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PHOTODISCOLORATION OF REACTIVE BLACK 5 DYE USING MECHANOCHEMICALLY ACTIVATED TiO_2-CeO_2 PHOTOCATALYSTS

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Abstract

The mechanochemical activation was used as a preparation method for obtaining nanosized mixed oxide TiO_2-CeO_2 photocatalysts. The commercial TiO_2 and CeO_2 oxides(Alfa Aesar GmbH & Co KG) were mixed at mass ratio: 1:1; 1:2 and 2:1 and then treated mechanochemically. The prepared nanostructured TiO_2-CeO_2 materials were physicochemically characterized with techniques such as X-ray diffraction analysis and Fourier transform infrared spectroscopy. The photodiscoloration tests of Reactive Black 5 dye solutions under UV light irradiation established that equal contents of TiO_2 and CeO_2 in mechanochemically activated TiO_2-CeO_2 mixtures lead to best photocatalytic activity of prepared catalyst samples (highest rate constant): TiO_2-CeO_2 (2:1) (2.5×10^{-3} min^{-1}) < TiO_2-CeO_2 (1:2) (2.6×10^{-3} min^{-1}) < TiO_2-CeO_2 (1:1) (2.8×10^{-3} min^{-1}).

Key words: *TiO_2-CeO_2 photocatalysts, mechanochemical treatment, photocatalytic degradation, Reactive Black 5 dye*

1. INTRODUCTION

The discharging of wastewaters from textile dye coloring facilities generates undesirable pollution and hypertrophication, which could result in the formation of dangerous byproducts occurring in the wastewater (Saquib et al. 2003). The presence of these synthetic organic compounds in water has potential carcinogenic and mutagenic effects (Rauf et al. 2011). Photocatalysis has been studied as a promising technique for the treatment of pollutants. Metal oxides, such as TiO_2 have widely ranging and important applications in environmental science. Amongst the photocatalytic materials, the titanium dioxide (TiO_2) has been intensively used to decolorize effluents mainly because of its optical-electronic properties, low-cost, chemical stability, and nontoxicity (Jaimes-Ramireza et al. 2012). TiO_2 photocatalytic efficiency may be improved when it is combined with other oxides. The selection of a dopant is very crucial in promoting the overall photocatalytic activities (Park et al. 2013). Doping usually gives a rise to lattice defects which can act as trapping sites for charge carriers, hence, slowing down the recombination rate of electron-hole pairs (Dedkova et al. 2013 and Ghasemi et al. 2012). Improvement of photocatalytic activity by addition of Ce atoms in TiO_2 has already been reported (Zuas et al. 2013, Magesh et al. 2009). It has been found out that the variable valences of Ce such as Ce^{4+} and Ce^{3+} make CeO_2 to manifest excellent characteristics in transferring electrons and enhancing the absorption capability in ultraviolet region (Pavasupree et al. 2005). Furthermore, Ce ions can function as O_2 storage sites. Due to the low redox potential a Ce ion can easily pass over from Ce^{4+} to Ce^{3+} state (Tanabe et al. 1978). There are many applications involving the Ce - doped TiO_2 photocatalytic activity for removal of many pollutants as follows: photocatalytic degradation of Methylene Blue (Magesh et al. 2009), Acid Orange 7 (Jaimes-Ramíreza et al. 2012), Reactive Red 195 (Ghasemi et al. 2012), Congo Red dye (Zuas et al. 2013), selective chemisorption of Methyl Orange (Fang et al. 2007). Other examples are sonocatalytic degradation of Acid Red B (Wang et al. 2010), 2-dichlorophenoxyacetic acid (Galindo et al. 2008), removal of phenol (Ko et al. 2010), photocatalytic elimination of methanol (Tiejun et al. 2009), gas sensor (Mohammadi et al. 2010), hydrogen generation from water (Sasikala et al. 2010), NH_3-SCR (Shan et al. 2012) and p-chlorophenol degradation (Liu et al. 2011). The effect of the method of preparation is important. Systems of mixed oxides TiO_2-CeO_2 were synthesized by polymer-assisted method (Magesh et al. 2009), co-precipitation (Zuas et al. 2013), homogenous precipitation (Shan et al. 2012) hydrothermal method (Liu et al. 2011) and sol-gel (Lopez et al. 2004, Pavasupree et al. 2005, Dedkova et al. 2013, Jaimes-Ramíreza et al. 2012, Ghasemi et al. 2012, Galindo et al. 2008, Fang et al. 2007, Ko et al. 2010, Tiejun et al. 2009). The TiO_2-CeO_2 composites were prepared by ultrasound (Wang et al. 2010), by

