

## Preparation and Characterization of Mg/TiO<sub>2</sub> for Visible Light Photooxidative-Extractive Deep Desulfurization

(Penyediaan dan Pencirian Mg/TiO<sub>2</sub> untuk Proses Nyahsulfur Fotopengoksidaan-Pengekstrakan di bawah Cahaya Nyata)

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### ABSTRACT

A series of Mg/TiO<sub>2</sub> photocatalysts were prepared using aqueous wet impregnation method at different Mg loading followed by calcination at different temperatures for 1 h duration. The photocatalysts were characterized using thermal gravimetry, Fourier-transform infrared spectroscopy, x-ray diffraction, field emission scanning electron microscopy and high-resolution transmission electron microscopy. The photocatalysts were investigated for photooxidative-extractive deep desulfurization of model oil containing dibenzothiophene at room temperature and under visible light irradiation. The model oil containing 100 ppm S was photooxidized followed by extraction using imidazolium-phosphate ionic liquids at room temperature. The best performing photocatalyst was 0.25 wt. % Mg/TiO<sub>2</sub> calcined at 400°C (0.25Mg400), in which 98.4% of dibenzothiophene (3.070 mmol DBT per g photocatalyst) was converted to dibenzothiophene sulfone. The highest extraction efficiency of 97.8% (0.01525 mmol S per mL ionic liquid) was displayed by 1,2-diethylimidazolium diethylphosphate.

**Keywords:** Desulfurization; Mg/TiO<sub>2</sub>; oxidation; photocatalyst; visible light

### ABSTRAK

Suatu siri Mg/TiO<sub>2</sub> fotomangkin telah disediakan menggunakan kaedah impregnasi basah akuas dengan komposisi Mg yang berlainan diikuti dengan pengkalsinan selama 1 jam pada suhu yang berlainan. Pencirian fotomangkin tersebut dijalankan menggunakan termogravimetri, spektroskopi transformasi Fourier inframerah, pembelauan sinar-X, pemancaran medan mikroskopi imbasan elektron dan mikroskopi transmisi elektron beresolusi tinggi. Seterusnya, fotomangkin tersebut dikaji untuk proses nyahsulfur fotopengoksidaan-pengekstrakan daripada model minyak diesel yang mengandungi dibenzotiofen pada suhu bilik dan di bawah sinaran cahaya nyata. Model minyak mengandungi 100 ppm S yang difoto-oksidakan diikuti dengan proses pengekstrakan menggunakan bendalir ionik imidazolium fosfat pada suhu bilik. Fotomangkin 0.25 % bt. Mg/TiO<sub>2</sub> yang dikalsin pada 400°C menunjukkan prestasi yang terbaik dengan 98.4% dibenzotiofen (3.070 mmol DBT per g fotomangkin) ditukar kepada dibenzotiofen sulfon. Tahap tertinggi pengekstrakan yang tercapai adalah 97.8% (0.01525 mmol S per mL bendalir ionik) yang ditunjukkan oleh 1,2-dietilimidazolium dietilfosfat.

**Kata kunci:** Cahaya nyata; fotomangkin; Mg/TiO<sub>2</sub>; nyahsulfur; pengoksidaan

### INTRODUCTION

In oil and gas industry, the emission of sulfur compounds from petroleum exhaust such as sulfur dioxide, SO<sub>2</sub>, or sulfur trioxide, SO<sub>3</sub>, into the atmosphere is undesirable. These pollutants are detrimental to both environment and human health; causing acid rain, corrosion of buildings and monuments, damaged trees, irritation to eyes, nose, throat and respiratory tract. The Malaysian Government has imposed the regulatory standards for sulfur content in diesel down to 10 ppm, to meet the EURO V standard (EPA 2011). The current industrial method to remove sulfur from diesel is called hydrodesulfurization (HDS). However, this process requires high operating temperature and pressure (approximately 400°C and 100 atm) leading to high operational cost and energy

consumption. Furthermore, HDS has its limitation in removing refractory sulfur compounds with high stearic hindrance (Campos-Martin et al. 2010; Jiang et al. 2011a). Therefore it is impossible to reduce the sulfur content in diesel down to less than 10 ppm via HDS.

There are few reported alternatives for sulfur removal that have been researched and investigated. Since the world is moving towards sustainable approach, utilization of the free and abundant sunlight for solar photocatalytic process (An'amt et al. 2014; Khalik et al. 2015) would be attractive. One of the promising processes is photooxidative desulfurization using titania, TiO<sub>2</sub> to remove heterocyclic sulfur compounds such as benzothiophenes (Abdel-Wahab & Gaber 1998; Matsuzawa et al. 2002) and dibenzothiophenes (Abdel-Wahab & Gaber 1998; Tao et al.

