorption at 224 nm (maximum absorption peak of DCB) was measured using a Perkin–Elmer 552A spectrophotometer. The change in concentration of DCB of the irradiated sample as a function of time was compared to that of the blank.

Amine titration method for determination of the surface acidity of a solid. The surface acidity of the samples was determined by titration with n-butylamine following a procedure established by Tamele (27). Catalyst powder (0.5 g) was dispersed in 50 ml of benzene using a glass stirring bar. Five drops of a 0.5 N indicator solution in benzene were added to the flask; 0.01 N n-butylamine was titrated against the powder and the amount of titer necessary to effect the color change on the surface of the powder was recorded. The acidity was then calculated in terms of mmole/g catalyst, and the acid strength was expressed by the Hammett acidity function, H_0, of the respective indicator used. The following indicators were used in this study: bromothymol blue ($pK_a = +7.2$, $H_0 \leq +7.2$), neutral red ($pK_a = +6.8$, $H_0 \leq +6.8$), methyl red ($pK_a = +4.8$, $H_0 \leq +4.8$), methyl yellow ($pK_a = +3.3$, $H_0 \leq +3.3$), fast garnet ($pK_a = +2.0$, $H_0 \leq +2.0$), and crystal violet ($pK_a = +0.8$, $H_0 \leq +0.8$). Although the titration technique has intrinsic limitations (28), precautions were taken to handle the samples in a consistent manner to ensue that the results were reproducible and could be confidently compared on a relative basis. The reproducibility was found to be 0.001 mmole/g.

RESULTS AND DISCUSSION

The photocatalytic activity of Nb_2O_5/TiO_2 powder samples was evaluated by the degradation of 1,4-dichlorobenzene (DCB). Samples were irradiated for 10 min with a xenon lamp. Figure 1 shows the change in concentration of DCB as a function of irradiation time for samples heat-treated at 550°C. It can be seen that Nb_2O_5/TiO_2 samples show an approximately 100% increase in photocatalytic activity over a pure TiO_2 sample which has been heat-treated at 550°C. The optimum loading of Nb_2O_5/TiO_2 (P25) particles was determined by measuring the activity of various Nb_2O_5/TiO_2 samples. The results of these measurements are plotted in Fig. 2. It can be seen that the optimum concentration of Nb_2O_5 on TiO_2 powders is in the range of 1.5 to 3 mole%. It is well known that this concentration corresponds to the amount required for monolayer coverage.

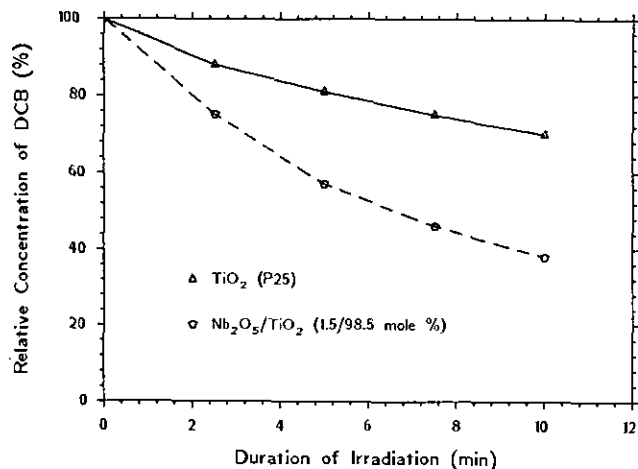It has been indicated by previous investigators that sur-

FIG. 1. Decomposition of DCB vs irradiation time of TiO₂ and Nb₂O₅/TiO₂ samples.

face hydroxy groups play an important role in the photocatalytic degradation of organic contaminants in water. Tanabe (29, 30) has established that the n-butylamine titration method is a means of determining surface acidity of metal oxides. The presence of a second metal oxide in contact with TiO₂, such as Nb₂O₅/TiO₂ (24), should cause an increase in acidity.