one-step flame spray (Chaisuk et al. 2004) and impregnation of TiO_2 on a CeO_2 support, synthesized by polyol method (Sasikala et al. 2010). It has been reported that nanocrystalline particles with controlled size have a greater number of active sites, enabling to enhance the photocatalytic activity (Galindo et al. 2008, Pavasupree et al. 2005), in particular nanostructured TiO_2-based materials offer advantages as materials with superior properties, like adsorption capacity and selectivity (Watanabe et al. 2004).

The goal of this paper was to investigate the photocatalytic activity of mechanochemically activated nanosized TiO_2-CeO_2 catalyst samples with different weight ratios of TiO_2 and CeO_2 in the mixture (1:1; 1:2 and 2:1) for discoloration of Reactive Black 5 dye under UV light irradiation. The relationship between different weight ratios and photocatalytic properties of synthesized by mechanochemical treatment TiO_2-CeO_2 photocatalytic materials is established. The X-ray diffraction analysis and FTIR spectroscopy were applied to characterize the obtained TiO_2-CeO_2 composite photocatalysts in details.

2. EXPERIMENTAL

2.1. Mechanochemical treatment of TiO_2-CeO_2 mixtures

The mechanochemical treatment of TiO_2-CeO_2 mixtures was carried out in a high-energy planetary ball mill type PM 100, Retsch, Germany using agate milling container of 80 ml volume. The mixtures with a total mass of 6 g commercially available TiO_2 and CeO_2 (Alfa Aesar GmbH & Co KG) and different weght ratios 1:1; 1:2 or 2:1 have been mechanochemically activated at milling speed 300 rpm for one hour in air medium. The mass ratio between TiO_2-CeO_2 mixture and the milling balls was 1:9.

2.2. Physicochemical characterization of the TiO_2-CeO_2 photocatalytic samples

The X-ray diffraction (XRD) analysis using TUR M62 apparatus with PC control and data acquisition, equipped with a HZG-4 goniometer and CoKα radiation was performed to establish the phase composition of the obtained TiO_2-CeO_2 photocatalyst samples. The presence of phases was determined using JCPDS database (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997). FTIR spectra were collected with a Fourier-transform infrared spectrometer Bruker-Vector 22 in the middle range (400-4000 cm^{-1}) by KBr tablets.

2.3. Photocatalytic study of TiO_2-CeO_2

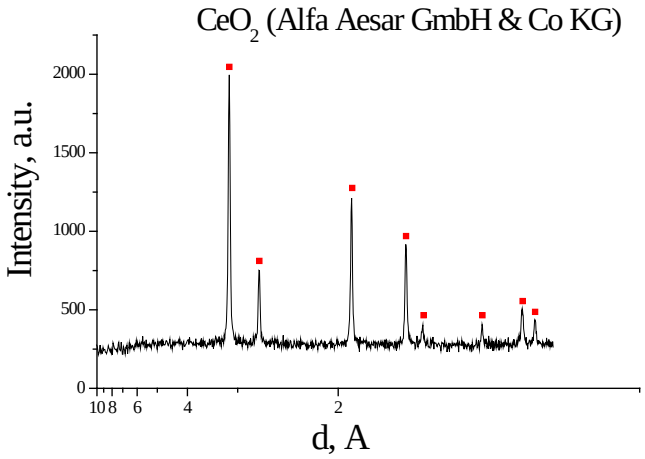
Reactive Black 5 (RB5) azo dye is commonly used in the textile industry and it can cause serious environmental problems. For this reason we selected this specific dye as model pollutant. The photocatalytic degree of discoloring of RB5 was determined using a volume of 150 ml of dye aqueous solution with 20 ppm initial concentration having pH 7. The photocatalytic activity tests have been carried out using polychromatic UV-A light lamp (Sylvania BLB, 18 W), with wavelength range 315-400 nm (λ_{max}=365 nm). The intensity of illumination upon the sample, evaluated using Cole Parmer radiometer, was 0.66 $mW.cm^{-2}$. The process of discoloring has been monitored by UV-Vis absorbance spectrophotometer BOECO S26 in the wavelength range from 200 to 800 nm. A semi-batch slurry photocatalytic reactor was used continuously feeding air flow. All photocatalytic activity tests have been carried out at a constant stirring rate (400 rpm) under ambient conditions. The samples reach adsorption-desorption equilibrium in the dark within about 30 min time interval before switching on the illumination. To test the photocatalytic activity of TiO_2-CeO_2 (1:1), TiO_2-CeO_2 (1:2) and TiO_2-CeO_2 (2:1) suspensions, aliquot samples of the suspension have been taken out of the reaction vessel after regular time intervals. The powder was then separated from the aliquot solution by centrifugation before the UV–Vis spectrophotometric measurement of residual dye concentration. After that, the aliquot solution, together with the photocatalyst powder, were returned back into the reaction vessel in order to operate at constant reaction volume. The degree of discoloration is expressed as $-\ln(C/C_0)$ (where C_0 and C are initial concentrations before switching on the illumination and the residual concentration of the solution after illumination for selected time interval, measured at 599 nm absorbance maximum, corresponding to the peak of the diazo bond (-N=N-).

