Photodegradation of carboxylic acids on Al$_2$O$_3$ and SiO$_2$ nanoparticles

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Al$_2$O$_3$ and SiO$_2$ nanoparticles effect photodegradation of carboxylic acids, and their photonic efficiencies are comparable to those of TiO$_2$ P25 Degussa, TiO$_2$ Hombikat, TiO$_2$ anatase, TiO$_2$ rutile, ZnO, SnO$_2$, and ZrO$_2$ nanosemiconductors. All the nanoparticles show sustainable photoactivity and the degradation rates increase linearly with oxalic acid-concentration and photon flux. The photonic efficiencies of degradation are in the order: formic acid > oxalic acid > acetic acid > citric acid. The mechanism of photodegradation is discussed.

Keywords: Photochemistry, Catalysis, Photocatalysis, Photodegradation, Nanomaterials, Oxides, Semiconductors, Electrical properties, Alumina, Silica

Photoreactions on the surfaces of semiconductors like TiO$_2$ and ZnO are well known. Al$_2$O$_3$ and SiO$_2$ are insulators and provide only non-reactive surfaces. However, calcination at 1073 K creates active sites enabling photoreactions on the surface of SiO$_2$ or Al$_2$O$_3$. Prior to the photoreaction, a kind of surface defect is generated through dehydroxylation at high temperature. This can be photoexcited to form the first surface intermediate. Some photocatalytic reactions that take place on the surface of SiO$_2$ or Al$_2$O$_3$ are photoinduced direct methane coupling, photometathesis, photoepoxidation of propylene by molecular oxygen and photodegradation.

Silica activated by evacuation at high temperatures catalyzes metathesis reactions of ethylene and propylene under photolysis. Photometathesis of propylene involves two photoexcitation steps. For both steps photolysis is essential, but the effective wavelength for each step is different. While UV light is necessary for the first step, visible light as well as UV light is effective for the second step. In the first step, photoabsorption sites, generated by evacuation at high temperature such as 1073 K, react with propylene under UV irradiation to form surface intermediates. In the second step, the intermediates thus formed react with propylene in presence of light including visible light to form metathesis products. Examination of the non-oxidative direct methane coupling reaction on amorphous and mesoporous silica reveals the non-bridging oxygen hole center (NBOHC) along with the co-generated E' center as the photoactive sites. The reported photooxidation on SiO$_2$ surface includes epoxidation of propylene and oxidation of carbon monoxide.

Alumina as well as silica gel catalyze the photochemical transformation of benzo[el]pyrene. Dibenzo-p-dioxin degrades on silica with UV-C light whereas the degradation of chrysene on silica gel occurs under Xe lamp. Photodegradation of methyl red, 4-chlorophenol, pyrene, phloxine B and uranine on silica have been reported. Perylene photodegrades on silica as well as alumina. Non-reactive solid supports, such as untreated alumina or silica-gel with a high and specific porosity, may significantly control photochemical reactivity of adsorbed molecules due to electronic interactions between the molecules. Norrish type II photoreaction of alkyl aryl ketones on alumina and silica have also been reported. However, the photocatalytic efficiencies of SiO$_2$ and Al$_2$O$_3$ are far less than those of the semiconductors, TiO$_2$ and ZnO. The reactions are very slow and the yields are poor. Herein, we report for the first time photodegradation of carboxylic acids by untreated Al$_2$O$_3$ and SiO$_2$ nanoparticles with the photonic efficiencies comparable to those of the widely used nanoparticulate semiconductors. Semiconductor-catalyzed photodegradation of oxalic acid has been investigated extensively and hence is taken up as the substrate for detailed study. In presence of air, it undergoes clean photomineralization without formation of any long lived intermediates and earlier workers have followed the reaction by measuring the CO$_2$-liberation.
Materials and Methods

Al₂O₃ (Sigma-Aldrich), SiO₂ (Sigma-Aldrich), TiO₂ P25 (Degussa), TiO₂ Hombikat (Fluka), TiO₂ anatase (Sigma-Aldrich), TiO₂ rutile (Sigma-Aldrich), ZnO (Sigma-Aldrich), SnO₂ (Sigma-Aldrich) and ZrO₂ (Sigma-Aldrich) nanoparticles and TiO₂ (Merck) and Al₂O₃ (Merck) submicron particles were used without any pre-treatment. Oxalic acid (Merck), sodium oxalate (Merck), formic acid (SD Fine) and acetic acid (SD Fine) used were of AR or LR grade. Acetic acid was purified by fractional distillation and citric acid by recrystallization. Solutions of formic, acetic and citric acids were standardized prior to the experiments.

