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Surface Acidity and Photocatalytic Activity of TiO_2, WO_3/TiO_2, and MoO_3/TiO_2 Photocatalysts

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TiO_2 powder samples (Degussa P25) were calcined at various temperatures and their photocatalytic activity toward the degradation of 1,4-dichlorobenzene was measured. The surface acidity of the samples was also determined by the *n*-butylamine titration method. A linear relationship between photocatalytic activity and surface acidity was observed for the TiO_2 samples. WO_3/TiO_2 mixed oxide powders and MoO_3/TiO_2 mixed oxide powders were prepared by an impregnation technique. The addition of WO_3 or MoO_3 to TiO_2 greatly enhanced its photocatalytic properties. The addition of WO_3 or MoO_3 to TiO_2 also increased the catalysts' surface acidity, as determined by the *n*-butylamine titration method. A correlation between the maximum photocatalytic activity and the maximum surface acidity was observed. Whereas acidity may not be the only factor which influences activity, it is certainly an important one.

Introduction

Photoassisted heterogeneous catalysis is currently of considerable interest as a means of removing harmful organic impurities from water. Many organic compounds can be decomposed in aqueous solution in the presence of titanium(IV) oxide powders illuminated with near UV or sunlight.[1–10]

It has been shown that the photocatalytic activity of titanium(IV) oxide is influenced by surface area, crystal structure (anatase and/or rutile) and density of surface hydroxyl groups.[11–14] Previous investigators have modified this density through the photodecomposition of the platinum group metals onto the surface of the titanium(IV) oxide catalyst.[15–24] Others have examined the role of hydroxyl groups in the photoadsorption of oxygen on TiO_2 surfaces.[25–28] Electrochemical experiments have confirmed the importance of hydroxy groups in promoting electron transfer from the conduction band of TiO_2 to chemisorbed oxygen molecules.[29,30] Thus, it is well-known that surface hydroxy groups play an important role in the photocatalytic degradation of organic water contaminants.

Boehm[31,32] showed that two types of OH groups exist on the surface of Degussa TiO_2 (P25), half of which are acidic in character while the other half are predominantly basic. Morterra et al.[33,34] 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 surface acidity over their individual end members because of an increase in the polarizability of the hydroxide groups present in the mixed oxide.[35,36] Recent investigators[37,38]

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have shown that for the WO_3/TiO_2 mixed oxide system increasing the mole percent of WO_3 loaded onto TiO_2 increased the total acidity. This was attributed to an excess of positive charge in the system, and this positive charge is considered to cause the generation of additional acidity. These stronger acid sites, produced on WO_3/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 amination of phenol and the isomerization of butene.[39–44]

Two previous studies[45,46] showed that both the WO_3/TiO_2 and MoO_3/TiO_2 mixed oxide systems have higher photocatalytic activity toward the oxidation of 1,4-dichlorobenzene (DCB) than does the pure titanium(IV) oxide powder. Both studies proposed that the similarity in bandgaps between MoO_3, WO_3, and TiO_2 (anatase, 3.2 eV; MoO_3, 3.0 eV; WO_3, 2.8 eV),[47] as well as the ease of reducibility of the surface MoO_3 and WO_3 species, made the electron-transfer rate-controlling step more efficient and hence increased the overall photocatalytic activity of the system. However, in light of the above discussion, an alternative proposal may involve surface hydroxy groups and surface acidity as important factors in determining the efficiency of the photocatalyst. This study of the surface acidity of these mixed oxide systems is appropriate in order to gain a greater understanding of the physical nature of these photocatalysts.

Experimental Section

Preparation of TiO_2 Polycrystalline Samples. TiO_2 powder (1.0 g Degussa P25) was moistened with 2.5 mL of distilled water, dried under an infrared lamp for 30 min, then dried at 120 °C for 16 h. The product was ground with a mortar and pestle. Finally, the sample was calcined in an oxygen gas stream (100 cm^3/min) at various annealing temperatures for 1 h. Samples were annealed at 250, 350, 450, and 500 °C.

