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## Abstract

The effect of transition metal co-catalysts on the photocatalytic properties of TiO<sub>2</sub> was investigated. Ruthenium (Ru), palladium, platinum, copper, silver, and gold, were loaded onto TiO<sub>2</sub> powders (anatase and mixed-phase P25) and screened for the decomposition of rhodamine B (RhB) under broad-band irradiation. The morphology and estimated chemical composition of photocatalysts were determined by scanning electron microscopy and energy dispersive spectroscopy, respectively. Brunhauer, Emmett and Teller (BET) analysis measured mass-specific surface area(s). X-ray diffraction analysis was performed to confirm the identity of titania phase(s) present. The BET surface area of anatase TiO<sub>2</sub>/Ru 1% (9.2 m<sup>2</sup>/gm) was one of the highest measured of all photocatalysts prepared in our laboratory. Photolyses conducted under air-saturated and nitrogen-saturated conditions revealed photodegradation efficiencies of 85 and 2 percent, respectively, after 60 min compared to 58 percent with no catalyst. The cause of low photocatalytic activity under an inert atmosphere is discussed. TiO<sub>2</sub>/Ru 1% showed a superior photocatalytic activity relative to P25-TiO<sub>2</sub> under broad-band irradiation. A potential deployment of photocatalytic technologies on a mission could be a reactor with modest enhancement in solar intensity brought about by a trough-style reactor, with reactants and catalyst flowing along the axis of the trough and therefore being illuminated for a controlled duration based on the flow rate.

## Nomenclature

Ag	Silver
BET	Brunauer-Emmett-Teller
C	final dye concentration
C <sub>o</sub>	initial dye concentration
Cu	Copper
EDS	energy dispersive spectroscopy (for elemental analysis)
P25	Degussa (Evonik) product, a mixed-phase (75 percent anatase/25 percent rutile) titanium dioxide powder
Pd	Palladium
Pt	Platinum
RhB	Rhodamine B
Ru	Ruthenium
SEM	Scanning electronic microscope(y)
TiO <sub>2</sub>	Titanium dioxide (or titania), most stable phase is rutile, other common phases: anatase and brookite

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<sup>1</sup> NASA Glenn Research Center, Summer Faculty Fellow from Southern University.

UV Ultraviolet light, roughly 400 to 800 nm  
UV-Vis Ultraviolet-visible (electronic absorption) spectroscopy  
XRD X-ray diffraction

## Introduction

Work is underway at NASA Glenn Research Center (GRC) and numerous other research laboratories to develop technologies based upon heterogeneous photocatalysis to decompose organics and/or decontaminate wastewaters (Refs. 1 to 7). The presence of these contaminants in water could pose potential health and environmental problems in a controlled environment such as on a space station or during long-term manned missions. There are also significant terrestrial concerns about chemicals such as azo dyes, herbicides, and pesticides that are present in rivers and lakes; many of these are toxic, carcinogenic, mutagenic, and/or resistant to biodegradation (Refs. 8 to 13). Additionally, conventional wastewater treatment techniques are usually ineffective in decontamination of these compounds. Thus developing energy efficient and “green” technologies to reduce or eliminate organic wastes has important potential dual-use applications.

To this end, semiconductors like titanium oxide ( $\text{TiO}_2$ ), zinc oxide ( $\text{ZnO}$ ) and other transition metal compounds (mostly oxides) are being studied for their photocatalytic properties to decompose a wide variety of toxic and persistent organic compounds into harmless inorganics such as mineral acids, carbon dioxide and water (Refs. 4, 5, 7, and 13). The basic principles concerning these catalysts are well understood: when a light source of sufficient energy illuminates a photocatalyst, electron/hole pairs will be produced as electrons absorb the light energy, being promoted to the conduction band and leaving (positively-charged) holes in the valence band. Thus produced, electron/hole pairs induce a complex series of reactions that potentially lead to the complete degradation of (dye or other) pollutants adsorbed on the semiconductor surface (Ref. 6). Transition metals serving as co-catalysts also trap free electrons, thus lowering the electron/hole pair-recombination rate resulting in an increase in the photocatalytic efficiency. Titania ( $\text{TiO}_2$ ) is the most commonly used photocatalyst due to its excellent optical properties and ability to facilitate very rapid light-induced reactions.  $\text{TiO}_2$  exists in three phases: rutile and anatase (most commonly) and brookite. Compared to most catalysts, titanium dioxide is quite inexpensive, chemically very stable, and readily available.