Characterization studies

The powder X-ray diffraction patterns were obtained using a Bruker D8 system employing Cu-Kα radiation ($\lambda = 1.5406 \text{ Å}$) with a tube current of 30 mA at 40 kV in a 20 range of 5-60° at a scan speed of 0.050° s⁻¹ or a Rich Seifert (model 3000) X-ray diffractrometer. A Perkin-Elmer Lambda 35 spectrophotometer was employed to record the UV-visible diffuse reflectance spectra of the oxides and Avatar 330FT-IR spectrometer was used to obtain the infrared spectra. The impedance spectra of the different forms of TiO₂ nanocrystals, Al₂O₃ nanocrystals and SiO₂ nanoparticles were obtained using a HP 4284A Precision LCR meter at room temperature in air over the frequency range of 1 MHz to 20 Hz. While the disk area was 0.5024 cm², the thickness of TiO₂ anatase, rutile, P25 and Hombikat, Al₂O₃, SiO₂ and SiO₂ (porous) pellets was 2.12, 1.53, 2.78, 1.80, 1.58, 1.54 and 1.40 mm, respectively. The surface areas of the submicron TiO₂ and Al₂O₃ particles were obtained from nitrogen adsorption-desorption isotherms using the BET (Brunauer-Emmett-Teller) equation.

Photodegradation studies

Photodegradation was carried out in a Heber micro-photoreactor (HMI SL W6) fitted with a 6 W 254 nm low-pressure mercury lamp and a 6 W 365 nm mercury lamp (Sankyo Denki, Japan). Quartz and borosilicate glass tubes (15 mm inner dia.) were used for the 254 and 365 nm lamps, respectively. Detailed photocatalytic studies were made with a Heber multilamp photoreactor (HML MP88) fitted with eight 8 W mercury UV lamps of wavelength 365 nm and highly polished anodized aluminum reflector. Four cooling fans were mounted at the bottom of the reactor to dissipate the generated heat. Borosilicate glass tube was employed as the reaction vessel and was placed at the centre of the photoreactor. The light intensity was varied by illuminating two or four or eight lamps and the angles sustained by the adjacent lamps at the sample were 180°, 90° and 45°, respectively. Under each experimental condition the photon flux was determined by ferrioxalate actinometry.

Photodegradation was studied with 10 and 25 mL of the acid solutions in the micro and multilamp photoreactors, respectively. All the oxides were used without any pretreatment. Air was bubbled through the solution that effectively stirred the solution and kept the suspended oxide (0.02 g) under continuous motion. The airflow rate, measured by soap bubble method, was 7.8 mL s⁻¹. After illumination, the oxide particles were recovered by centrifugation and the undecomposed carboxylic acid was estimated by alkaliometry and also by permanganometry. TiO₂ rutile nanocrystals failed to separate on centrifugation and were removed by filtration using 0.45 μm-nylon filter membrane (Sigma-Aldrich). The decrease in the acid-concentration for a finite time of illumination provided the degradation rate and the results were reproducible to ±5%. A time lag of at least 15 min was provided before illumination to ensure pre-adsorption of the acids on the oxides. The non-purgable organic carbon (total organic carbon) in the reaction solution was analyzed using Shimadzu TOC-VCPn (by catalytic oxidation). The pH of the acid solution was unadjusted and measured using Systronics pH System 361. The dissolved oxygen was measured using Elico dissolved oxygen analyzer PE 135 and the UV-visible spectra were recorded with UV-1650 Shimadzu spectrophotometer.