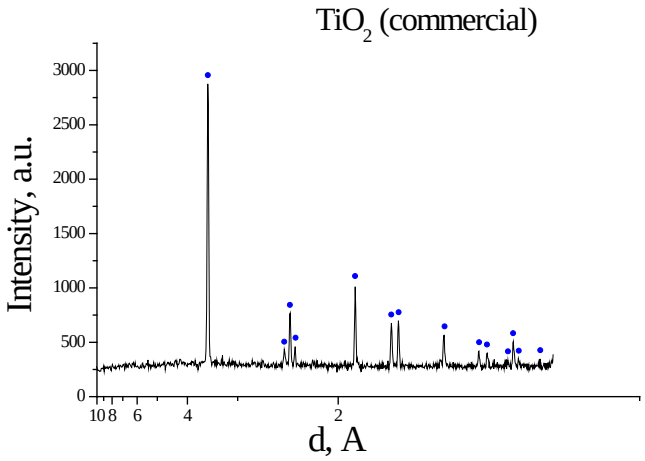
3. RESULTS AND DISCUSSION

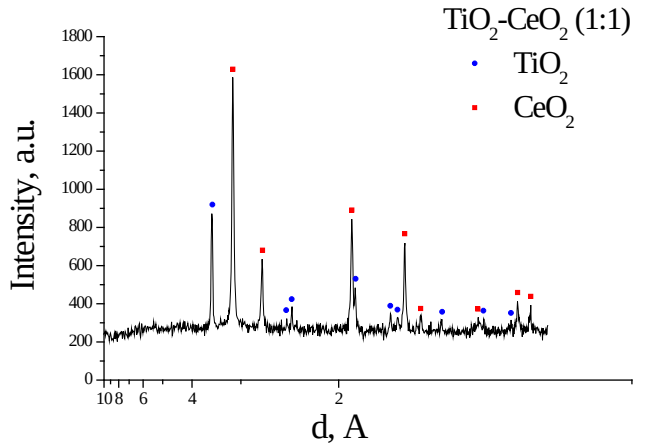
Fig. 1 illustrates the X-ray diffraction patterns of commercial TiO_2 and CeO_2 (Alfa Aesar GmbH & Co KG) and mechanochemically activated nanosized TiO_2-CeO_2 photocatalyst samples. The pure CeO_2 phase (PDF-81-0792) and mono-phase TiO_2 (anatase modification PDF-21-1272) have been registered in the XRD patterns of the starting materials CeO_2 and TiO_2. Different phase compositions were observed in the diffractograms of

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mechanochemically treated nanosized TiO_2-CeO_2 powder mixtures – the diffraction peaks are corresponding to different contents of TiO_2 (PDF-21-1272) and CeO_2 (PDF-81-0792) phases due to the different initial mass ratios 1:1; 1:2 and 2:1 of TiO_2 and CeO_2 used for composing the starting mixtures. The higher crystallinity degree of initial and prepared samples is established based on the recorded X-ray diffraction patterns.







