Synthesis of ZrO$_2$ and ZrO$_2$/SiO$_2$ particles and photocatalytic degradation of methylene blue

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SiO$_2$ particles (0.6 µm dia.) have been synthesized from tetraethyl orthosilicate and then decorated with ZrO$_2$ synthesized from zirconium tetrabutoxide. X-ray diffraction, infrared spectra, scanning electron microscopy, energy dispersive X-ray spectroscopy and transmission electron microscopy have been used to characterize the ZrO$_2$ and ZrO$_2$/SiO$_2$ catalysts. The results reveal that there are Si-O-Zr bridges between SiO$_2$ and ZrO$_2$ particles and ZrO$_2$ deposited on the SiO$_2$ surface. FT-IR analysis shows Si-O-Zr bonding at 1073 cm$^{-1}$. XRD analysis shows that amorphous SiO$_2$ and tetragonal ZrO$_2$ particles are formed at 500 °C. SEM and TEM analyses show that SiO$_2$ and ZrO$_2$/SiO$_2$ nanocomposite particles have a spherical morphology with diameter of 700-750 nm and a uniform particle size. Photoactivity of ZrO$_2$ and ZrO$_2$/SiO$_2$ particles has been investigated in the presence of ozone under UV light with methylene blue as a sample pollutant. Pseudo-first order kinetic model gives $R^2$ values to be 0.69-0.97 and 0.79-0.93 for ZrO$_2$ and ZrO$_2$/SiO$_2$ respectively. This study proves that ozone assisted ZrO$_2$/SiO$_2$ catalyst is an effective and fast-reacting system for photocatalytic removal of organic pollutants present in wastewater.

Keywords: Photocatalytic degradation, Dye degradation, Composites, Nanocomposites, Zirconia, Silica, Methylene blue

Composite particles are being effectively used as chemical components in many applications such as catalyst, electromagnetic fields, photocatalytic degradation etc. The composites with properties have been the focus of extensive research. There are many methods such as thermal evaporation, electroless plating, sol–gel method and via encapsulation to synthesize composite particles. However, the most common methods are sol–gel and vacuum evaporation.

Industrial wastes such as rubber, paper, plastics and food cause environmental pollution due to azo dyes. These azo dyes significantly affect the health of people and other living things. Recently, photocatalytic degradation method was used as an effective method for the elimination of azo dyes. In this, semiconductor composite materials play an important role in the photocatalytic process.

ZrO$_2$ is an n-type semiconductor oxide and its photocatalytic activity has been successfully tested by Herrman et al. Relatively wide band gap value and the high negative value of the conduction band allow it to be used as a photocatalyst in the production of hydrogen through water decomposition. In ZrO$_2$/SiO$_2$ related studies, researchers have focused on the design of composite particles and even the deposition of ZrO$_2$ on spherical SiO$_2$ surfaces. However, there are no photocatalytic studies with ZrO$_2$/SiO$_2$ mixed oxide. In addition, ozone assisted ZrO$_2$/SiO$_2$ catalyst has not been studied for photocatalytic application under UV light.

In the present study, we have synthesized ZrO$_2$ and ZrO$_2$/SiO$_2$ spherical nanocomposite catalysts by using a simple sol–gel process. The structure and texture are characterized by FT-IR, SEM-EDAX, TEM and XRD techniques, and their photocatalytic activity has been assessed using methylene blue (MB) as a sample pollutant. The suspension pH, catalyst concentration and temperature were kept constant in all experiments. We have also investigated how SiO$_2$ and ozone affect the photocatalytic activity of ZrO$_2$ in the spherical composite form.

Materials and Methods

Preparation of SiO$_2$ and ZrO$_2$ particles and ZrO$_2$/SiO$_2$ nanocomposite

SiO$_2$ particles were synthesized by using sol–gel method. Initially, 50 mL NH$_3$ solution and 25 mL absolute ethanol and 50 mL water were mixed.
Then, 20 mL tetraethyl orthosilicate was added to this solution drop by drop and mixed for 4 h. The particles obtained were filtered and washed with water three times and dried at 80 °C in an oven and calcined for 3 h.