2009) from fuel (Abdel-Wahab & Gaber 1998; Matsuzawa et al. 2002) and kerosene (Tao et al. 2009) in the presence of oxidizing agent.  $\text{TiO}_2$  is a semiconductor photocatalyst which shows high activity under ultraviolet rays only.  $\text{TiO}_2$  has a band gap of 3.2 eV which confines its photocatalytic activity within the range of UV light ( $\lambda < 388$  nm). Since sunlight consists of less than 5% UV portion, only a small fraction of solar spectrum can be utilized. In order to harvest the visible light portion of the sun, modification by metal doping has been proven to be effective (Afshar et al. 2011; Choi et al. 2010; Feng et al. 2013; Kudo et al. 2007; Linsebigler et al. 1995; Wongpisutpaisan et al. 2013). In principle, the metal dopants can reduce the band gap energy and thus extend the active region of  $\text{TiO}_2$  from UV to visible light.

Feng et al. (2013) has reported that modification of  $\text{TiO}_2$  with magnesium (Mg) was able to improve its photocatalytic performance under solar radiation. In addition, the photocatalysts also showed impressive recyclability of up to five photocatalytic activity cycles (Feng et al. 2013). The applications of magnesium oxide (MgO) nanomaterials are extremely wide extending from areas in catalysis (Carabineiro et al. 2011; Ganguly et al. 2011; Heidari et al. 2009), to superconductivity (Yuan et al. 1996). This is due to its unique physical and chemical properties. During photocatalyst preparation, the optimum calcination temperature was reported in the range from 400–500°C (Ileperuma et al. 1990; Peng et al. 2004). The presence of magnesium ion, ( $\text{Mg}^{2+}$ ) resulted in the photocatalytic activity being extended to the visible region. The incorporation of  $\text{Mg}^{2+}$  on  $\text{TiO}_2$  did not influence the crystal patterns of  $\text{TiO}_2$  particles (Avasarala et al. 2011) as was indicated by XRD data which showed the presence of single anatase phase.  $\text{Mg/TiO}_2$  has been employed in photoreduction process, converting nitrogen into ammonia (Ileperuma et al. 1990) and also in photocatalytic degradation of organophosphate pesticide (monochrotophos) (Avasarala et al. 2011). However, to date it has not been reported by other researchers for deep desulfurization process. In a UV-visible absorption study, the presence of Mg shifted the absorption region to higher wavelength in the visible region (400–550 nm). This observation indicated reduction in band gap. In addition, Avasarala et al. (2011) also proved that the presence of Mg could also reduce the recombination rate of the photogenerated electrons and holes. Combined oxidative-extractive desulfurization (Jiang et al. 2011b; Zhang et al. 2009a, 2009b) has also been reported as one of the desulfurization methods where imidazolium-phosphate ionic liquids displayed good extractive performance (Zaid 2011; Zhang et al. 2009b). Other reported ionic liquid alternatives were quaternary ammonium ionic liquids such as  $\text{Et}_3\text{NHCl}\cdot\text{FeCl}_3$  (Zhao et al. 2011) and choline chloride-glycerol (Zaid et al. 2015) used as extractants.

This paper investigates the performance of  $\text{Mg/TiO}_2$  for photooxidation of dibenzothiophene (DBT) in model oil under visible light irradiation. This was followed by extraction of the photooxidized model oil using

imidazolium-phosphate ionic liquid. The morphological and structural properties of the  $\text{Mg/TiO}_2$  photocatalysts were also investigated.

## MATERIALS AND METHODS

### PREPARATION OF $\text{Mg/TiO}_2$

A series of  $\text{Mg/TiO}_2$  photocatalysts were prepared using wet impregnation method in aqueous solution. Based on previously reported study on  $\text{Mg/TiO}_2$  photocatalyst (Avasarala et al. 2011), it was shown that the optimum performance was achieved employing 1.00 wt. % Mg loading. Therefore, for this study, the amount of Mg loaded onto  $\text{TiO}_2$  (Degussa P25) was investigated in the range from 0.10 to 4.00 wt. %. The Mg precursor used for the photocatalyst preparation was magnesium nitrate hexahydrate,  $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ . All chemicals were used as received.

A premeasured amount of  $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  was dissolved in distilled water followed by addition of predetermined amount of  $\text{TiO}_2$ . The suspension was continuously stirred for 1 h followed by slow evaporation of the solvent in a water bath at 80°C. Then the material was further dried in an oven at 120°C for 18 h. The dried photocatalyst, termed as uncalcined photocatalyst was ground into fine powder in order to maximize its surface area for calcination. Calcination process was conducted in static air to activate the uncalcined photocatalyst at 300, 400 and 500°C for 1 h duration. Denotation was used to represent the photocatalyst: aMgT where 'a' refers to the Mg loading in wt. % on  $\text{TiO}_2$  and 'T' refers to the calcination temperature in °C. For example, 0.25Mg400 represents 0.25 wt. % Mg loaded onto  $\text{TiO}_2$  and calcined at 400°C.