Rhodamine B (RhB), an organic dye (see Fig. 1), a model compound for organic waste, was decomposed by  $\text{TiO}_2$  photocatalysts with various transition metals added as co-catalysts by traditional catalyst processing methods, and were characterized by X-ray diffraction, scanning electron microscopy, Brunauer, Emmett and Teller analysis (BET). This research intends to probe  $\text{TiO}_2$  photocatalytic activity by enhancing its efficacy with different transition metal co-catalysts such as: ruthenium (Ru), palladium (Pd), platinum (Pt), copper (Cu), silver (Ag), and gold (Au). To achieve this purpose, different metal-co-catalyst-titania photocatalysts were synthesized on either anatase or a 4:1 mixture of anatase and rutile (P25), one of the better reference photocatalysts. All photocatalysts were tested in a broadband photoreactor to determine their effectiveness in dye degradation.

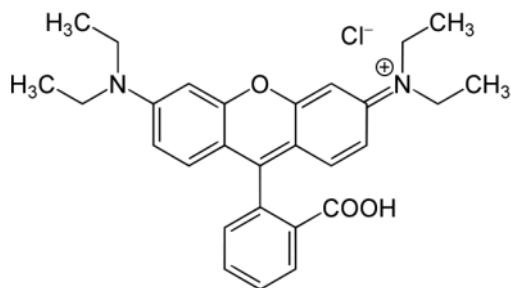


Figure 1.—Molecular structure of Rhodamine B.

RhB is a common dye in the triphenylmethane family, which contains four N-ethyl groups at either side of the xantheno ring (Fig. 1). It is reddish violet, highly soluble in water, and harmful if swallowed by human beings and animals. The maximum absorbance ( $\lambda_{\text{max}}$ ) of RhB is around 550 to 555 nm (Ref. 14). The color of this family of dyes results from conjugated chains or rings that absorb light at visible wavelength (Ref. 10).

## Materials and Methods

All chemicals were of high purity (> 99 percent) and used as received. To process the promoter-loaded photocatalysts, a Büchi Rotavapor 210 with a Vacuum Pump (V-700) was used, see Figure 2. Experimental and instrumentation details not given below are described in a recent report from the group at NASA Glenn Research Center (Ref. 15).

### Chemicals and Rhodamine B Solution

The following promoters or co-catalyst precursors were used: tetraamine platinum (II) nitrate ( $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ ), ruthenium (III) nitrosyl nitrate ( $\text{RuNO}(\text{NO}_3)_3$ ), palladium (II) chloride ( $\text{PdCl}_2$ ), and sodium tetrachloroaurate (III) dihydrate 99.99 percent ( $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ ); all were packaged under argon and obtained from Alfa Aesar of Ward Hill, MA. Silver nitrate ( $\text{Ag}(\text{NO}_3)_3$ ) and RhB (packaged under argon) were obtained from Acros Organics, Morris Plains, NJ and cupric nitrate ( $\text{Cu}(\text{NO}_3)_2$ ) was obtained from Fisher Scientific of Pittsburgh, PA. A  $8.0 \times 10^{-6}$  M RhB solution was prepared from a stock solution containing 0.447 g of RhB dissolved into 100 ml of deionized water. The stock and the diluted solutions had very dark reddish-purple and pink colors, respectively.

