Kinetics Study of Photocatalytic Activity of Core-Shell Structured Magnetic 
Fe$_3$O$_4$/SiO$_2$/CeO$_2$ and their Application as Photocatalyst

Duangdao Chanheii$^1$, Burapat Inceesungvorn$^1$, Natda Wetchakun$^2$, Sukon Phanichphant$^3$.  

$^1$Department of Chemistry, Faculty of Science Chiang Mai University, Chiang Mai 50200, Thailand  
$^2$Department of Physics and Materials Science, Faculty of Science Chiang Mai University, Chiang Mai 50200, Thailand  
$^3$Materials Science Research Center, Faculty of Science Chiang Mai University, Chiang Mai 50200, Thailand  

*E-mail: sphanichphant@yahoo.com

The magnetic catalyst is considered as a new method to separate the catalyst from the treated suspension in photoreactors in which the catalyst can be easily recovered by applying an external magnetic field. The first step, CeO$_2$ photocatalyst was prepared by coating directly onto the surface of magnetic Fe$_3$O$_4$ particles via homogeneous precipitation and followed by a calcination process. However a direct contact of CeO$_2$ onto the surface of magnetic Fe$_3$O$_4$ particles presented unfavorable heterojunction due to the small band gap of Fe$_3$O$_4$ can act as electron-hole recombination center, leading to lowering the photocatalytic activity of formic and oxalic acids, thus the SiO$_2$ barrier layer between magnetic Fe$_3$O$_4$ and CeO$_2$ was prepared to reduce the negative effect. Then, the core-shell structured Fe$_3$O$_4$/SiO$_2$/CeO$_2$ has been prepared by combining three steps of the hydrothermal, sonochemical and homogeneous precipitation. The phase compositions of prepared samples were identified by X-ray diffraction (XRD). It was clearly confirmed from high resolution electron microscopy (HRTEM) that core-shell structured Fe$_3$O$_4$/SiO$_2$/CeO$_2$ exhibited core-shell structure including a magnetic Fe$_3$O$_4$ core, a SiO$_2$ middle layer and CeO$_2$ particle coating as expected. From the BET nitrogen adsorption-desorption isotherm, core-shell structured Fe$_3$O$_4$/SiO$_2$/CeO$_2$ exhibited a bigger pore volume, larger average pore size and higher specific surface area than the others. These surface properties could be provided more surface active sites for the adsorption of organic molecules, causing the higher efficiency in photocatalytic activity. The magnetic property of Fe$_3$O$_4$, Fe$_3$O$_4$/CeO$_2$, Fe$_3$O$_4$/SiO$_2$ and core-shell structured Fe$_3$O$_4$/SiO$_2$/CeO$_2$ were investigated with vibrating sample magnetometer (VSM) at room temperature. In order to estimate the band energy of the prepared samples, the reflectance spectra were obtained by using UV-visible diffuse reflectance spectrophotometry (UV-vis DRS) equipped with integrating sphere detector. To know the chemical environment and oxidation states of Fe, Ce, O, and Si in the material, X-ray photoelectron spectroscopy (XPS) was carried out. The results of the photocatalytic activity revealed that the pseudo-first order rate constants for formic and oxalic acid degradation was increased in the following order: core-shell structured Fe$_3$O$_4$/SiO$_2$/CeO$_2$ > single-phase CeO$_2$ > Fe$_3$O$_4$/CeO$_2$. The good photocatalytic activity of the core-shell structured Fe$_3$O$_4$/SiO$_2$/CeO$_2$ may be caused by SiO$_2$ middle layer and their surface properties. Furthermore the possible mechanism of the photoexcited electron-hole separation and transport processes was proposed in this research. Another important real world application for photocatalytic systems is long term stability. The core-shell structured Fe$_3$O$_4$/SiO$_2$/CeO$_2$ was compared and recovered in the consecutive cycles of use by external magnetic field. The material showed good stability with regards to photocatalytic performance for three cycles with less than 15% decreased from its initial activity during process.