Preparation of WO_3/TiO_2 Polycrystalline Samples. The procedure for the preparation of the WO_3/TiO_2 polycrystalline samples has been reported in detail in a previous publication.[45] WO_3 was dispersed onto TiO_2 by the following method: A stock aqueous ammonia solution of H_2WO_4 (Allied Chemical & Dye Corp., No. 1204), containing 2.0 mg/mL of tungstic acid, was prepared. A fixed weight of TiO_2 was ultrasonically dispersed in varying aliquots of the aqueous ammonia solution of tungstic acid, in order to prepare samples with varying concentrations of WO_3. Each solution was then evaporated to dryness over a hot water bath. The product was subsequently dried at 120 °C for 16 h and ground with a mortar and pestle. Finally, the product was heated at a rate of 100 °C/h to 450 °C in flowing oxygen (100 cm^3/min) and held at 450 °C for 1 h. Pure WO_3 powder samples were also made by drying an ammonia solution of tungstic acid, followed by a heat treatment analogous to that described above.

Preparation of MoO_3/TiO_2 Polycrystalline Samples. The procedure for the preparation of the MoO_3/TiO_2 polycrystalline samples has been reported in detail in a previous publication.[46] Dispersed samples of MoO_3 on TiO_2 were prepared as follows: A stock aqueous solution of ammonium paramolybdate (Mallinckrodt Chemical Works) containing 2.0 mg/mL of ammonium paramolybdate was prepared. A fixed weight of TiO_2 was ultrasonically dispersed in varying aliquots of the aqueous ammonium paramolybdate, in order to prepare samples with varying concentrations of MoO_3. The solutions were stirred and slowly evaporated over a hot water bath. The products were subsequently dried in an air oven at 120 °C for 16 h and ground with a mortar and pestle. The products were heated at a rate of 100 °C/h up to 450 °C in flowing oxygen (100 cm^3/min). They were then held at 450 °C for 1 h. Pure MoO_3 powder samples were also made by drying an aqueous solution of ammonium paramolybdate, followed by a heat treatment analogous to that described above.

Measurement of Photocatalytic Activity. The photocatalytic activities of various powder samples were evaluated by the degradation of 1,4-dichlorobenzene (DCB). This technique was suggested by Peterson and Gregg.[48] A saturated DCB solution was prepared by adding an excess of DCB to distilled water and stirring for 8 h. The solubility of DCB in water at room temperature is 76 ppm.[49] The solution was capped and preserved in darkness. The powdered sample (1.5 mg) was ultrasonically dispersed in 100 mL of distilled water. The TiO_2 suspension (3 mL) was placed in a silica cuvette, and 0.2 mL of saturated aqueous solution of 1,4-dichlorobenzene was added. The initial concentration of 1,4-dichlorobenzene was 5 ppm. A second sample that contained 0.2 mL of distilled water and 3 mL of the TiO_2 suspension was used as a blank and maintained in the dark. The sample to be measured was then irradiated with a 150-W Xe 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 with that of the sample kept in darkness.

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.[50] Catalyst powder (0.5 g) was dispersed in 50 mL of benzene using a glass stirring bar. Five drops of a 0.05 N indicator solution in benzene were added to the flask. N-Butylamine (0.01 N) was titrated against the powder, and the amount of titre necessary to effect the color change on the surface of the powder was recorded. The acidity was then calculated in terms of mmol/g of 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 ($pKa = +6.8$, $H_0 \leq +6.8$), methyl red ($pK_a = +4.8$, $H_0 \leq +4.8$), methyl yellow ($pK_a = 3.3$, $H_0 \leq +3.3$), fast garnet ($pKa = +2.0$, $H_0 \leq +2.0$), and crystal violet ($pK_a = +0.8$, $H_0 \leq +0.8$). Although the titration technique has intrinsic limitations,[51] precautions were taken to handle the samples in a consistent manner to ensure that the results were reproducible and could be confidently compared on a relative basis. The reproducibility was found to be 0.001 mm/g.