### Preparation of Transition Metal-Promoted $\text{TiO}_2$ Photocatalysts

Either 1 or 5 percent of the metal complex was dissolved in 20 ml of water. The only exception was the catalyst using 1% Pd. In the latter case, a few drops of HCl were added to the solution and stirred overnight to completely dissolve the palladium complex ( $\text{H}_2\text{PdCl}_4$ ). The solution (metal complex + water) was added dropwise to 10 g of  $\text{TiO}_2$ , either anatase or Degussa P25. Then, it was dried in a rotary evaporator (rotovap) at 200 torr in an 80 °C water bath (Fig. 2). Occasionally, the photocatalyst was scraped off the walls with a spatula and the flask was placed back on the rotovap. When the powder was dry, it was stored in an oven until calcinations were performed. Prior to calcining, the photocatalysts were ground with an alumina mortar and pestle. All the catalysts were calcined using a Thermolyne 21100 Tube Furnace at 400 °C for 2 hr under a flow of dry air. Calcining removes the volatile substances in the photocatalyst, typically nitrate released as nitric oxide (NO) or chloride released as HCl or  $\text{Cl}_2$ . Air is allowed to flow through the tube at about 5 ml/min to ensure that the catalyst does not decompose. After that, photocatalysts were characterized and screened for decomposition of RhB in a broadband photoreactor (Ace Glass).

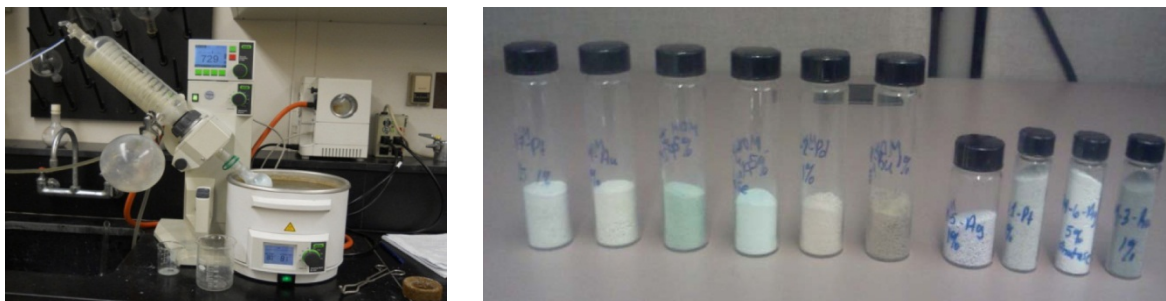


Figure 2.—(a) Assembly of a Büchi Rotavapor 210, a heating bath, and a Vacuum Pump (V-700) used to remove water from the photocatalyst. (b) Photocatalysts after the drying process in the rotovap, storage in a furnace and calcination at 400 °C.

## Transition Metal-Promoted TiO<sub>2</sub> Photocatalytic Studies

Photocatalytic experiments were carried out with 10 mg of catalyst added to 10 ml of an  $8.0 \times 10^{-6}$  molar RhB solution in a quartz photoreactor. The solution was irradiated with broadband light in air and nitrogen from pressurized cylinder tanks through a bubbler. The gas flow effectively stirred the solution and kept the suspended catalyst under constant motion. Aliquots of reaction (1.5 ml) were taken using a Pasteur pipette at pre-determined time intervals for up to one hour and centrifuged. The concentration of RhB was measured by a Perkin Elmer Lambda 950 UV/Vis spectrophotometer; UV/Vis spectra were recorded to monitor dye decomposition.

## Results and Discussion

Native or metal co-promoted (enhanced) titania (TiO<sub>2</sub>) photocatalyst powders were subsequently characterized by traditional methods and then screened for organic matter decomposition efficacy as discussed below. Obviously, exploiting this technology for space missions would entail design, testing and construction of a light-driven system that utilizes photocatalysis, as briefly described in the following section.