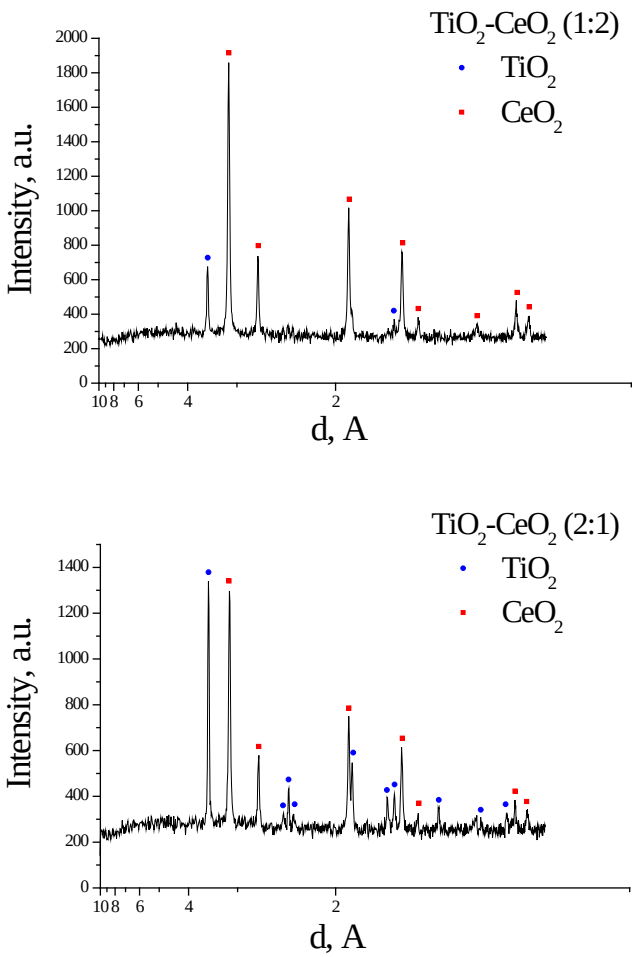


Fig. 1. XRD patterns of CeO_2 (Alfa Aesar GmbH & Co KG); commercial TiO_2 and prepared TiO_2-CeO_2 catalysts.

The average crystallite size, the lattice strain and the unit cell parameters of TiO_2 and CeO_2 phases are determined by PowderCell program based on the Williamson–Hall equation (G.K. Williamson et al. 1953) and they are represented in Table 1. The calculated values of mean particle size of TiO_2 and CeO_2 are about 9.5 and 13.5 nm respectively.

Table 1. Mean crystallite size (D), lattice strain (**ε**) and unit cell parameter (a) of TiO_2-CeO_2 catalysts.

Sample	Phase	D, nm	ε, a.u	a, A
TiO_2-CeO_2 (1:1)	TiO_2	9,1	$4{,}2.10^{-3}$	3.7833
	CeO_2	13,9	3.10^{-3}	5.4079
TiO_2-CeO_2 (1:2)	TiO_2	10,8	$4{,}2.10^{-3}$	3.7810
	CeO_2	13,3	3.10^{-3}	5.4084
TiO_2-CeO_2 (2:1)	TiO_2	8,6	$4{,}2.10^{-3}$	3.7836
	CeO_2	13,2	3.10^{-3}	5.4119

The FTIR spectra are displayed in Fig. 2. The vibrations registered in the region below 700 cm^{-1} are attributed to the presence of the metal oxides: titanium dioxide (titania) and cerium dioxide (ceria) (Mazaheri et al. 2009, Guo and Qiao 2008, Dos Santos et al. 2008). The presence of a peak at about 1200 cm^{-1} has also been observed by Hamza et al. (2013) in FTIR spectra of pure TiO_2. The broad absorption bands observed at about 3422 and 1624 cm^{-1} are assigned to the stretching O-H vibration of the water molecules (Mazaheri et al. 2009).