### DESULFURIZATION PROCESS

Deep desulfurization was conducted in two consecutive steps: Photooxidation followed by extraction processes. Sulfur species in the form of dibenzothiophene (DBT) was the model refractory sulfur species used in this work. It was added into dodecane to prepare model oil containing 100 ppm S (equivalent to 3.118 mM DBT) simulating diesel fuel. Photooxidation was conducted in the presence of visible light radiation followed by extraction using ionic liquids. A mixture containing 10 mL model oil and 0.01 g of photocatalyst giving concentration of 1.00 g  $\text{L}^{-1}$   $\text{Mg/TiO}_2$  nanoparticles was stirred in the dark for 30 min to ensure homogeneous mixing between DBT and photocatalyst. The mixture was then irradiated with a 500 W halogen lamp. The photoreactor was positioned below the light source (500W halogen lamp ( $\lambda > 400$  nm)) with a distance of 15 cm between the lamp and the top of the model oil. The reaction was carried out for 6 h. Intermittent sampling of the model oil during photoreaction was conducted at different time intervals (every 15 min for the first hour followed by 30 min for

the second hour and every hour after that). The suspended photocatalyst was separated by filtration prior to analysis using GC-SCD (Agilent 7890A gas chromatograph coupled with Agilent 355 sulfur chemiluminescence detector). It was equipped with DB-1 J & W 123-1033 column (30 m × 320 mm × 1 mm) referring to the column dimension maintained at 325°C with helium carrier gas flowing at 1.1 mL min<sup>-1</sup>. The samples were analyzed to determine the amount of S as DBT and also dibenzothiophene sulfone (DBTO<sub>2</sub>).

During the photooxidation process, no oxidant was required. The amount of DBT (mmol) being converted to DBTO<sub>2</sub> per unit mass of photocatalyst was determined using (1):

$$DBT\ conversion = \frac{10}{1000} \times \frac{(DBT_i - DBT_f)}{\text{mass photocat}}, \quad (1)$$

where DBT<sub>i</sub> and DBT<sub>f</sub> are the initial and final concentrations of DBT (mM), respectively, in the model oil.

On the other hand, the % DBT conversion was calculated using (2):

$$\% DBT\ conversion = \frac{S_i - S_f}{S_i} \times 100\%, \quad (2)$$

where S<sub>i</sub> and S<sub>f</sub> are the initial and final concentrations of S (ppm), respectively, in the model oil.

The oxidized model oil (5.0 mL) was further extracted using three different types of ionic liquids (1.0 mL), namely 1,3-dibutyl-imidazolium dibutylphosphate (BBIM[DBP]), 1-butyl-2-ethyl imidazolium diethylphosphate (BEIM[DEP]) and 1,2-diethyl imidazolium diethylphosphate (EEIM[DEP]) to extract the sulfur species (both DBT and DBTO<sub>2</sub>). These three ionic liquids were selected based on their outstanding performance reported from previous work on integrated catalytic oxidation-extraction for desulfurization (Zaid 2011). The total amount of S (mmol), both as DBT and DBTO<sub>2</sub> that were extracted per unit volume of ionic liquid was determined using (3):

$$S_{\text{extracted}} = \frac{5}{1000} \times (S_o - S_e) \times \frac{1}{\text{volume ionic liquid}}, \quad (3)$$

where S<sub>o</sub> and S<sub>e</sub> are the total concentrations of sulfur species (mM), as DBT and DBTO<sub>2</sub> in the model oil after photooxidation process and extraction process, respectively.

In order to determine the % S<sub>removal</sub>, (4) was used:

$$\% S_{\text{removal}} = \frac{S_o - S_e}{S_o} \times 100\%, \quad (4)$$

where S<sub>o</sub> and S<sub>e</sub> are the total concentrations of sulfur species (ppm) as DBT and DBTO<sub>2</sub> in the model oil after photooxidation process and extraction process, respectively.