### Characterization of Photocatalyst Samples

Analyses of promoted-titania photocatalysts were performed on BET, X-ray diffraction (XRD), and scanning electron microscopy (SEM)-energy dispersive spectroscopy (EDS) instruments. The BET analysis (Table 1) determined that the photocatalysts with the largest surface areas were anatase-TiO<sub>2</sub>/Ru 1% and anatase-TiO<sub>2</sub>/Pt 1%; while that with the smallest surface area was anatase-TiO<sub>2</sub>/Ag 5%, although all samples differed by at most 2 m<sup>2</sup>/g. The surface area of our native anatase TiO<sub>2</sub> was 10 m<sup>2</sup>/g; this is much lower than the surface area of unmodified P25 TiO<sub>2</sub> (~50 m<sup>2</sup>/g). It was anticipated that for the lower percent metal-containing samples, the specific surface area would be higher because the metal promoter would not occupy as many surface sites. EDS analysis confirmed the presence of metal promoters on the surface of titania photocatalysts. The analysis for the promoter shows a weight percent range of 1.11 to 2.48 percent for the photocatalysts with a target value of 1 percent loading. In the case of the desired 5 percent promoter loading, the range was 3.78 to 8.68 percent. Each catalyst had the same promoter wt% calculated and added but the EDS analysis showed that samples often either exceeded or were under their desired loadings as a result of processing variability. A typical XRD powder pattern is shown in Figure 3 for a 1% Ru-promoted anatase sample.

TABLE 1.—EDS AND BET ANALYSIS FOR METAL-DOPED TITANIA PHOTOCATALYSTS  
[EDS catalyst elemental composition—the weight percentage of each element in each sample is the average of three EDS runs.]

Sample	% wt. Ti	% wt. O	% wt. Promoter	% Degradation after 60 min	BET surface area (m <sup>2</sup> /g)
Anatase TiO <sub>2</sub> /Ag 1%	47.00	51.90	1.11 (Ag)	66%	8.38
Anatase TiO <sub>2</sub> /Pd 1%	47.24	51.36	1.40 (Pd)	74%	8.75
Anatase TiO <sub>2</sub> /Pt 1%	48.74	48.84	2.24 (Pt)	72%	9.49
P25 TiO <sub>2</sub> /Cu 5%	42.51	48.80	8.68 (Cu)	40%	8.35
Anatase TiO <sub>2</sub> /Cu 5%	48.10	45.59	6.31 (Cu)	28%	8.35
Anatase TiO <sub>2</sub> /Ag 5%	46.84	49.38	4.94 (Ag)	76%	7.52
Anatase TiO <sub>2</sub> /Ru 1%	51.85	46.20	1.95 (Ru)	85%	9.26



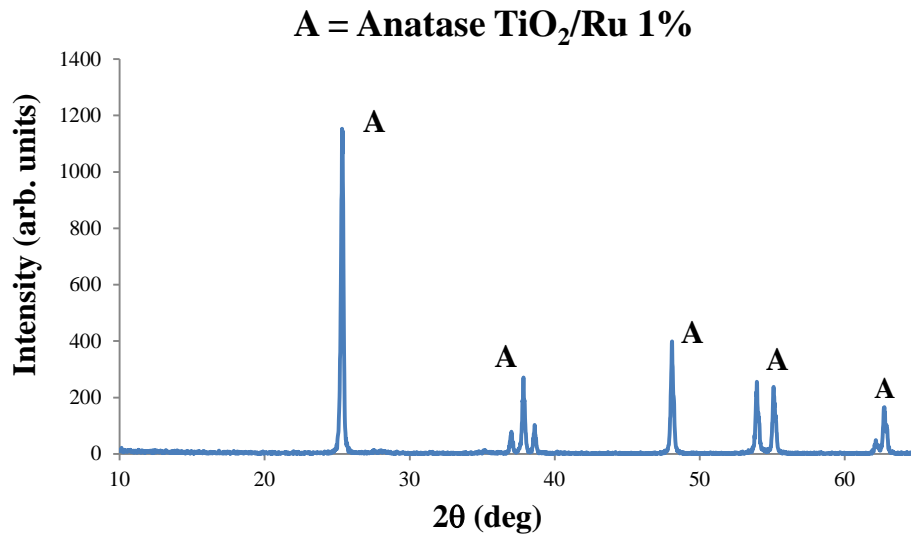


Figure 3.—X-ray diffraction powder pattern of the anatase/1% ruthenium sample.