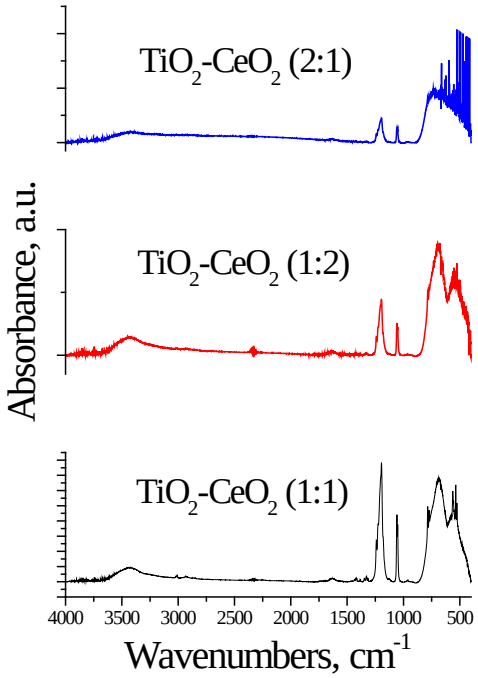


Fig. 2. FTIR spectra of the obtained TiO_2-CeO_2 photocatalyst samples.

Fig. 3 represents the concentration ratio C/C_0 during the photocatalytic degradation of the dye as a function of the time interval of illumination. The photocatalytic activity has been tested in the reaction of Reactive Black 5 discoloration under UV-light irradiation. Among all the investigated photocatalyst samples it is the TiO_2-CeO_2 (1:1) sample that showed the highest photocatalytic activity (Fig. 3). According to Pavasupree et al. (2005) the highest catalytic activity under visible light has been observed with the 50 mol% TiO_2–50 mol CeO_2%.

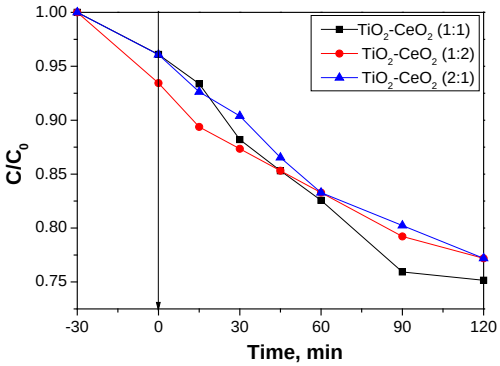


Fig. 3. Concentration ratio varying during the photocatalytic oxidative degradation of an initial concentration (C_0) of 20 ppm RB5 dye, based on changes in the intensity of the absorbance peak, corresponding to azo bond (-N=N-) as a function of the time interval of illumination.

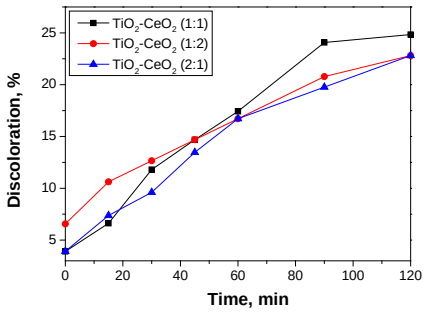


Fig. 4. Degree of discoloration of the dye solution after 120 minutes of UV-A illumination over TiO_2-CeO_2 (1:1), TiO_2-CeO_2 (1:2) and TiO_2-CeO_2 (2:1) samples.

Fig. 4 illustrates comparatively the obtained data on the degree of discoloration of the dye over the studied materials. The efficiency for dye RB5 removal over both samples TiO_2-CeO_2 (1:2) and TiO_2-CeO_2 (2:1) shows a similar value - 23% after 120 minutes of illumination. The best photocatalytic efficiency - 25% conversion, is exhibited by the TiO_2-CeO_2 (1:1) system. Some authors reported that the photocatalytic reactivities of TiO_2-CeO_2 systems were strongly related to the several factors. Magesh et al. (2009) estimated that modifying TiO_2 with Ce considerably enhanced activity under UV light illumination. They demonstrated the existence of a synergistic effect between two oxides. Ce loading reduces the recombination of charge carriers because of the easy redox transition of Ce^{4+}/Ce^{3+} couple (Magesh et al. 2009). On the other hand the photocatalytic activities increased also as a result of the physical and photophysical properties of the TiO_2–CeO_2 mixed oxides (Galindo et al. 2008). According to Ghasemi et al. (2012) the photocatalytic activities were increased upon increasing the amount of cerium dopant until a maximum is reached. There are two factors which are limiting the amount of Ce loading: partial blocking of active sites by excess amounts of Ce, introduced in the photocatalysts, and an increase in the opacity and light scattering of CeO_2–TiO_2 nanoparticles at a high concentration leading to a decrease in the percentage of light photons passing through the sample.