## CHARACTERIZATION OF PHOTOCATALYST

Selected photocatalysts were characterized using thermal gravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM). TGA was conducted using Perkin Elmer Thermal Analyzer (Pyris V3.81) to estimate suitable calcination temperatures for activating the raw photocatalyst. In FTIR, the IR spectrum was collected by scanning the sample from 4000 to 400 cm<sup>-1</sup> in the transmission mode using Perkin Elmer spectrophotometer (Spectrum One). The resulting FTIR spectra were used to analyse and identify the functional groups present in the photocatalyst. The effect of incorporating Mg onto the crystal structure of TiO<sub>2</sub> was analyzed using powder XRD (Bruker D8 Advance) conducted with CuKα radiation (40 kV, 40 mA) at 2θ angles from 2° to 80° and a scan speed of 4°·min<sup>-1</sup>. This technique is used to identify the type of TiO<sub>2</sub> phases and Mg-species present. The morphology of the Mg/TiO<sub>2</sub> photocatalysts was determined using FESEM (Zeiss Supra 35VP). The samples were coated with a layer of platinum-palladium prior to scanning at 100 kX magnification. HRTEM was performed using Zeiss Libra 200 microscopy technique whereby a beam of electrons was transmitted through an ultra-thin sample. The image formed from the interaction of the electrons transmitted through the sample is magnified and focused onto an imaging device.

## RESULTS AND DISCUSSION

### PRETREATMENT OF PHOTOCATALYST

The thermograms for the raw and calcined Mg/TiO<sub>2</sub> photocatalysts are displayed in Figure 1. The raw materials were thermally stable. Slight decomposition was observed (less than 10%) when the temperature was increased to 800°C. The raw photocatalyst (0.25 Mg uncalcined) decomposed slightly more than the calcined samples

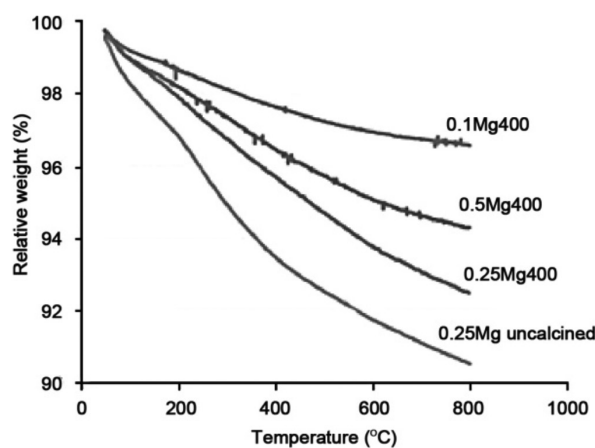
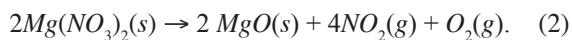


FIGURE 1. Thermogram of uncalcined and calcined photocatalysts with different Mg loading

which may be related to the presence of hydrates (50–200°C). Higher degradation temperature displayed on the thermograms may indicate the decomposition of  $Mg(NO_3)_2$  as proposed in (2) (Clark 2005).



#### DESULFURIZATION PROCESS

Photooxidation which is the first step in deep desulfurization process was conducted using Mg/TiO<sub>2</sub> photocatalysts for a duration of 6 h under visible light irradiation. No oxidant was added. The effect of calcination temperature and Mg loading on DBT conversion were investigated and the results are shown in Figure 2. Equations (2) and (3) were used to calculate DBT conversion. Calcination temperature at 300°C was not producing active photocatalysts where the performance was less than 5% (0.130 mmol DBT per g photocatalyst). After calcination at 400°C, photocatalyst with 0.5 wt. % Mg loading (0.5 Mg400) showed the best performance of 45.7% DBT conversion to DTBO<sub>2</sub> (1.426 mmol DBT per g photocatalyst). Therefore, lower Mg loading photocatalysts were further investigated (0.10–0.25 wt. %) to determine its effect on activity.

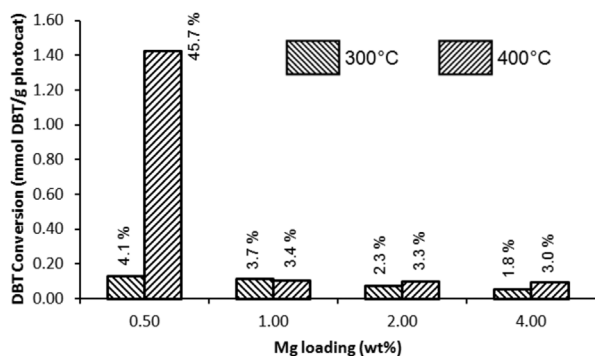


FIGURE 2. Effect of Mg loading and calcination temperature on DBT conversion to DBTO<sub>2</sub>