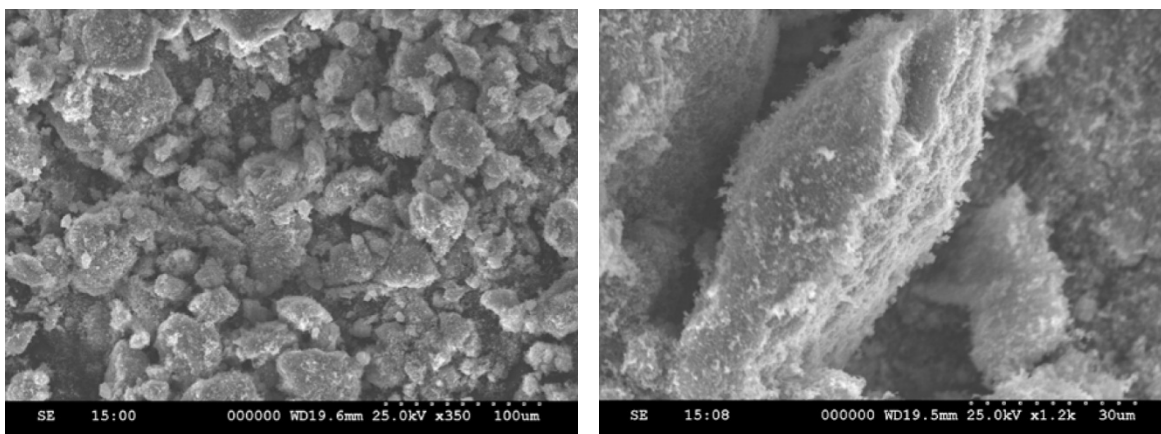


Figure 4.—Morphology of the anatase TiO<sub>2</sub>/Ru 1% photocatalyst from scanning electron micrographs.

Morphological analysis of the photocatalysts was accomplished by SEM (Fig. 4). Photocatalyst surfaces look rough with small particles that are not evenly distributed. The particles of the photocatalysts have different shapes and also various sizes (25 to 100  $\mu\text{m}$  in diameter). XRD analysis confirms that the synthesized photocatalysts are polycrystalline (Fig. 3). As shown in Table 1, the percent degradation of RhB after 60 min. was in excess of 70 percent for anatase-TiO<sub>2</sub>/Ag 5%; the anatase-TiO<sub>2</sub>/Ru 1%, showed the highest efficiency (85 percent), with the lowest being P25 TiO<sub>2</sub>/Cu 5% (40 percent). A higher specific surface area typically corresponds to higher catalytic activity as observed for anatase TiO<sub>2</sub>/Ru 1% (Refs. 5 to 7).

## Photocatalytic Results

Figure 5 shows a typical absorbance versus wavelength relationship for UV/Vis spectra of  $8.0 \times 10^{-6}$  M RhB irradiated with UV light in the absence of a catalyst. The initial (0 min) and final (60 min) absorbance values were 0.82 and 0.39, respectively. Figure 6 illustrates the degradation of a RhB solution in air, in the absence and the presence of a catalyst, and saturated with nitrogen gas with the catalyst present. The highest and lowest efficiency of degradation of RhB was found in a reaction with anatase-TiO<sub>2</sub>/Ru 1% (under aerobic conditions) and anatase-TiO<sub>2</sub>/Ru 1% (under nitrogen saturated conditions), respectively. RhB can react even in the absence of a catalyst under UV light as shown by the red line in Figure 6, however, the presence of anatase TiO<sub>2</sub>/Ru 1% accelerates this photoreaction significantly.