Physical Characterization of the Polycrystalline Powders. X-ray powder diffraction patterns of these powder samples were obtained using a Philips diffractometer and monochromated high intensity Cu $K_{\alpha1}$ radiation ($\lambda = 1.5404$ Å). Diffraction patterns were taken with a scan rate of 1° 2θ/min over the range $12° \leq 2\theta \leq 80°$.

All of the polycrystalline samples used in this study were prepared from Degussa P-25 (70% anatase, 30% rutile). The sizes of the particles were determined from the measured line broadening of the major peaks of both anatase and rutile. The average size of the anatase particles was 17 nm, and 25 nm for the rutile particles.

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 degrased at 170 °C for 2 h and the adsorbate gas consisted of 30% N_2/70% He.

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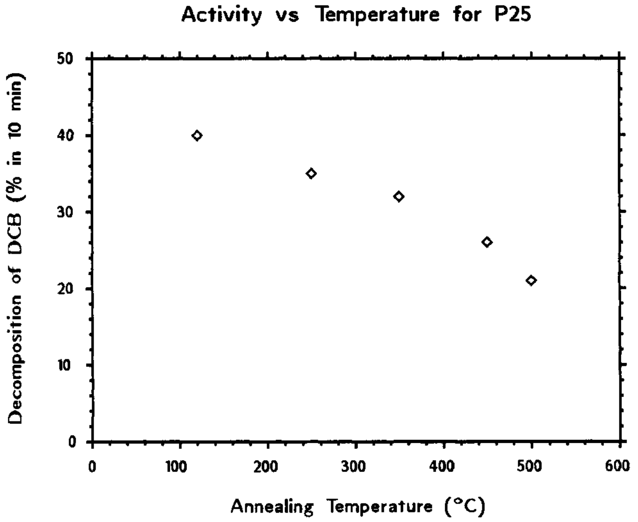

Figure 1. Effect of annealing temperature on the decomposition of DCB by P25.

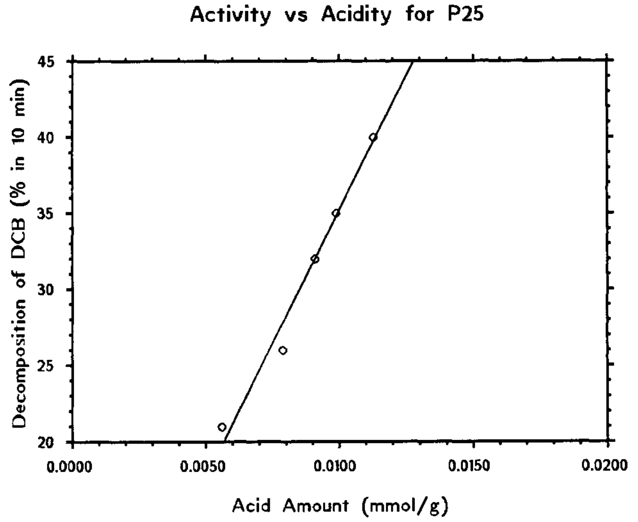

Figure 2. Correlation between surface acidity determined with methyl red and the decomposition of DCB by P25.

Results and Discussion

It has been indicated by previous investigators that surface hydroxy groups play an important role in the photocatalytic degradation of organic water contaminants. The importance of surface hydroxyl groups in photoadsorption on TiO_2 surfaces, as well as in promoting electron transfer from the conduction band of TiO_2 to chemisorbed oxygen molecules, has been discussed in the literature.[25–30] It has also been established that the surface acidity of TiO_2 (anatase) is primarily Lewis in nature.[31–34] The results presented here indicate a correlation between the surface acidity of the catalysts and their resulting photocatalytic activity.

Tanabe[35,37,39,52,53] 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 contrast with TiO_2, such as WO_3/TiO_2,[37] should cause an increase in acidity. The discussion on surface acidity presented in this research is based on the earlier work of Tanabe.

A commercially available titanium(IV) oxide, Degussa P25, was used as the standard TiO_2 powder catalyst. One-gram samples were treated as described in the Experimental Section and annealed for 1 h at various temperatures in flowing oxygen. It can be seen from Table 1 that these samples show little difference in surface area, anatase to rutile ratio, or crystallite size. The photocatalytic activity of the TiO_2 samples was evaluated by the degradation of 1,4-dichlorobenzene. Figure 1 shows the change in percent of DCB decomposed in 10 min as a function of annealing temperature. It can be seen that there is a decrease in the percent of DCB decomposed as the annealing temperature is increased.