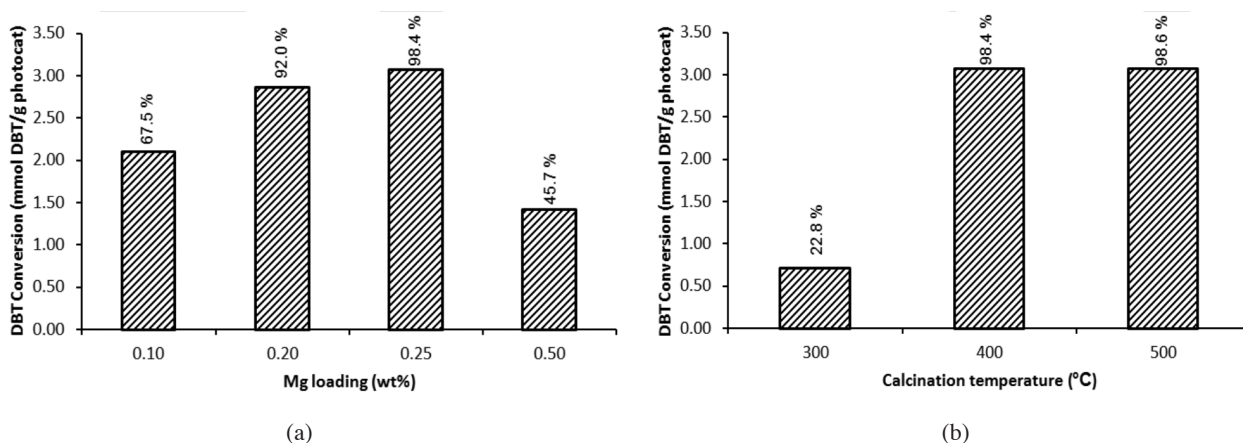


FIGURE 3. Effect of (a) Mg loading and (b) calcination temperature on DBT conversion

Figure 3(a) shows the improved performance of Mg/TiO<sub>2</sub> photocatalysts with lower Mg loading calcined at 400°C. The best performing photocatalyst was that with 0.25 wt. % Mg loading (0.25 Mg400) giving 98.4% DBT conversion (3.070 mmol DBT per g photocatalyst) after 5 h reaction. Then, the effect of calcination temperature (300 and 500°C) on the performance of 0.25 wt. % Mg/TiO<sub>2</sub> photocatalysts was further investigated. Based on Figure 3(b), although the photocatalyst calcined at 500°C displayed better performance (3.073 mmol DBT per g photocatalyst), it could only outperform 0.25 Mg400 by 0.2%, thus, 400°C is still the preferred optimum calcination temperature since it is less energy intensive.

Photolysis of DBT was negligible (0.02%). The oxidized model oil (containing both DBT and DBTO<sub>2</sub>) was further extracted by using three imidazolium-phosphate type ionic liquids, (BBIM[DBP]), (BEIM[DEP]) and (EEIM[DEP]). The extraction efficiencies were determined using (3) and (4). Figure 4 shows the extraction efficiency of the three imidazolium-phosphate-based ionic liquids. The performance of all three ionic liquids were comparable with the extraction efficiencies of BBIM[DBP], BEIM[DEP] and EEIM[DEP] at 97.2% (0.01515 mmol S per mL ionic liquid), 97.7% (0.01523 mmol S per mL ionic liquid) and 97.8% (0.01525 mmol S per mL ionic liquid), respectively. Previous work on the oxidative-extractive desulfurization from 1000 ppm DBT (with addition of H<sub>2</sub>O<sub>2</sub>) (Zaid 2011) showed that the sulfur removal was in the range from 78.2–85.2% following the sequence of BBIMDBP > EEIMDEP > BEIMDEP. To date, no other work has been reported on similar Mg/TiO<sub>2</sub> photocatalyst for deep desulfurization process. Photooxidative-extractive desulfurization process under UV (Zhao et al. 2011) and visible light irradiation (Zaid et al. 2015) using TiO<sub>2</sub>-based photocatalyst and quaternary ammonium ionic liquids have been reported with comparative sulfur removal efficiency of more than 98% and 97.1%, respectively.



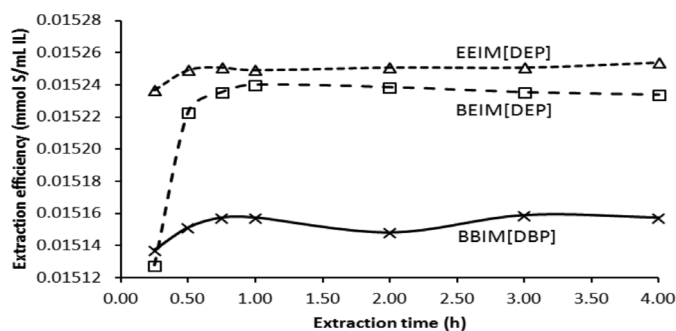


FIGURE 4. Extraction efficiency of total sulfur species using different ionic liquids