For ZrO$_2$ particles, 10 mL zirconium tetrabutoxide was dissolved in 150 mL aqueous ethanol and then ammonia solution was added drop by drop to this mixture. The pH was adjusted to 6 and then mixed for 12 h. The obtained solution was filtered and calcined at 500 °C for 3 h.

For synthesizing ZrO$_2$/SiO$_2$ spherical nanocomposite particles, SiO$_2$ particles (1 g) obtained by the above procedure were added to ethanol-water mixture (50 mL), then 20 mL TBOZ and 30 mL ethanol were added to the solution and mixed for 3 h. The obtained particles were filtered and calcined at 500 °C, washed three times and dried in an oven at 80 °C for 12 h.

Characterization

The crystalline phase structure of the sample was examined by XRD (Rigaku-Smart Lab) using copper K radiation ($\lambda = 0.154056$ nm). The FT-IR spectra these particles were recorded on Thermo-Scientific, (Nicolet IS10-ATR) spectrophotometers. The size and shape of the particles were investigated by SEM (JEOL JSM-7600F) and TEM (JEOL JEM 2100F HRTEM). Elemental analysis was carried out using (JEOL JSM-7600F) EDAX analyzer with SEM. The Brunauer-Emmett-Teller (BET) surface area was measured using ASAP 2010 (Micromeritics Instrument Corporation, USA) with N$_2$ adsorption at 77.35 K.

Particle size was determined from X-ray diffraction analysis, carried out using Cu-Kα radiation (1.540 Å). The crystallite size of ZrO$_2$ and ZrO$_2$/SiO$_2$ spherical nanocomposite particles were calculated Å using Scherer equation;

$$d = \frac{B\lambda}{\beta_{1/2}\cos\theta}$$

where $d$ is the average particle size, $B$ is the Scherrer constant (0.91), $\lambda$ is wavelength of the radiation $\beta_{1/2}$ is full width at half maximum of the diffraction peak and $\theta$ is the diffraction is the diffraction angle.

The band gap energies of samples were determined by the diffuse reflectance spectra recorded on UV-visible-DRS Shimadzu spectrophotometer in the wavelength range of 200-800 nm. The approximate optical band gap ($E_g$) was determined as $E_g = 1240/\lambda$.

Photocatalytic studies

The aqueous solution of MB was prepared by dissolving known quantity of C$_{16}$H$_{18}$ClN$_3$S.xH$_2$O (Fluka, 97%) in doubly distilled water. It was further diluted to obtain standard solutions. All the reagents used were of analytical grade.

In photolytic experiments, a specially designed UV reactor was used. This reactor consists of a closed system having an UV lamp, properties of fixed mixing and water cooling and ozone entry (Fig. 1). The color of MB was analyzed by using Dr. Lange spectrophotometer and maximum wavelength in the visible area was determined to be 664 nm. All color changes were investigated at this wavelength. All photocatalytic experiments were carried out in UV reactor under the following experimental conditions. The amount of catalyst, ozone flow rate, and concentration of MB and volume of MB solution were: 1 g, 1.5 g/mL, 50 mg/L and 50 mL respectively.

The amount of degradation was calculated every 30 min. The degradation percentage of MB was calculated as:

$$\%\text{Degradation} = \frac{(C_0 - C)/C_0}{},$$

where $C_0$ is the initial concentration of MB and $C$ is the MB concentration at time $t$. Degradation efficiency was compared from the difference between degradation percentages of each parameter.

Results and Discussion

XRD analysis of ZrO$_2$ and ZrO$_2$/SiO$_2$ particles

Figure 2 shows XRD pattern of the ZrO$_2$, SiO$_2$ and ZrO$_2$/SiO$_2$ spherical nanocomposite particles respectively. In Fig. 2a the XRD patterns of ZrO$_2$ show peaks appearing at 20: 28.09°, 30.08°.
31.23°, 35.19°, attribute to the tetragonal ZrO$_2$ (JCPDS-17-0923). There is only one broad peak centered at 2θ = 23.42°, suggesting that amorphous SiO$_2$ was formed during calcination at 500 °C (Fig. 2b). For ZrO$_2$/SiO$_2$ spherical nanocomposite particles, there are four peaks appearing at 2θ: 28.09°, 30.13°, 31.26°, 34.42°, corresponding to the tetragonal ZrO$_2$ besides one peak at 23.81°, which may be attributed to amorphous SiO$_2$ (Fig. 2c). This indicates that the transformation of ZrO$_2$ from $t$-ZrO$_2$ to $m$-ZrO$_2$ does not occur because of stabilization of tetragonal ZrO$_2$ by SiO$_2$. Calculated crystalline size from XRD analysis showed particle size to be 1.12 nm for SiO$_2$ particles and 11.52 nm for ZrO$_2$/SiO$_2$ spherical nanocomposite particles.