Table 1. Surface Area, Anatase/Rutile Ratio, and Crystallite Size Data for TiO_2 (P25)

annealing temp (°C)	surface area (m^2/g)	anatase/rutile ratio	crystallite size (nm) anatase	crystallite size (nm) rutile
120	48	67/33	17.5	27.0
250	46	67/33	17.5	26.5
350	47	67/33	17.0	26.8
450	46	67/33	17.8	26.5
500	46	67/33	17.8	26.5

Table 2. Activity and Acidity Data for TiO_2 (P25)

annealing temp (°C)	photocatalytic activity (rel)	acidity (mmol/g)
120	40 (2)	0.0113
250	35 (2)	0.0099
350	32 (2)	0.0091
450	26 (2)	0.0079
500	21 (2)	0.0056

The surface acidity of these samples was evaluated by the *n*-butylamine titration method with methyl red ($pK_a = +4.8$) as the indicator. The total acidity is related to the number of sites having acid strengths with $H_0 \leq +4.8$. Figure 2 shows the change in the percent of DCB decomposed in 10 min vs the acidity of the samples. It can be seen that a linear relationship between the catalyst's activity and its surface acidity exists for the TiO_2 samples. Table 2 summarizes the data shown in Figure 1 and 2.

The thermal treatment of TiO_2 (Degussa P25) causes a decrease in the photocatalytic activity, and this corresponds directly to a decrease in the surface acidity. High annealing temperatures alter the surface of the catalyst and reduce surface acid sites. The corresponding decrease in photocatalytic activity indicates the importance of surface acid sites in the photocatalytic process. This importance is emphasized by the observation that there was little difference in the surface area, anatase to rutile ratio, or crystallite sizes of all samples studied.

WO_3 and MoO_3 were introduced onto TiO_2 (Degussa P25) by the impregnation technique described above. It was shown[45,46] that in both the WO_3/TiO_2 and MoO_3/TiO_2 mixed oxide systems, no detectable change in the cell parameters of TiO_2 was observed, which limits the degree of solid solution of WO_3 or MoO_3 in TiO_2 to less than 2 mol. %. No diffraction peaks of WO_3 or MoO_3 appeared in the patterns up to a loading of 7 mol ‰. This indicated a high degree of dispersion of MoO_3 and WO_3 on the TiO_2 surface. There was also shown to be little difference in the surface areas and crystallite sizes of the prepared WO_3/TiO_2 or MoO_3/TiO_2 and TiO_2 (Degussa P25) samples. The optimum loading of WO_3 or MoO_3 on TiO_2 was determined by measuring the activity of various WO_3/TiO_2 and MoO_3/TiO_2 samples. The photocatalytic activity of the prepared

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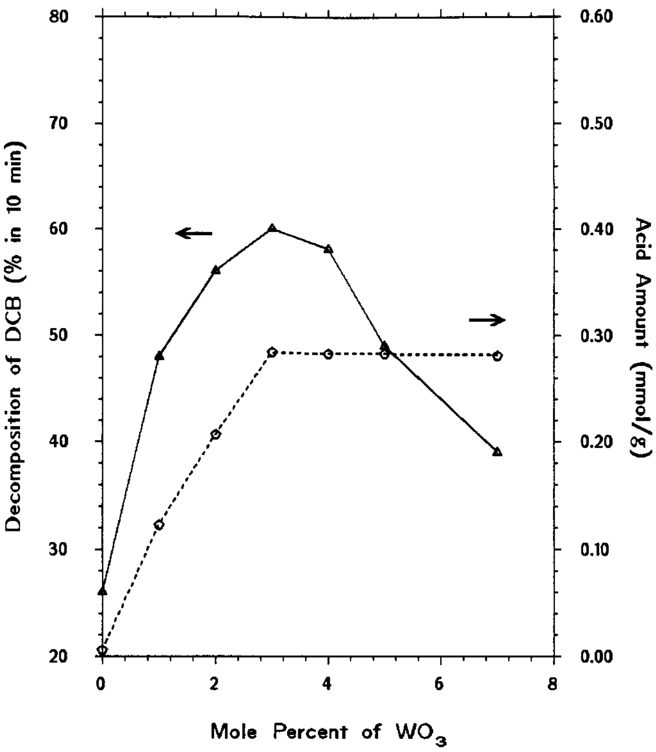