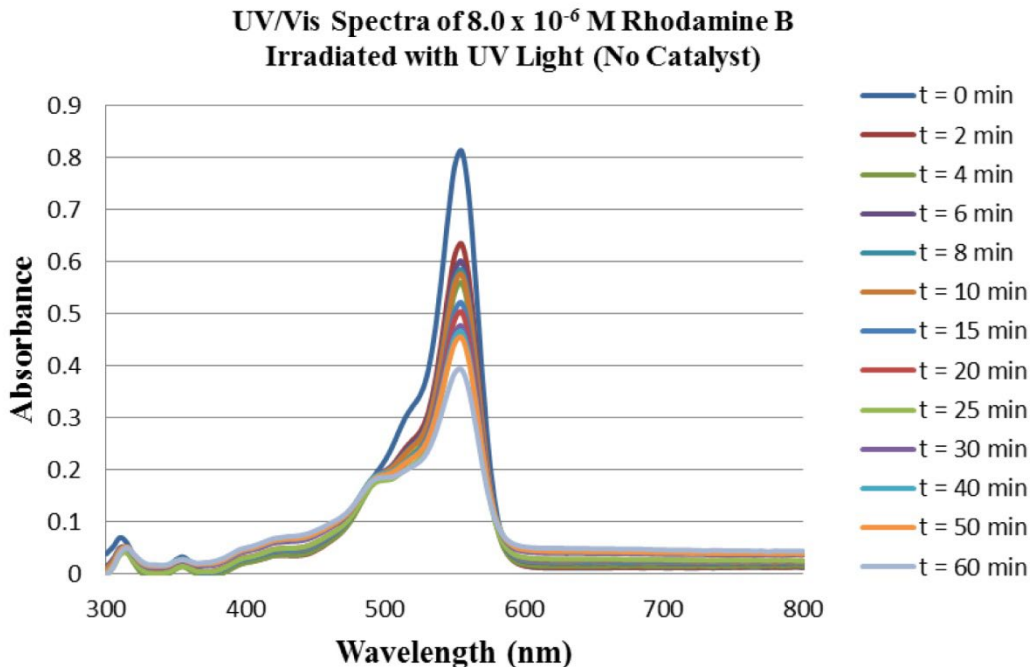


Figure 5.—UV-Vis spectra of RhB irradiated without a catalyst for 60 min.