The surface acidity of the prepared powder samples was evaluated by the n-butylamine titration method. Samples were prepared with 0.5, 1.5, 2.3, 3, 5, and 7%
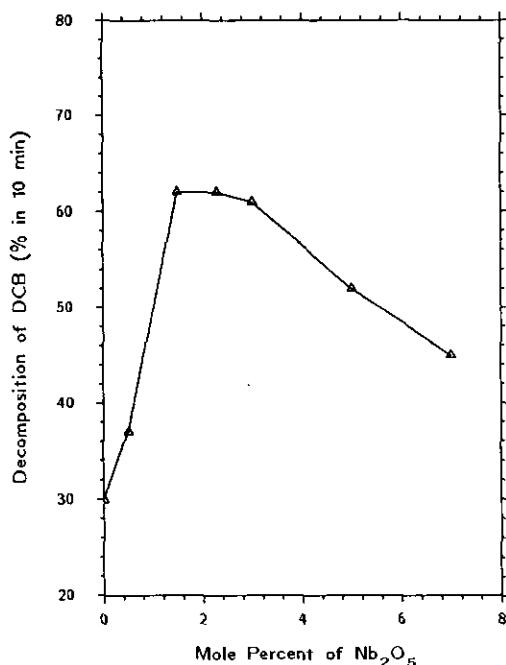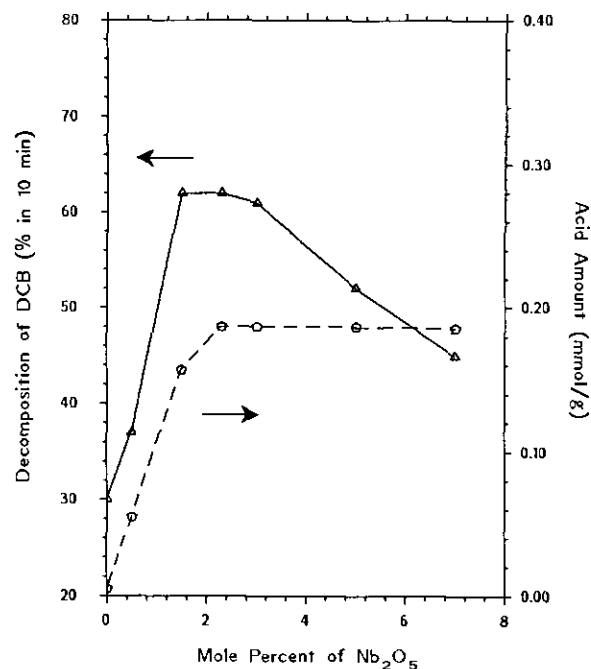

FIG. 3. Decomposition of DCB and the surface acidity determined with methyl red as a function of concentration of Nb₂O₅ on TiO₂.

Nb₂O₅ on TiO₂. Figure 3 shows the change in percent of DCB decomposed in 10 min and the change in acid amount is determined with the indicator methyl red plotted against increasing mole% of Nb₂O₅. It can be seen that the point at which the optimum photocatalytic activity is reached (1.5 mole% Nb₂O₅) approximately corresponds to the point at which the acid site density is maximized. It has been reported (31) that TiO₂ is covered with a monolayer of Nb₂O₅ at approximately 2.2 mole%. Beyond 3 mole% of Nb₂O₅ concentration, the number of acid sites remains constant. The observed activity decreases as the concentration of Nb₂O₅ is increased from 3 to 7 mole%, which is consistent with a build-up of inactive Nb₂O₅. Table 1 summarizes the data shown in Figs. 2 and 3. Table 1 shows that there is little variation in the surface area of the Nb₂O₅/TiO₂ samples as a function of Nb₂O₅ loading. Therefore, the increased photocatalytic efficiency observed in the Nb₂O₅/TiO₂ system can be related to the same structural feature that enhances the adsorption of n-butylamine. Samples of Nb₂O₅/TiO₂ prepared at 650°C gave similar results to those of the samples prepared at 550°C. Surface areas, acidities, and activities remained unchanged. Hence, Nb₂O₅ appears to improve the properties of titanium photocatalysts.