Results and Discussion

Crystal structure

The X-ray diffractogram of the Al₂O₃ nanocrystals employed reveals the presence of gamma (γ) and delta (δ) phases; the XRD is the combined JCPDS patterns of γ (00-001-1303 (D), cubic, $a 7.9000 \text{ Å}$) and δ (00-016-0394 (D), tetragonal, $a 7.9430 \text{ Å}, c 23.5000 \text{ Å}$) forms. The percentages of γ and δ phases are 65 and 35, respectively. The XRD of anatase TiO₂ nanocrystals matches with the standard JCPDS pattern of anatase TiO₂ (89-4921) and the rutile lines are absent. The diffraction pattern of the used TiO₂ rutile sample matches with the standard JCPDS pattern of rutile TiO₂ (89-4202) and no anatase peaks are seen.
The X-ray diffraction pattern of the TiO$_2$ P25 employed confirms the presence of anatase and rutile phases in the sample; the standard JCPDS patterns of anatase (00-021-1272) as well as rutile (01-089-0553) are present. The phase percentages have been obtained from the integrated intensity of the peaks at 2$\theta$ value of 25.3° for anatase (101) and 27.4° for rutile (110). The percentage of anatase is given by $A$ (%) = 100/(1 + 1.265($I_a/I_R$)), where $I_a$ is the intensity of the anatase peak at 2$\theta$ = 25.3° and $I_R$ is that of the rutile peak at 2$\theta$ = 27.4°. The phase composition thus obtained is 81% anatase and 19% rutile, which is in accordance with that provided by the manufacturer. The diffraction pattern of TiO$_2$ Hombikat reveals the presence of anatase as well as rutile forms; the peak fitting conforms to the JCPDS patterns of anatase [89-4921] and rutile [110, 211, etc., lines]. The percentages of anatase and rutile, determined using the intensities of 101 peak of anatase and 110 peak of rutile, are 69 and 31, respectively. The diffraction pattern of ZnO confirms its hexagonal wurtzite structure. The peak fitting is highly satisfactory with the JCPDS pattern 89-7102. The XRD of SnO$_2$ is in accordance with its tetragonal structure; the observed diffractogram totally matches with the standard JCPDS pattern (88-0287). The diffractogram of ZrO$_2$ matches with JCPDS 89-9066; the crystal structure is monoclinic primitive. The TiO$_2$ submicron crystals used are of anatase phase; the XRD is identical with the standard pattern of anatase (JCPDS 00-021-1272) and the rutile lines (00-034-0180 D) are absent. The XRD pattern of the employed Al$_2$O$_3$ submicron particles agrees with the standard JCPDS patterns of $\gamma$-Al$_2$O$_3$ (00-001-1308 D, cubic: $a$ 7.900 Å) and $\chi$-Al$_2$O$_3$ (00-004-0880 N, cubic: $a$ 7.950 Å) thus revealing the presence of both the phases ($\gamma$:$\chi$:52:48).

The average crystal size of the nanocrystals has been determined from the half-width of the full maximum (HWFM) of the most intense peaks of the different nanocrystals using the Scherrer equation, $D = 0.9\lambda/b\cos\theta$, where $D$ is the mean crystallite size, $\lambda$ is the X-ray wavelength, $\theta$ is the Bragg angle and $b$ is the corrected line broadening of the sample. The specific surface areas of the nanocrystals have been obtained using the relationship, $S = 6/\rho D$, where $S$ is the specific surface area, $D$ is the average particle size and $\rho$ is the material density. The results are presented in Table 1. The listed particle sizes and surface areas of the amorphous SiO$_2$ are those provided by Sigma Aldrich. The average crystal sizes of submicron particles of TiO$_2$ and Al$_2$O$_3$ have been deduced from the determined BET surface areas.

### Optical and electrical properties

The diffuse reflectance spectra (DRS) of the studied oxides are displayed in Fig. 1; the reflectance data are reported as $F(R)$ value, obtained by application of the Kubelka-Munk algorithm $[F(R) = (1 - R^2)/2R]$, where $R$ is the reflectance. The DRS show that ZnO, SnO$_2$ and all the forms of TiO$_2$ absorb at the wavelength of illumination, whereas ZrO$_2$, Al$_2$O$_3$ and SiO$_2$ do not. Defects in nanocrystals strongly influence the electrical properties of the materials. Impedance spectroscopy (IS) is a relatively new and powerful tool to probe the

<table>
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<th>Oxide</th>
<th>$D$ (nm)</th>
<th>$S$ ($m^2g^{-1}$)</th>
<th>$\xi^a$ (%)</th>
<th>$\xi^b$ (%)</th>
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<td>640±50</td>
<td>90</td>
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<td>68</td>
<td>84</td>
<td>94</td>
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<td>18</td>
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<td>94</td>
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<td>-</td>
<td>-</td>
<td>7</td>
<td>3</td>
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*$\lambda$ = 365 nm; $\lambda$ = 254 nm; $^a$oxide loading = 0.10 g.