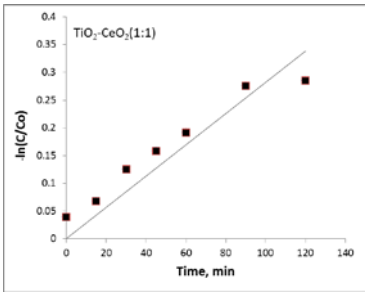


Fig. 5. Reaction course as a linear dependence of the illumination time –ln (C/C_0) of TiO_2-CeO_2 (1:1) powders; where C_0 is initial concentration of the dye, C is the dye concentration after illumination.

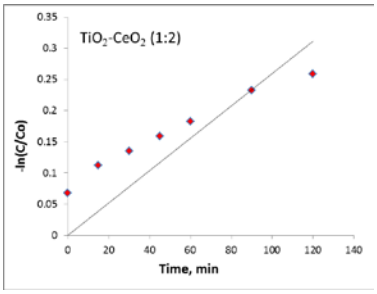


Fig. 6. Reaction course as a linear dependence of the illumination time –ln (C/C_0) of TiO_2-CeO_2 (1:2) powders; where C_0 is initial concentration of the dye, C is the dye concentration after illumination.

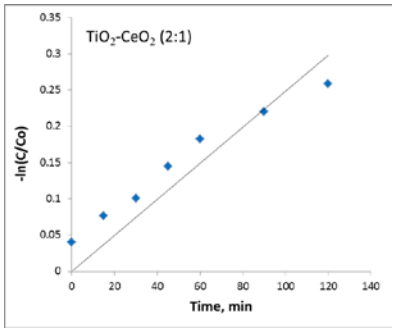


Fig. 7. Reaction course as a linear dependence of the illumination time –ln (C/C_0) of TiO_2-CeO_2 (2:1) powders; where C_0 is initial concentration of the dye, C is the dye concentration after illumination.

More or less acceptable linearity of the time (t) dependence was observed upon applying the first order kinetic equation: $-\ln(C/C_0) = k.t$ (see Fig. 5-7). The values calculated from the selected slopes (rate constants) are listed in Table 2. A maximum in the rate constant was observed with the sample TiO_2-CeO_2 (1:1) ($k = 2.8 \times 10^{-3}$ min^{-1}).

Table 2. Rate constants of nanodimensional TiO_2- CeO_2 photocatalysts.

Sample	K ($x10^{-3}$ min^{-1})
TiO_2-CeO_2 (1:1)	2.8
TiO_2-CeO_2 (1:2)	2.6
TiO_2-CeO_2 (2:1)	2.5

4. CONCLUSIONS

Nanosized TiO_2-CeO_2 photocatalyst samples have been activated mechanochemically. The mean crystallite size of TiO_2 and CeO_2 phases in TiO_2-CeO_2 samples are calculated to be 9.3 and 8.7 nm based on the XRD data. The mechanochemically treated nanodimensional TiO_2-CeO_2 systems show good photocatalytic properties in the reaction of Reactive Black 5 dye oxidative discoloration under UV-light illumination. The TiO_2-CeO_2 (1:1) photocatalyst sample possesses the highest photocatalytic activity – rate constant $k=2.8 \times 10^{-3}$ min^{-1}. The performed photocatalytic activity tests established dependence on the photocatalytic activity on the mass ratio of TiO_2 and CeO_2 with the mechanochemically prepared nanostructured TiO_2-CeO_2 photocatalyst samples. The equal content weight ratio of TiO_2 and CeO_2 leads to formation of a photocatalyst sample with the highest photocatalytic efficiency, compared to those of the other samples. The synthesized samples can be used as photocatalysts for wastewater purification.