The use of various indicators with different pK_a values, and thus different Hammett acidity functions, enables a determination of the total acidity at various acid strengths by the n-butylamine titration method. Table 1

FIG. 2. Photocatalytic activity of TiO₂ powders as a function of concentration of Nb₂O₅ on TiO₂.

TABLE 1
Photocatalytic Activity, Surface Area, and Acidity Distribution for TiO_2, Nb_2O_5/TiO_2 Polycrystalline Samples

Sample	Activity (rel)*	Surface area (m^2/g)**	Acidity Distribution $(mmole/g)$***					
			Bromothymol blue $H_0 \leq +7.2$	Neutral red $H_0 \leq +6.8$	Methyl red $H_0 \leq +4.8$	Methyl yellow $H_0 \leq +3.3$	Fast garnet $H_0 \leq +2.0$	Crystal violet $H_0 \leq +0.8$
P25(RT)	40	49	0.071	0.071	0.011	0	0	0
P25(550°C)	30	45	0.038	0.037	0.005			
Nb_2O_5	3	6	0.162	0.139	0.035	0.035	0.035	0
Nb_2O_5/TiO_2								
0.5%	37	45	0.220	0.200	0.055	0.055	0.055	0.019
1.5%	62	47	0.386	0.300	0.157	0.157	0.157	0.052
2.3%	62	47	0.425	0.327	0.187	0.188	0.188	0.060
3%	61	47	0.426	0.328	0.187	0.189	0.187	0.060
5%	52	46	0.424	0.326	0.187	0.187	0.187	0.059
7%	45	44	0.425	0.325	0.186	0.186	0.187	0.058

* Reproducible within ± 2.
** Reproducible within ± 2 m^2/g.
*** Reproducible within ± 0.001 mmole/g.

shows acid site distribution and surface acidity for TiO_2 and Nb_2O_5/TiO_2 samples. It can be seen that the total acidity of Nb_2O_5/TiO_2 samples increases with increasing mole percent of Nb_2O_5 at all pK_a's studied until the surface of the TiO_2 is effectively covered. Beyond this concentration, the total acidity remains constant. Figure 4 shows the acid site disstribution for two Nb_2O_5/TiO_2 samples listed in Table 1. The total acidity of the 1.5% Nb_2O_5 sample is higher than that of the 0.5% Nb_2O_5 sample in the range of $+0.8 \leq H_0 \leq +7.2$.

CONCLUSIONS

The photocatalytic activity of TiO_2 toward the oxidation of 1,4-dichlorobenzene (DCB) can be increased by approximately 100% by the introduction of Nb_2O_5. The optimum concentration of Nb_2O_5 on TiO_2 powders is in the range of 1.5 to 3 mole% of Nb_2O_5. The observed increase in the photocatalytic activity of the mixed Nb_2O_5/TiO_2 catalysts corresponded with an increase in their submonolayer surface coverage and acidity. It appears that the surface acidity plays an important role in determining the activity of the photocatalyst.

ACKNOWLEDGMENT

FIG. 4. Acid site distribution of two Nb_2O_5/TiO_2 samples.

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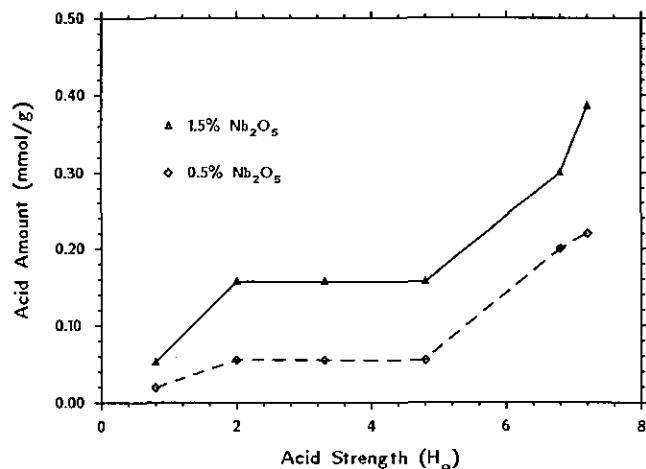10. H. Gerishcer and A. Heller, *J. Phys. Chem.* **95**, 5261 (1991).

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