![Fig. 1—The UV-visible diffuse reflectance spectra of the studied oxides.](image-url)
electrical properties of the oxides and may be employed to investigate the dynamics of the bound and mobile charges in the bulk or interfacial region of the semiconductors. In polycrystalline materials, the overall sample resistance may be a combination of the intragranular or bulk crystal resistance and intergranular or grain boundary resistance. The impedance spectra (the variation of impedance with frequency) of the different forms of TiO$_2$ used show decrease of impedance with increase of frequency indicating the capacitance of the oxides (not displayed). As expected, the IS of porous SiO$_2$ reveals the insulating nature of the oxide. However, the impedance spectra of Al$_2$O$_3$ and nonporous SiO$_2$ are similar to those of the semiconductor oxides exhibiting their defective structures.

The Nyquist plots suggest that the structure of porous SiO$_2$ is free of electrical defects (Fig. 2). The Nyquist plots of Al$_2$O$_3$ and nonporous SiO$_2$ are similar to those of the semiconductor oxides, indicating the structural defects in the solids. The ohmic or uncompensated resistance ($R_\Omega$) corresponds to the grain boundary or intergranular resistance while the polarization or electron-transfer (charge-transfer) resistance ($R_\text{CT}$) refers to the intragranular or bulk crystal resistance; the latter is related to the resistance to mass transfer, which is controlled by the specific conductance, $\sigma$. The constant phase element (CPE) is equivalent to a double layer capacitance, C. The Nyquist plot of Hombikat displays a large charge-transfer resistance, thus suggesting the predominance of kinetic control. The Nyquist plots of all other TiO$_2$ show large regions of mass-transfer with significant kinetic control at low and high frequencies, respectively. Further, the Nyquist plots reveal the presence of significant series capacitance in the equivalent circuit.

Table 2 presents the determined specific conductance, capacitance and the ohmic and charge-transfer resistances of the different forms of TiO$_2$, Al$_2$O$_3$ and non-porous SiO$_2$. Among the TiO$_2$ nanocrystals, the specific conductance of anatase is larger than that of rutile. However, the benchmark photocatalyst P25 Degussa, which is a blend of anatase (81%) and rutile (19%) phases, exhibits surprisingly higher specific conductance than anatase and rutile. On the other hand, Hombikat, which also contains anatase (69%) and rutile (31%) phases, does not show similar characteristics; its specific conductance is even less than that of rutile. Further, P25 Degussa shows the largest capacitance among the TiO$_2$ examined. The measured specific conductance, capacitance, and ohmic and charge-transfer resistances of Al$_2$O$_3$ and nonporous SiO$_2$ are comparable to those of TiO$_2$. 

![Nyquist plots of the studied oxides.](image-url)
Photodegradation

While photocatalysis by semiconductors is well known it is surprising that carboxylic acids degrade on the surfaces of untreated Al₂O₃ and SiO₂ nanoparticles under UV irradiation. In presence of air, Al₂O₃, SiO₂ and porous SiO₂, without any pre-treatment, effect photodegradation of oxalic acid and the photonic efficiencies with illumination at 365 and 254 nm are comparable to those of semiconductor nanocrystals under identical conditions. Table 1 presents the photonic efficiencies of Al₂O₃ and SiO₂ nanoparticles along with those of TiO₂ P25 Degussa, TiO₂ Hombikat, TiO₂ anatase, TiO₂ rutile, ZnO, SnO₂ and ZrO₂ nanocrystals. The reported photonic efficiency (ξ) is the number of acid molecules degraded per incident photon. Submicron particles of Al₂O₃ (167 nm, 10.63 m² g⁻¹) at 5-times loading under identical conditions, fail to effect the photodegradation. However, under the same experimental conditions, TiO₂ anatase submicron particles photocatalyze the degradation. The estimation of un-decomposed oxalic acid by permanganometry and by alkalimetry shows identical results, indicating clean mineralization of oxalic acid under continuous purging of air. Further, TOC (total organic carbon) analysis of the acid solution before and after illumination with Al₂O₃ and SiO₂ nanoparticles confirms mineralization of the acid. The measured TOC/TOC₀ value of the acid solution decreases from 1.0 to 0.003, 0.007 and 0.006 after 4 h of illumination with Al₂O₃, SiO₂ and porous SiO₂, respectively. Earlier reports also confirm clean mineralization of the acid without formation of stable intermediates. The results of direct photolysis, under identical conditions but without the oxide, are also presented in Table 1. These results clearly show that the photodegradation is mediated by the surfaces of the particles. All the active oxides show sustainable photoactivities. Reuse of the catalysts without any treatment provides identical results (data not presented).