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REFERENCES

Chaisuk, C., Wehatoranawee, A., Preampiyawat, S., Netiphat, S., Shotipruk, A., Panpranot, J., Jongsomjit, B., Mekasuwandumrong, O 2011, "Preparation and characterization of CeO_2/TiO_2 nanoparticles by flame spray pyrolysis", *Ceramics International*, vol. 37, pp. 1459–1463.

Dedkova, K., Matejova, L., Matejova, K., Peikertova, P., Mamulova Kutlakova, K., Kukutschova, J 2013, " Study of the antibacterial activity of cerium doped TiO_2 photocatalysts", paper presented at the scientific meeting of the Nanocon, Brno, Czech Republic 16 – 18 October.

Dos Santos, M.L., Lima, R.C., Riccardi, C.S., Tranquilin, R.L., Bueno, P.R., Varela, J.A., Longo, E 2008, "Preparation and characterization of ceria nanospheres by microwave-hydrothermal method", *Materials Letters*, vol. 62, pp. 4509–4511.

Fang, J., Bao, H., He, B., Wang, F., Si, D., Jiang, Z., Pan, Z., Wei, S., Huang, W 2007, "Interfacial and Surface Structures of CeO_2-TiO_2 Mixed Oxides", *J. Phys. Chem. C*, vol. 111, pp. 19078-19085.

Galindo, F., Gomez, R., Aguilar, M 2008, "Photodegradation of the herbicide 2,4-dichlorophenoxyacetic acid on nanocrystalline TiO_2–CeO_2 sol–gel catalysts", *J Mol Catal Chem*, vol. 281, pp. 119–125.

Ghasemi, S., Setayesh, S., Habibi-Yangjeh, A., Hormozi-Nezhad, M., Gholami, M 2012, "Assembly of CeO_2–TiO_2 nanoparticles prepared in room temperature ionic liquid on graphene nanosheets for photocatalytic degradation of pollutants" *J Hazard Mater*, vol. 199– 200, pp. 170–178.

Guo, H., Qiao, Y. 2008, "Preparation, structural and photoluminescent properties of CeO_2:Eu^{3+} films derived by Pechini sol–gel process", *Applied Surface Science*, vol. 254, pp. 1961–1965.

Hamza, M.A., Saiof, F. N., Al-ithawi, A. S., Ameen, M. A., Yaseen, H. M 2013, "Prepared of Nd: TiO_2 Nano Particles Powder as IR Filter via Sol-Gel", *Advances in Materials Physics and Chemistry*, vol. 3, pp. 174-177.

Huheey, J.E 1978, *Inorganic Chemistry*, Harper & Row Pub. Inc., New York, p. 74.

Jaimes-Ramireza, R., Vergara-Sanchezb, J., Silva-Martinez, S 2012, "Solar assisted degradation of Acid Orange 7 textile dye in aqueous solutions by Ce-doped TiO_2", *Mexican Journal of Scientific Research*, vol. 1, No. 1, pp. 42-55.

Ko, J.-B., Choi, S.-M., Kang, I.-C., Han, J.-K 2010, "Synthesis and visible light photocatalytic activity of porous CeO_2-TiO_2 composite powders", *Journal of Ceramic Processing Research.*, vol. 11, No. 1, pp. 123-125.

Liu, H., Wang, M., Wang, Y., Liang, Y., Cao, W., Su, Y 2011," Ionic liquid-templated synthesis of mesoporous CeO_2–TiO_2 nanoparticles and their enhanced photocatalytic activities under UV or visible light", *J Photochem Photobiol Chem*, vol. 223, pp. 157– 164.

Lopez, T., Rojas, F., Alexander-Katz, R., Galindo, F., Balankin, A., Buljanc, A 2004, "Porosity, structural and fractal study of sol–gel TiO_2–CeO_2 mixed oxides", *J Solid State Chem*, vol. 177, pp. 1873–1885.

Magesh, G., Viswanathan, B., Vishwanath, R. P., Vardarajan, T. K 2009, "Photocatalytic behavior of CeO_2-TiO_2 system for the degradation of Methylene Blue", *Indian J Chem*, vol. 48A, pp. 480-488.