## CHARACTERIZATION RESULTS

### FTIR

Figure 5(a) compares the FTIR spectra of the uncalcined and calcined photocatalysts showing the presence of nitrate functional group at wavenumber  $1384\text{ cm}^{-1}$  (Nakagawa & Walter 1969) on the raw photocatalyst. There was no indication of the presence of nitrate group in the calcined samples indicating that the nitrate group was completely removed during calcination process (Clark 2005). This

is in agreement with the results obtained from TGA. Based on Figure 5(a) and 5(b), all photocatalysts displayed the absorption bands corresponding to O–H stretching and bending around  $3400$  and  $1600\text{ cm}^{-1}$ , respectively. However, the % transmittance of the characteristic peaks before calcination was higher compared to that after calcination. This indicates that most of the hydrates were removed during calcination, in agreement with the TGA results. An absorption band between  $400$  and  $900\text{ cm}^{-1}$  was attributed to Ti–O stretching vibrations (Wang & Zhou 2010).

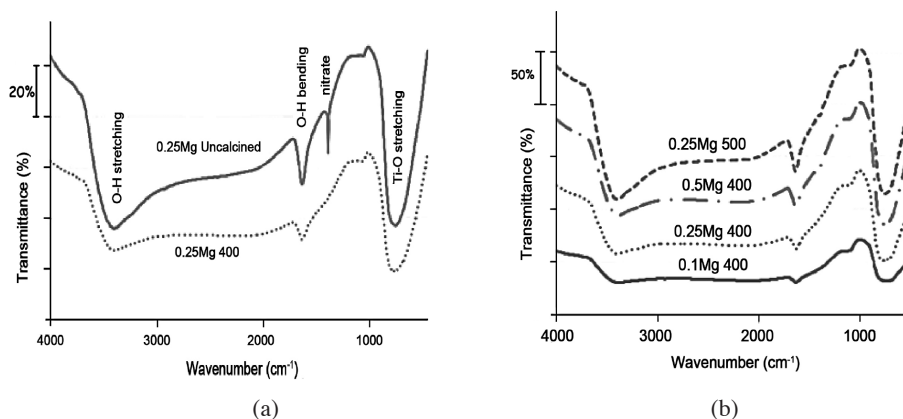


FIGURE 5. FTIR spectra for (a) uncalcined and calcined  $\text{Mg}/\text{TiO}_2$  photocatalysts and (b)  $\text{Mg}/\text{TiO}_2$  photocatalysts

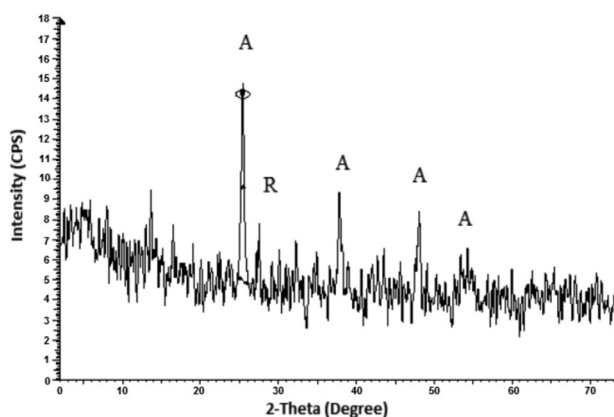


FIGURE 6. XRD pattern of 0.24  $\text{Mg}400$

## XRD

The XRD pattern of 0.25 Mg400 displayed in Figure 6 shows the characteristic peaks for TiO<sub>2</sub> dominated by the anatase phase (A) ( $2\theta = 25.3^\circ, 33.8^\circ, 47.8^\circ, 53.8^\circ$ ) and a small amount of rutile phase (R) ( $2\theta = 27.4^\circ$ ).

No peaks corresponding to Mg-species were detected indicating high Mg dispersion on TiO<sub>2</sub>. Similar results were also observed by Avasarala et al. (2011). The XRD patterns for the other photocatalysts with different Mg loadings and calcined at different temperatures were similar to that represented in Figure 6.

## FESEM

Figure 7(a)-7(d) displays the FESEM images for Mg/TiO<sub>2</sub> photocatalysts with different Mg loading calcined at 400°C for 1 h duration. The average particle size and particle size distribution of the photocatalysts are shown in Table 1. Figure 7(a)-7(c) shows irregular spherical-shaped particles with size ranging from 17-62 nm. The photocatalysts maintained their average size within 26-31 nm, comparable to as reported the literature (Avasarala et al. 2011; Hwang et al. 2009). As the Mg loading increased, the particle size also increased in addition to the presence of cubical-shaped structural materials (indicated by white

circle in Figure 7(d)). This may represent the presence of separate Mg particles (Su et al. 2011). Agglomeration and sintering of the nanoparticles were also observed with the increase in size distribution.