The photonic efficiencies of degradation of oxalic acid are slightly higher with UV-C radiation than with UV-A illumination. This is evident from the results of the degradation using a 6 W 365 nm mercury lamp of photon flux 17.8 µEinstein L⁻¹ s⁻¹ and a 6 W 254 nm low-pressure mercury lamp of photon flux 6.2 µEinstein L⁻¹ s⁻¹, separately, in the micro-reactor under identical conditions (Table 1). A possible reason may be better absorption of UV-C radiation than UV-A illumination by the oxides.

In the case of semiconductors, another explanation stems from the recombination of photogenerated electron-hole pairs. Electrons that absorb photons of energy much larger than the band gap are promoted to an energy level higher than the conductance band minimum, and their recombination with the valence band holes is not as fast as in the case of electrons at the conduction band minimum.

The dependence of photodegradation on the acid-concentration as well as the photon flux has been studied by using the multilamp photoreactor with mercury UV lamps of wavelength 365 nm. Rate measurements at different oxalic acid concentrations show linear increase of the degradation rates with oxalic acid concentration and in absence of the oxide the degradation is slow (Fig. 3). This linear dependence indicates first-order degradation.

\[ \text{Degradation rate} = k \times [\text{Acid}] \]

where \( k \) is the rate constant and \([\text{Acid}]\) is the concentration of oxalic acid.

Fig. 3—Degradation of oxalic acid as a function of concentration: [Catalyst loading = 0.02 g; λ = 365 nm; \( I = 25.4 \, \mu\text{Einstein L}^{-1} \, \text{s}^{-1} \); illumination time: 30 min; airflow rate = 7.8 mL s⁻¹; \([\text{O}_2]\)dissolved = 24.7 mg L⁻¹; vol. of acid solution = 25 mL].
kinetics. Generally, heterogeneous photocatalyzed reactions conform to Langmuir-Hinshelwood model exhibiting saturation kinetics, i.e., a linear increase of the reaction rate with the substrate concentration at low substrate and the rate becoming independent of the substrate concentration at high substrate\textsuperscript{12,33}. However, the first-order kinetics observed in the present study may satisfy Langmuir-Hinshelwood model provided the adsorption of acid on the oxide is low, which is found to be so.

The UV spectra of oxalic acid solution illuminated with Al\textsubscript{2}O\textsubscript{3} nanoparticles and recorded at different time of illumination but after recovery of the oxide shows continuous removal of oxalic acid on UV-A illumination. The concentration of undegraded oxalic acid, estimated titrimetrically, decreases exponentially with illumination time revealing a clean first order kinetics. Generally, the enhancement of heterogeneous-photocatalysis with photon flux is nonlinear\textsuperscript{32-34}. The reaction enhances linearly with the light intensity at low photon flux but at high light intensity the photoreaction rate is to depend on the square-root of photon flux\textsuperscript{35}. In the present study, linear enhancement of degradation with light intensity is observed. Dissolved oxygen is essential for the photodegradation. The oxalic acid-degradation rates on Al\textsubscript{2}O\textsubscript{3}, porous SiO\textsubscript{2}, and SiO\textsubscript{2} nanoparticles at dissolved oxygen of 24.7 (air-purging) and 2.6 mg L\textsuperscript{-1} (nitrogen-purging) are 3.9, 6.8, 3.2 and 0.03, 0.03, 0.05 \(\mu\)M s\textsuperscript{-1}, respectively (25 mL 0.05 M oxalic acid, 0.02 g oxide loading, 32 W-illumination at 365 nm, 25.4 \(\mu\)Einstein L\textsuperscript{-1} s\textsuperscript{-1} photon flux).

Mechanism

The diffuse reflectance spectra of bare Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} confirm that these do not significantly absorb UV-A radiation (Fig. 1). It is known that the emission spectrum of the medium pressure Hg-lamp, in addition to the strong 365 nm line (I-line), shows a number of less intense other lines at 254, 405 (H-line), and 436 nm (G-line). The borosilicate reaction vessel used screens the UV-C light (254 nm line). Hence, the possibility of direct band gap-excitation of these oxides with the employed 365 nm-illumination is excluded. Water molecules are physically adsorbed and also chemically bound on Al\textsubscript{2}O\textsubscript{3} as well as SiO\textsubscript{2} surfaces\textsuperscript{36}.