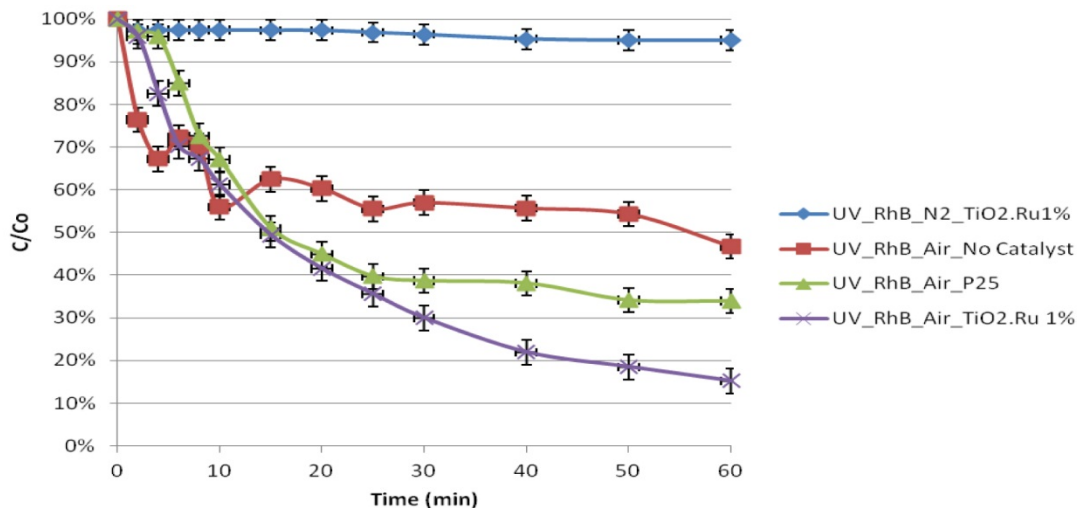


Figure 6.—UV-Vis spectra of photocatalytic studies of a metal doped Titania catalyst. The photo-degradation efficiency decreases as follows: Air\_TiO<sub>2</sub> Ru 1% > Air\_TiO<sub>2</sub> (P25) > Air\_No Catalyst > N<sub>2</sub>TiO<sub>2</sub>.Ru 1%.

## Mechanism of Photocatalysis

There have been a number of investigations to evaluate photocatalytic activity under both nitrogen-rich and oxygen-rich conditions. Ali et al. investigated photocatalyzed oxidation of methyl blue using ZnO thin films and suggested the reaction occurs (at least partially) by a Mars Van Krevlen-type mechanism (i.e., lattice oxygen atoms are used for oxidation, causing degradation of the ZnO lattice over time) (Ref. 16). This analysis suggests that applying oxygen-rich conditions either minimizes or prevents lattice oxygen from participating in the photocatalyzed oxidation reaction, or replacement of the lattice oxygen atoms removed during this reaction. It is hypothesized that oxygen atoms from the photocatalyst lattice are removed and utilized in the radical initiation and propagation phase of the follow-on reactions.

Physical degradation of photocatalysts is observed, as the reaction progresses under oxygen-limited conditions, because there is only a limited oxygen supply to replenish the lattice oxygen atoms used (Ref. 16). Consequently, under oxygen-rich conditions, the catalyst degradation is reduced because of the regeneration of the lattice oxygen atoms and maintenance of the physical structure. The Mars Van Krevlen-type mechanism has also been reported for TiO<sub>2</sub> and other (doped) ZnO-containing catalysts. For example, Lee and Falconer have shown that lattice oxygen atoms are extracted from mixed-phase TiO<sub>2</sub> (Degussa P25) during the photocatalytic decomposition of formic acid (Ref. 17).

In a related study of the photodegradation of RhB, under ultraviolet and visible light irradiation, by Shenawi-Khalil et al. a new family of BiO(Cl<sub>x</sub>Br<sub>1-x</sub>) (x = 0, 0.1, 0.2, 0.5, 0.7, 1) was synthesized by hydrothermal processing (Ref. 18). The Bi-based photoactive material with x = 0.5 exhibited a 74.2 percent degradation efficiency in 60 min, about 10 percent less compared to anatase-TiO<sub>2</sub>/Ru 1% (Table 1).

Zhong et al. carried out the photocatalytic degradation of RhB using TiO<sub>2</sub> supported on activated carbon (TiO<sub>2</sub>-AC) under microwave irradiation (Ref. 19). The decomposition of RhB in microwave-enhanced photocatalysis (MPC) 30 mg/L was 96 percent after 20 min. The reaction rate constant of RhB, a pseudo first-order reaction, using this photocatalyst material was 4.16 times greater than that using Degussa P25.

Houšková et al. investigated the photocatalytic activity of Ru-doped titania in the gas phase by the decomposition of acetone during irradiation at both 365 and 400 nm (Ref. 20). The method of UV-Vis diffuse reflectance spectroscopy was employed to estimate the band-gap of the as-prepared Ru-doped titania samples. They established that the intensity of the absorbance in the visible region increases with the concentration of doped Ru ions; a value of 3.20 eV is reported in the literature for pure anatase (Ref. 21). The band-gap is also dependent on the extent of doping and decreases with increasing content of Ru ions. Typically, doping with Ru ions results in an increase of the titania surface area, a decrease of the anatase particle size and a diminished band-gap energy, and is accompanied by an improvement in photocatalytic activity (Ref. 5).