## HRTEM

Figure 8(a)-8(d) displays the HRTEM images and lattice fringes of the Mg/TiO<sub>2</sub> photocatalysts with different Mg loading and calcined at 400°C. Two different morphologies were observed; irregular spherical-shaped and also cubical-shaped particles (indicated by white circle in Figure 8(c)) which may represent TiO<sub>2</sub> and Mg-species, respectively (Su et al. 2011). Two different length of lattice fringes were also identified from which were tabulated in Table 2. The shorter and more consistent d-spacing of 0.332-0.361 nm was assigned to anatase TiO<sub>2</sub> (101) (Lu et al. 2008; Parra et al. 2008; Zhang et al. 2011). No surface lattice distortion on TiO<sub>2</sub> was observed even when incorporated with higher Mg loading (Zhang et al. 2011). The longer d-spacing ranging from 0.753-1.230 nm may be related to Mg-species. The reported lattice fringes for Mg-species were 0.21 nm for MgO (200) (Ganguly et al. 2011; Kim et al. 2006; Su et al. 2011); 1.64 and 1.07 nm for lamellar Mg(OH)<sub>2</sub> (200) and (300) (Ranjit & Klabunde 2005); 0.72 nm for mixture of

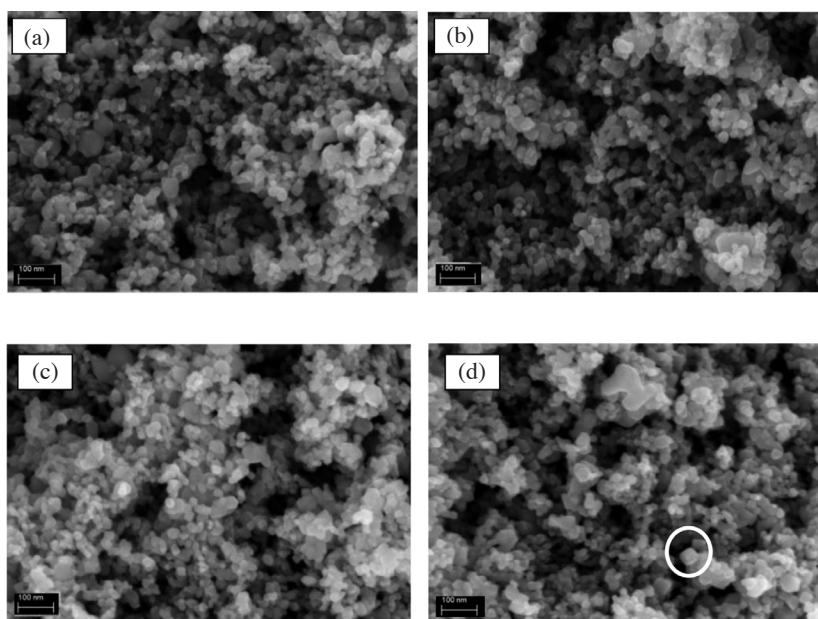


FIGURE 7. FESEM images for (a) 0.10 Mg, (b) 0.25 Mg, (c) 0.50 Mg and (d) 1.00 Mg photocatalysts

TABLE 1. Particle size distribution and average size of Mg/TiO<sub>2</sub> photocatalyst

Mg loading (%)	Average particle size (nm)	Particle size range (nm)
0.10	26	17-57
0.25	31	20-62
0.50	31	23-45
1.00	35	22-62

MgO and Mg(OH)<sub>2</sub> (Mc Kelvy et al. 2001) and 0.89-0.96 nm for lamellar Mg-oxyhydroxide intermediates (Mc Kelvy et al. 2001).

Based on the d-spacings indicated in Table 2, co-existence of MgO and Mg(OH)<sub>2</sub> was observed at low Mg loading while the presence of lamellar Mg-oxyhydroxide intermediate was observed on 0.25 Mg400. At higher Mg loading, lamellar Mg(OH)<sub>2</sub> was present. The best performing

photocatalyst for deep desulfurization was 0.25 Mg (Zaid 2011) indicating that the active species required for the process was lamellar Mg-oxyhydroxide intermediates.