Figure 3. Decomposition of DCB and the surface acidity determined with methyl red as functions of concentrations of WO_3 impregnated on P25.

powder samples was evaluated by the degradation of DCB. The concentration which gives maximum activity is 3 mol % for WO_3 and 2.5 mol % for MoO_3.

The surface acidity of the prepared powder samples was evaluated by the *n*-butylamine titration method. Samples were prepared with 1%, 2%, 3%, 4%, 5%, and 7% WO_3 on TiO_2. Figure 3 shows the change in percent of DCB decomposed in 10 min and the change in acid amount as determined with the indicator methyl red plotted against increasing mole percent of WO_3. It can be seen that the point at which the optimum photocatalytic activity is reached (3 mol % WO_3) corresponds to the point at which the number of acid sites is maximized. At this concentration, it has been reported[54] that TiO_2 is covered with a monolayer of WO_3. Beyond 3 mol % WO_3, the surface of the TiO_2 particles is effectively covered by WO_3, and the acidity remains constant from 3 to 7 mol %. The observed activity decreases as the concentration of WO_3 is increased from 3 to 7 mol %, which is consistent with a buildup of inactive WO_3. It has been shown that there is little difference in surface areas and crystallite sizes of the WO_3/TiO_2 samples. Therefore, the increased acidity in the WO_3/TiO_2 samples is clearly related to the increased photocatalytic efficiency of the mixed oxide system. The addition of a higher valence cation (W^{6+}) introduces excess positive charge onto the surface of the catalyst.[37]

Samples were prepared with 1%, 2%, 2.5%, 3%, 4%, 5%, and 7% MoO_3 on TiO_2. Figure 4 shows the change in percent of DCB decomposed in 10 min and the change in acid amount as determined with the indicator methyl red plotted against increasing mole percent of MoO_3. It can be seen that the point at which the optimum photocatalytic acidity is reached (2.5 mol % MoO_3) corresponds to the point at which the surface acidity is maximized. This concentration of MoO_3 also effectively covers the surface of TiO_2 with a monolayer.[55] Samples with concentrations of MoO_3 greater than 2.5 mol % show constant surface acidity. All of these samples have the same surface areas and crystallite sizes. The addition of a higher valence cation (Mo^{6+}) onto the surface of the TiO_2 catalyst introduces excess positive charges on the surface and creates additional acid sites on the surface, similar to the WO_3/TiO_2 system. The increased acidity in the MoO_3/TiO_2 samples is clearly indicated as playing an important role in the increased photocatalytic activity of the mixed oxide system.