Reaction kinetics gives information about the reaction rates and the mechanisms by which the reactants are converted to the products. Kinetics is determined by both the catalyst and the substrate concentration. A recent study confirms the use of pseudo-first order kinetics to describe the photocatalytic degradation of RhB with a rate expression of  $-dC/dt = k_{obs}C$  (Ref. 22). Specific rate constants and correlation to factors such as (photo)catalyst loading, co-promoter and reaction conditions are currently being analyzed and will be reported in a future publication.

## Integration of Photocatalysis into Space Missions

Of particular interest for space missions is the potential applicability of photocatalysis for the decomposition of organics in order to mitigate potential health and environmental problems in the controlled environment of a spacecraft or space station, particularly for long-term manned missions. One resource common to all manned missions in the immediate future is an abundance of sunlight, which

presents an opportunity to use concentrated sunlight, through the use of solar concentrators (Ref. 23), to possibly enhance or augment photocatalytic process(es). Other methods may also be considered for more distant long-term missions.

The most likely scenario for a photocatalytic reactor could include a modest enhancement in the solar intensity brought about by a trough-style reactor, with reactants and catalyst flowing along the axis of the trough and therefore being illuminated for a controlled duration based on flow rate. A rigid concentrator providing a 2000:1 concentration ratio increases the intensity substantially with concurrent undesirable increases in temperature (and potential recombination of electrons and holes). A less stringent concentrator is likely to be far more desirable, one providing a modest concentration ratio, perhaps a factor of 10:1, akin to flexible Fresnel concentrators developed in the 1990s for photovoltaics (Ref. 24).

Other concepts utilizing mass produced-composite strips, developed more recently as part of a Small Business Innovative Research effort funded by NASA GRC, may also be considered as they also provide a line focus which is conducive to illuminating a lengthy reactor tube over an extended period of time when utilizing a sun tracking system (Ref. 25). More research is needed to better understand the requirements of the receiving tube that would be located along the line focus, including such parameters as transparency, diameter and length. With the degradation reaction occurring in tens of minutes, a modest flow rate on the order of a liter per minute, and a reasonable diameter tubing machined to ensure mixing, one could envision a trough system on the order of a few meters in length to process a few liters of fluid over a few hours, suggesting a reasonable trough size. Identifying mechanisms and technologies for separating gas(es) generated from photocatalytic reactions and recycling the catalyst, in a microgravity environment, also warrant further study.

Another scenario for a photocatalytic reactor could include illumination of the reactants and catalyst utilizing energy derived from fluorescent lamps or light emitting diodes (Ref. 26). Of course, such a scenario would need abundant electrical power for the lamps or diodes. Missions in the distant future, to locations beyond Mars where sunlight is far less abundant, could be powered via nuclear reactors, and such fluorescent lamp or light emitting diode concepts could be facilitated by greater available power.

## Conclusions

Our materials characterization analysis shows that we have successfully produced different photocatalysts promoted using transition metal co-catalysts with various concentrations (1 to 5 percent) and using anatase or mixed anatase and rutile (P25). EDS confirms an approximate elemental composition of each of the promoted photocatalysts. However, some of them did not yield the expected weight percent target. As seen in the SEM, the catalyst conglomerate in particles and there are smaller particles on the surface, probably from co-promoters. Five weight-percent Cu on anatase and P25 proved to be ineffective photocatalysts. 1% wt. Pt on P25 was shown to be effective. The best catalyst in this study was 1% wt. Ru on anatase. Future work will include testing of the photocatalysts in a UV reactor to determine how effective they are in the decomposition of other dye systems such as LDS-698 and fluorescein. The potential applicability of photocatalysis to the decomposition of organics in order to mitigate potential health and environmental problems in the controlled environment of a spacecraft or space station, particularly for long-term manned missions, provides an impetus to further develop and deploy technologies that exploit plentiful and cost-effective resources such as (ultraviolet) solar radiation.

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