## CONCLUSION

Mg/TiO<sub>2</sub> was successfully synthesized using aqueous wet impregnation method. 0.25 Mg400 has successfully

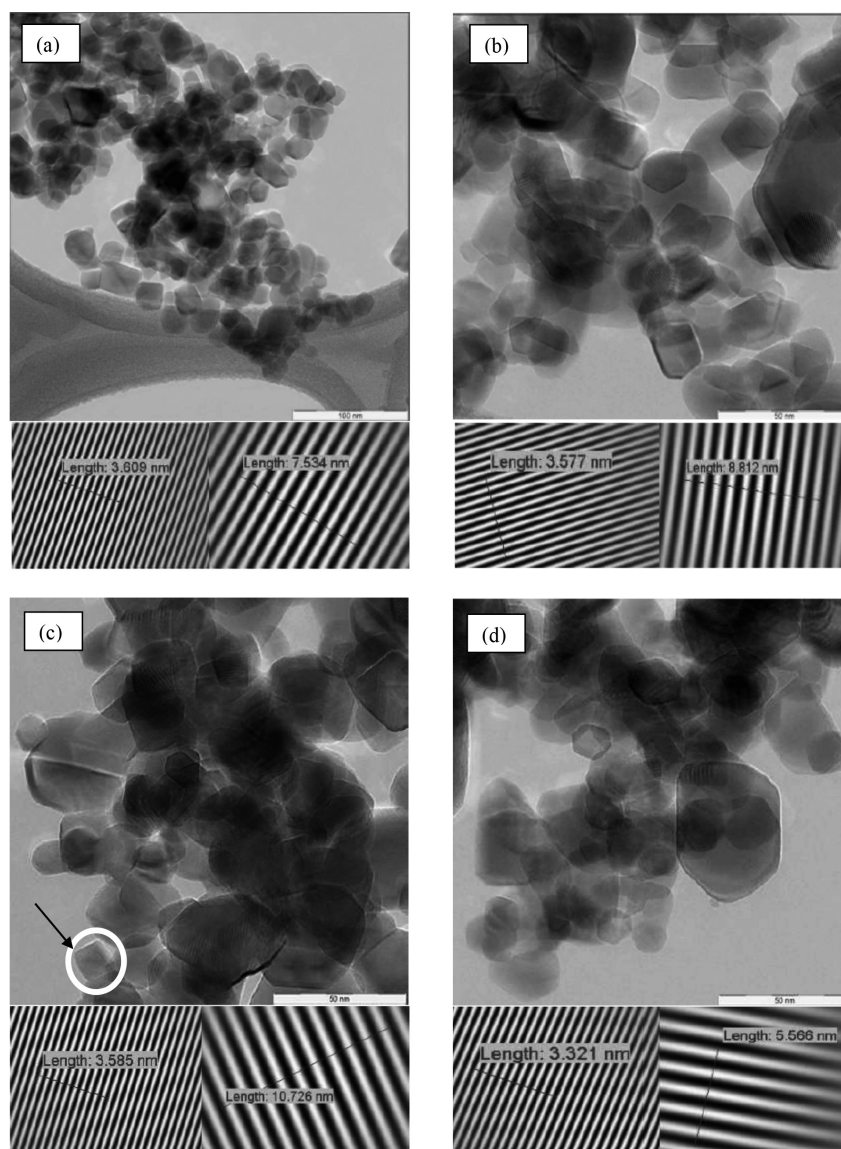


FIGURE 8. HRTEM images for (a) 0.10 Mg, (b) 0.25 Mg, (c) 0.50 Mg and (d) 1.00 Mg photocatalysts

TABLE 2. HRTEM d-spacings of Mg/TiO<sub>2</sub> photocatalyst

Mg loading (%)	d-spacing of TiO <sub>2</sub> (nm)	Mg-Species	
		d-spacing (nm)	Type of Mg-Species
0.10	0.361	0.753	MgO + Mg(OH) <sub>2</sub> mixture
0.25	0.358	0.881	Mg-oxyhydroxide lamellar
0.50	0.359	1.073	Mg(OH) <sub>2</sub>
1.00	0.332	1.113	Mg(OH) <sub>2</sub>

photooxidized 98.4% of DBT (3.070 mmol DBT per g photocatalyst) into DBTO<sub>2</sub>. The sulfur removal observed after subsequent extraction with 1,2-diethyl imidazolium diethylphosphate (EEM[DEP]) ionic liquid gave the highest performance of 97.8 % (0.01525 mmol S per mL ionic liquid). Mg/TiO<sub>2</sub> exist as irregular spherical-shaped particles. As the Mg loading increased, cubical shaped structure materials could be observed. The average particle size ranged from 26-36 nm. Incorporation of Mg on TiO<sub>2</sub> did not lead to any lattice distortion. At low Mg loading, the presence of MgO + Mg(OH)<sub>2</sub> mixture was detected while at higher Mg loading, the presence of lamellar Mg-oxyhydroxide intermediates and Mg(OH)<sub>2</sub> was observed. Lamellar Mg-oxyhydroxide intermediates were the active species for high photooxidative performance.

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