**FT-IR analysis**

The presence of chemical bonding between SiO$_2$ and ZrO$_2$ was investigated with FT-IR analysis. Si-O-Si asymmetric stretching at 1100 cm$^{-1}$ corresponding to SiO$_2$ is observed. The characteristic peaks of Si–OH at 799 cm$^{-1}$ may be attributed to the silanol groups on the SiO$_2$ particles. In both spectra, the peaks which appear at about 3226 cm$^{-1}$ and 3381 cm$^{-1}$ are due to the bending vibration of OH from water. In the FT-IR spectrum of ZrO$_2$/SiO$_2$ spherical nanocomposite particles, it was observed that the peak shifted from 1100 cm$^{-1}$ to 1073 cm$^{-1}$. According to Zhan et al. and Lee et al., this shift arises from zirconia in a Si-O-Zr bond because of strong electropositivity of ZrO$_2$. Dang et al. reported that stretching vibration modes of Zr-O-Si bonds may be assigned at 967 cm$^{-1}$; however an increase in the number of Si-O-Zr bonds leads to increased shifts in FT-IR spectrum. Chen et al. reported that Si-O-Zr bonds can be assigned at 1050 cm$^{-1}$ which is attributed to the silica network forming the Si-O-Zr band. These reports are consistent with our findings and verified the oxygen bridge between Si and Zr.

**SEM and EDAX**

SEM images of SiO$_2$ and ZrO$_2$/SiO$_2$ nanocomposite microsphere were recorded (Fig. 3). Smooth and co-shaped SiO$_2$ particles are observed. The average diameter of ZrO$_2$/SiO$_2$ spherical nanocomposite particles is increased due to the ZrO$_2$ on the SiO$_2$ surface (Fig. 3(b,c)). EDAX analysis shows the qualitative presence of Zr, O, and Si as the main elements and confirms that ZrO$_2$ particles are on the surface of SiO$_2$ particles (Fig. 4).

**TEM analysis**

Figure 5 shows the TEM image of ZrO$_2$/SiO$_2$ spherical nanocomposite particles. The presence of ZrO$_2$ on SiO$_2$ surface with roughness was clearly observed. Self-aggregations of ZrO$_2$ occurred because of high generation rate of ZrO$_2$ particles. Therefore, the rate of generation of ZrO$_2$ particles during the hydrolysis and condensation reactions must be controlled in the sol-gel process.
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Fig. 3 – SEM images of (a) SiO$_2$ particles, and, (b,c) ZrO$_2$/SiO$_2$ particles.

Fig. 4 – EDAX analysis of ZrO$_2$/SiO$_2$ particles.

Fig. 5 – TEM analysis of ZrO$_2$/SiO$_2$ particles.
Table 1 – Kinetic parameters for the degradation of MB by ZrO$_2$ and ZrO$_2$/SiO$_2$ particles as catalyst

<table>
<thead>
<tr>
<th>System</th>
<th>ZrO$_2$</th>
<th>ZrO$_2$/SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>$k 	imes 10^{-3}$ (min$^{-1}$)</td>
</tr>
<tr>
<td>UV</td>
<td>0.69</td>
<td>0.20</td>
</tr>
<tr>
<td>Catalyst only</td>
<td>0.69</td>
<td>0.21</td>
</tr>
<tr>
<td>UV/Catalyst</td>
<td>0.82</td>
<td>3.54</td>
</tr>
<tr>
<td>UV/O$_3$</td>
<td>0.94</td>
<td>4.71</td>
</tr>
<tr>
<td>UV/O$_3$/Catalyst</td>
<td>0.97</td>
<td>11.01</td>
</tr>
</tbody>
</table>

The pseudo-first order kinetic model explains the kinetics of photocatalytic degradation of MB as

$$\ln\left(\frac{C_0}{C}\right) = kt,$$

where $C_0$ is the initial concentration of MB and $C$ is the concentration in solution at time.