Mazaheri, M., Hassanzadeh-Tabrizi, S. A., Aminzare, M., Sadrnezhaad, S.K 2009, "Synthesis of CeO_2 Nanocrystalline Powder by Precipitation Method", *Proceedings of the 11th ECERS Conference*, Krakow, 2009, pp. 655-658.

Mohammadi, M.R., Fray, D.J 2010," Nanostructured TiO_2–CeO_2 mixed oxides by an aqueous sol–gel process: Effect of Ce:Ti molar ratio on physical and sensing properties", vol. 150, pp. 631–640.

Park, H., Park, Y., Kim, W., Choi, W 2013, "Surface modification of TiO_2 photocatalyst for environmental applications". *J Photochem Photobiol C Photochem Rev*, vol. 15, pp.1–20.

Pavasupree, S., Suzuki, Y., Pivsa-Ar, S., Yoshikaw, S 2005, "Preparation and characterization of mesoporous TiO_2–CeO_2 nanopowders respond to visible wavelength", J Solid State Chem, vol. 178, pp. 128–134.

Rauf, A., Meetani, A., Hisaindee, S 2011, "An overview on the photocatalytic degradation of azo dyes in the presence of TiO_2 doped with selective transition metals", *Desalination*, vol. 276, pp. 13-27.

Saquib, M., Muneer, M 2003, "TiO_2-mediated photocatalytic degradation of a triphenylmethane dye (Gentian Violet), in aqueous suspensions", *Dyes Pigments*, vol. 56, pp. 37-49.

Sasikala, R., Shirole, A.R., Sudarsan, V., Kamble, V.S., Sudakar, C., Naik, R., Rao, R., Bharadwaj, S.R 2010, "Role of support on the photocatalytic activity of titanium oxide", *Appl Catal Gen*, vol. 390, pp. 245–252.

Shana, W., Liua, F., Hea, H., Shia, X., Zhanga, C 2012, "An environmentally-benign CeO_2-TiO_2 catalyst for the selective catalytic reduction of NO_x with NH_3 in simulated diesel exhaust", *Catal Today*, vol. 184, pp. 160– 165.

Tanabe, K., Hattori, H., Sumiyoshi, T., Tamaru, K., Condo, T 1978, "Surface property and catalytic activity of MgO-TiO_2", *J. Catal*., vol. 53, pp. 1-8.

Tiejun, C., Yuchao, L., Zhenshan, P., Yunfei, L., Zongyuan, W., Qian, D 2009, "Photocatalytic performance of TiO_2 catalysts modified by $H_3PW_{12}O_{40}$, ZrO_2 and CeO_2", *J Environ Sci*, vol. 21 pp. 997–1004.

Wang, J., Lv Y., Zhang, L., Liu, B., Jiang, R., Han, G., Xu R., Zhang X 2010, "Sonocatalytic degradation of organic dyes and comparison of catalytic activities of CeO_2/TiO_2, SnO_2/TiO_2 and ZrO_2/TiO_2 composites under ultrasonic irradiation", *Ultrason Sonochem*, vol. 17, pp. 642–648.

Watanabe, S., Ma, X., Song, C 2004, "Selective Sulfur Removal from Liquid Hydrocarbon Over Regenerable CeO_2-TiO_2 Adsorbent for Fuel Cell Application" *Paper Am Chem Soc Div Petrol Chem*, vol. 49, pp. 511 – 513.

Williamson, G.K., Hall, W.H 1953, "X-ray line broadening from filed aluminium and wolfram", *Acta Metall*, vol. 1, pp. 22-31.

Zaharescu, M., Wittmar, A., Teodorescu, V., Andronescu, C., Wittmar, M., Veith, M 2009, "TiO_2-CeO_2 Nanometric Powders Prepared by Sol-Gel Method", *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 635, № 12, pp. 1915–1924.

Zuas, O., Hamim, N 2013, "Synthesis, Characterization and Properties of CeO_2-doped TiO_2 Composite Nanocrystals", *Materials Science (MedŽiagotyra)*, vol. 19, No. 4, pp. 443-447.

Zhou, W., Liu, K., Fu, H., Pan, K., Zhang, L., Wang, L., Sun, C 2008, "Multi-modalmesoporous TiO_2–ZrO_2 composites with high photocatalytic activity and hydrophilicity", *Nanotechnology*, vol. 19, pp. 035610–035616.