Infrared spectra of the dried catalysts, prior to illumination but after allowed to attain equilibrium with oxalic acid solution show characteristic absorbance of >C=O and –OH groups, indicating adsorption of the acid on the nanomaterials. Further, the infrared spectra of oxalic acid adsorbed catalysts and those of oxalic acid crystals mixed with the nanoparticles show that the acid is chemisorbed on the oxides. While oxalic acid adsorbed nanoparticles show absorbance at 3440, 1693, 1441, 1257 (Al\textsubscript{2}O\textsubscript{3}), 3420, 1687, 1401, 1266 (porous SiO\textsubscript{2}) and 3422, 1688, 1401, 1274 cm\textsuperscript{-1} (SiO\textsubscript{2}), oxalic acid crystals mixed with the oxides absorb at 3426, 1697,1408, 1264 (Al\textsubscript{2}O\textsubscript{3}), 3429, 1632, 1405 (porous SiO\textsubscript{2}) and 3437, 1631 cm\textsuperscript{-1} (SiO\textsubscript{2}), respectively. Similarly, formic, acetic and citric acids are also adsorbed on the catalysts. The IR frequencies of the mixed and adsorbed-formic, acetic and citric acids, respectively are: 1588, 1380 and 1633, 1384 (Al\textsubscript{2}O\textsubscript{3}), 1636, 1394, 1208 and 1636 (porous SiO\textsubscript{2}), 1636, 1394, 1209 and 1631 (SiO\textsubscript{2}); 1630, 1420 and 1637, 1384 (Al\textsubscript{2}O\textsubscript{3}), 1637, 1394 and 1634 (porous SiO\textsubscript{2}), 1637, 1394 and 1636, 1397 (SiO\textsubscript{2}); 1635, 1398, 1219 and 1634, 1398, 1225 (Al\textsubscript{2}O\textsubscript{3}), 1629, 1400, 1198 and 1640, 1369, 1233 (porous SiO\textsubscript{2}), 1634, 1399, 1214 and 1633, 1398, 1203 (SiO\textsubscript{2}). On the surface of Al\textsubscript{2}O\textsubscript{3} besides the acidic (Al\textsuperscript{3+}) and basic (O\textsuperscript{2-}) sites, hydroxyl groups are also present. The acidic sites may coordinate to the carbonyl oxygen (the Bronsted OH groups and Lewis aluminum ions provide a strong polar environment for the carbonyl group in the ground or excited state) and the basic O\textsuperscript{2-} group may be involved in hydrogen bonding with the OH group of the acid\textsuperscript{19}. Hence, the possible mechanism is the light absorption by the carboxylic acid chemisorbed on Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} nanoparticles leading to electron transfer to the defective solid matrix. The diffuse reflectance spectra of oxalic acid-adsorbed Al\textsubscript{2}O\textsubscript{3}, porous SiO\textsubscript{2} and SiO\textsubscript{2} along with those of bare nanoparticles, confirms the same (Fig. 4). While bare Al\textsubscript{2}O\textsubscript{3}, porous SiO\textsubscript{2} and SiO\textsubscript{2} do not absorb UV-A radiation, the corresponding oxalic acid-adsorbed nanomaterials absorb at 384 nm (Al\textsubscript{2}O\textsubscript{3}), 426 and 383 (porous SiO\textsubscript{2}), and 422 and 384 nm (nonporous SiO\textsubscript{2}), respectively.

Transfer of an electron from the adsorbed carboxylic acid to surface Al\textsuperscript{3+} or Si\textsuperscript{4+} may be the initiation step of the photodegradation process. Further transfer of the electron to a neighboring adsorbed oxygen molecule, through the solid state defects, may facilitate the degradation process. The rest of the mechanism may be similar to that in semiconductor photocatalysis. The report that 2,4,5-trichlorophenol forms a charge-transfer complex with TiO\textsubscript{2} which is activated by light of wavelength as
long as 520 nm resulting in photochemical reaction also supports the above proposition. Although porous SiO$_2$, inferred from its Nyquist plot, is free of defects, its porous nature and very large surface area may be responsible for the observed photodegradation. The similarity in characteristics of the reactions on semiconductor and insulator surfaces suggests similarity in the adsorption and desorption steps of the two processes. A plausible explanation for the observed photocatalytic activity of Al$_2$O$_3$ nanocrystals and the inertness of the submicron particles is the active surface of Al$_2$O$_3$ nanocrystals. Bare ZrO$_2$ also.