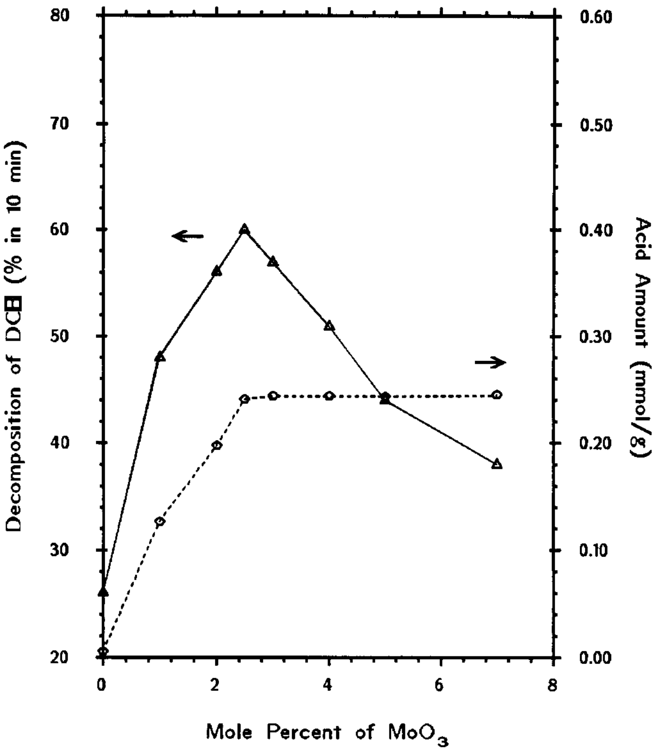

Figure 4. Decomposition of DCB and surface acidity determined with methyl red as f unctions of concentration of MoO_3 impregnated on P25.

The use of various indicators with different pK_a values, and thus different Hammett acidity functions, enables a determination of the amount of acid at various acid strengths by the *n*-butylamine titration method. To determine the total acidity at various acid strengths, several different indicators were used with the *n*-butylamine titration method. Table 3 summarizes the indicators used and shows the acidity distribution for WO_3/TiO_2 and MoO_3/TiO_2 samples. It can be seen for both series of samples that the acid number and strength increase with increasing mole percent of WO_3 or MoO_3 until the surface of the TiO_2 is effectively covered. Beyond this concentration, the acid number and strength remain constant.

Conclusions

The first part of this study showed a linear relationship between the photocatalytic activity of Degussa TiO_2 (P25) and its surface acidity as indicated by titration with *n*-butylamine. Several TiO_2 samples were prepared by heating Degussa TiO_2 at temperatures between 250 and

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Table 3. Photocatalytic Activity, Surface Activity, and Acidity Distribution for TiO_2, WO_3, MoO_3, WO_3/TiO_2, and MoO_3/TiO_2 Polycrystalline Samples

sample	activity (rel)	surface area (m^2/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[a]	40	48	0.070 mmol/g[b]	0.070	0.011	0	0	0
WO_3	2	3	0.103	0.101	0.043	0.031	0.18	0
WO_3/TiO_2								
1%	48	47	0.225	0.224	0.123	0.083	0.046	0
2%	56	47	0.314	0.310	0.207	0.162	0.119	0
3%	60	45	0.388	0.387	0.285	0.194	0.152	0.051
4%	58	46	0.387	0.387	0.280	0.193	0.152	0.050
5%	49	44	0.388	0.389	0.282	0.194	0.154	0.052
7%	39	43	0.391	0.392	0.281	0.191	0.155	0.050
MoO_3	2	2.5	0.095	0.096	0.034	0.027	0.011	0
MoO_3/TiO_3								
1%	48	48	0.215	0.211	0.127	0.068	0.038	0
2%	56	46	0.278	0.277	0.198	0.124	0.095	0
2.5%	60	47	0.330	0.327	0.241	0.172	0.132	0.048
3%	57	46	0.333	0.330	0.244	0.171	0.131	0.047
4%	51	45	0.334	0.331	0.244	0.174	0.134	0.049
5%	44	45	0.334	0.333	0.242	0.174	0.135	0.050
7%	38	44	0.335	0.334	0.245	0.176	0.135	0.049

[a] P25 heated to 450 °C has an activity of 26 and methyl red acidity of 0.008. [b] Reproducible within ±0.001 mm/g.

500 °C. The photocatalytic activity of TiO_2 decreased as the annealing temperature was increased. This decrease corresponded directly to a decrease in the surface acidity of the TiO_2 samples.

The second part of this study showed that an observed increase in the photocatalytic activity of the mixed oxide/TiO_2 catalysts corresponded with an increase in their surface acidity. Samples of WO_3/Degussa TiO_2 (P25) and MoO_3/Degussa TiO_2 (P25) were prepared by impregnation. The concentrations of WO_3 and MoO_3 which gave maximum photocatalytic activity were 3 and 2.5 mol %, respectively. These concentrations also gave maximum surface acidities. Beyond these concentrations, the surface acidity remained constant, and the photoactivities decreased. It appears that surface acidity plays an important role in determining the activity of the photocatalyst.

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