The band gap values of ZrO$_2$ and SiO$_2$/ZrO$_2$ catalyst were calculated to be 4.13 eV and 2.48 eV respectively (Fig. 7). The band absorptions of the SiO$_2$/ZrO$_2$ spherical nanocomposite particles shift to longer wavelengths, indicating decrease in the band gap level. In this case, more photogenerated e/$h^+$ pairs are involved in the photocatalytic reactions.

ZrO$_2$ exhibit low photoactivity because of low absorbance in the UV range.$^{22}$ When photo-activity of ZrO$_2$ is compared with that of ZrO$_2$/SiO$_2$ particles, it is seen that ZrO$_2$/SiO$_2$ spherical nanocomposite particles were more active than ZrO$_2$ because of lattice deformation which is confirmed by unchanged t-ZrO$_2$ phases from the XRD results.$^{23}$
formation of Si-O-Zr and Si-O' bonds. The lattice deformation caused the band gap energy of ZrO$_2$ ($E_g$) to shift to lower energy due to strain at SiO$_2$/ZrO$_2$ interface which provides an easier excitation of the electrons of ZrO$_2$ resulting in more effective photoactivity.

In addition, SiO$_2$ provides the better dispersion stability which allows increased contact of MB molecules with the catalyst surface per unit time. Both particles did not show any photoactivity under only UV and only catalyst conditions however we observed that O$_3$ (ozone) degraded some MB even without catalyst. This can be explained as ozone transforming into O$_2$ and OH being used to oxidize organic molecules and chlorinated organic compounds.

$$\text{O}_3 + \text{H}_2\text{O} + 2e^- \rightarrow \text{O}_2 + 2\text{OH}$$

The BET surface area of SiO$_2$, ZrO$_2$, and ZrO$_2$/SiO$_2$ are 159.4, 23.5 and 52.3 m$^2$/g respectively. Compared to that of SiO$_2$, the surface area of ZrO$_2$/SiO$_2$ decreases due to agglomeration of ZrO$_2$ particles on the SiO$_2$ surface, which can be clearly seen from SEM images.

We noticed that the best photoactivity under the experimental conditions occurred on using UV/O$_3$/ZrO$_2$/SiO$_2$ catalyst. In general, the photocatalytic reaction begins when photons excited electrons from valence band to conductivity band in semiconductor materials, then continues with the diffusion of charge carriers to the particle surface where the reaction with water molecules reveals highly reactive species of peroxide (O$_2^-$) and hydroxyl radical (OH') responsible for the degradation of adsorbed organic molecules.

Ozone used in the photocatalytic degradation produce O$_2$ molecule and OH' ion which cause formation of peroxide and hydroxyl radicals in conductivity and valence band respectively; in this case photocatalytic efficiency increases because of peroxide and hydroxyl radicals from both ozone and adsorbed water.

The photocatalytic reactions for degradation of MB can be expressed as:

$$\text{ZrO}_2^{**} + \text{hv} \rightarrow \text{ZrO}_2 (h^+ + e^-)$$
$$h^+ + \text{OH}^- \rightarrow \text{OH}^* (\text{OH}^* \text{from both O}_3 \text{ and water})$$
$$e^- + \text{O}_2^{ads} \rightarrow \text{O}_2^{ads} (\text{O}_2 \text{ from both O}_3 \text{ and water})$$

**Conclusions**

SiO$_2$ particles decorated with ZrO$_2$ particles were obtained using sol-gel method. Electron microscopy X-ray diffraction and infrared spectroscopy were used to reveal the presence of Si-O-Zr bridges between SiO$_2$ and ZrO$_2$ particles. The particle size of ZrO$_2$ on SiO$_2$ surface was ~10 nm. Compared with ZrO$_2$, the ZrO$_2$/SiO$_2$ spherical nanocomposite microspheres exhibit enhanced photocatalytic efficiency. Ozone contributed to the photoactivity of catalyst by producing peroxide and hydroxyl radicals.

**References**