![Fig. 4—UV-visible diffuse reflectance spectra of oxalic acid-adsorbed oxides.](image)

**Table 3—Degradation and adsorption of carboxylic acids on nanoparticles and photocatalytic efficiencies ($\xi$) of degradation (multilamp reactor). \([\text{acid}] = 0.05 \text{ M}; \text{catalyst loading} = 0.02 \text{ g}; \lambda = 365 \text{ nm}; \text{photon flux} = 25.4 \mu \text{Einstein L}^{-1} \text{s}^{-1}; \text{illumination} = 64 \text{ W}; \text{time} = 30 \text{ min.}; \text{airflow rate} = 7.8 \text{ mL s}^{-1}; [\text{O}_2]_{\text{dissolved}} = 24.7 \text{ mg L}^{-1}; \text{acid solution} = 25 \text{ mL}]

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<tr>
<th>Catalyst</th>
<th>Formic acid</th>
<th>Oxalic acid</th>
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<th>Citric acid</th>
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<td>30</td>
<td>28 (0.4)</td>
<td>21</td>
<td>19 (1.5)</td>
</tr>
<tr>
<td>TiO$_2$ rutile</td>
<td>35</td>
<td>44 (0.4)</td>
<td>14</td>
<td>13 (0.7)</td>
</tr>
<tr>
<td>ZnO</td>
<td>69</td>
<td>63 (0.4)</td>
<td>46</td>
<td>42 (2.6)</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>31</td>
<td>28 (0.2)</td>
<td>22</td>
<td>20 (0.7)</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>45</td>
<td>41 (0.4)</td>
<td>24</td>
<td>22 (0.7)</td>
</tr>
<tr>
<td>Nil</td>
<td>8</td>
<td>6</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>pH</td>
<td>2.43</td>
<td>0.90</td>
<td>2.50</td>
<td>2.30</td>
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</tbody>
</table>

Table 3—Degradation and adsorption of carboxylic acids on nanoparticles and photocatalytic efficiencies ($\xi$) of degradation (multilamp reactor). \([\text{acid}] = 0.05 \text{ M}; \text{catalyst loading} = 0.02 \text{ g}; \lambda = 365 \text{ nm}; \text{photon flux} = 25.4 \mu \text{Einstein L}^{-1} \text{s}^{-1}; \text{illumination} = 64 \text{ W}; \text{time} = 30 \text{ min.}; \text{airflow rate} = 7.8 \text{ mL s}^{-1}; [\text{O}_2]_{\text{dissolved}} = 24.7 \text{ mg L}^{-1}; \text{acid solution} = 25 \text{ mL}|

Fig. 4—UV-visible diffuse reflectance spectra of oxalic acid-adsorbed oxides.
does not absorb UV-A illumination while the acid-adsorbed ZrO$_2$ does, suggesting a similar mechanism of photodegradation; the oxalic acid adsorbed ZrO$_2$ show absorbance maximum at 422 and 384 nm.

Study of the degradation of formic, acetic, oxalic and citric acids by the nanomaterial reveals formic acid as the most easily degradable acid and citric acid as the most difficult to oxidize (Table 3). The order of susceptibility of degradation, on the surfaces of the insulators as well as the semiconductors studied is: formic acid > oxalic acid > acetic acid > citric acid. It is interesting to note that with all the oxides the susceptibility to degradation falls with increase in the number of carbon atoms. Although oxalic acid and acetic acid have the same number of carbon atoms, the oxygen-carbon ratio is higher in the case of the former.

Conclusions

SiO$_2$ and Al$_2$O$_3$ nanoparticles photodegrade formic, oxalic, acetic and citric acids and the photonic efficiencies are comparable to those of widely used nanoparticulate semiconductors. The acids are chemisorbed on Al$_2$O$_3$ and SiO$_2$. Transfer of electron form the adsorbed carboxylic acid to the defective solid matrix of Al$_2$O$_3$ or SiO$_2$ may initiate the reaction. The rest of the mechanism may be similar to that in semiconductor photocatalysis. The similarity in the characteristics of reaction on the surfaces of insulator and semiconductor suggests similarity in the adsorption and desorption steps of the two processes.

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References