การนำไทเทเนียมไดออกไซด์เจือซัมมาเรียมไปใช้เป็นตัวเร่งปฏิกิริยาในการย่อยสลายสารประกอบฟีแนนทรีนด้วยแสง

SYNTHESIS OF SAMARIUM DOPED TiO_2 CATALYSTS FOR PHOTODREGADATION OF PHENANTHRENE

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บทคัดย่อ: ไทเทเนียมไดออกไซด์เจือซัมมาเรียมซึ่งถูกเผาที่อุณหภูมิ 500 องศาเซลเซียส สามารถเร่งปฏิกิริยาการย่อยสลายสารประกอบฟีแนนทรีนภายใต้แสงวิซิเบิลได้ โดยสามารถย่อยสลายสารละลายฟีแนนทรีนเข้มข้น 20 ppm ได้ร้อยละ 90 ภายในระยะเวลา 7 ชั่วโมง ในขณะที่ตัวเร่งปฏิกิริยาตัวอื่นๆ ต้องใช้เวลานานกว่าในการย่อยสลายเพื่อให้มีประสิทธิภาพที่ทัดเทียมกัน โดยที่ตัวเร่งปฏิกิริยาทั้งหมดเตรียมโดยวิธีโซล-เจล จากการพิสูจน์เอกลักษณ์ของตัวเร่งที่เตรียมได้โดยวิธีการเลี้ยวเบนด้วยรังสีเอ็กซ์ (XRD) สามารถยืนยันโครงสร้างของไทเทเนียมไดออกไซด์เจือซัมมาเรียมและการเปลี่ยนแปลงเฟสของไทเทเนียมไดออกไซด์เจือซัมมาเรียม เมื่อใช้อุณหภูมิเผาที่แตกต่างกันได้ ขนาดของไทเทเนียมไดออกไซด์เจือซัมมาเรียมคำนวณจากสมการ Scherrer อยู่ในช่วง 8 ถึง 10 นาโนเมตร และขึ้นกับอุณหภูมิที่ใช้ในการเผารวมทั้งปริมาณซัมมาเรียมที่ใช้เจือ ข้อมูลจากการย่อยสลายสารประกอบฟีแนนทรีนภายใต้แสงวิซิเบิลยังแสดงให้เห็นว่า อุณหภูมิที่ใช้เผาและปริมาณซัมมาเรียมที่เจือมีผลต่อประสิทธิภาพในการเร่งปฏิกิริยาของตัวเร่ง

Abstract: Sm doped TiO_2 calcined at 500 ^oC catalyzed the photodegradation reaction of 20 ppm aqueous solution of Phenanthrene under visible light with 90% conversion within 7 hours. All catalysts were prepared via sol-gel process by using Titanium(IV)bis(ethyl acetoacetato)diisopropoxide as a Ti precursor and Samarium(III)acetylacetone hydrate as Sm source. Sm doped TiO_2 was calcined at various temperatures from 400 ^oC to 600 ^oC and all prepared catalysts were characterized by XRD and Raman spectroscopy. The results suggested that Sm doped TiO_2 catalyst remained in anatase phase. The particle sizes calculated by Scherrer's equation were in the range of 8-10 nm, depended on calcination temperature and amount of Sm on doping. The condition for preparing catalysts has effect on activities of catalyst in photodegradation reaction of Phenanthrene.

Introduction: Polycyclic aromatic hydrocarbons (PAHs) are widely well-known as toxicant organic compounds in environment, consisting of two or more fused benzene rings in linear, angular or cluster arrangement. PAHs are usually produced naturally by combustion processes, e.g. forest fires, volcanic activity and anthropogenically via industrial processes, particularly the combustion of fossil fuels for heating, power and transport. Many kinds of PAHs are strongly considered to be possible or probable human carcinogenic. Due to their properties, chronic health effect and carcinogenicity, microbial recalcitrance, high bioaccumulation potential and low removal efficiency in treatment process [2]. Therefore, to study about how to remove or degrade these toxicant compounds is necessary.

Titania (TiO_2) is an effective photocatalyst that widely uses for degradation of many organic compounds. Due to its good properties such as mechanical, thermal and anticorrosive properties, therefore its can be use as effective catalyst for oxidation or photodecomposition reaction [1, 2]. However, there is disadvantage of TiO_2, high band gap energy, which limits its wide application in the visible light range also the charge carrier recombination and phase transfer occurs very fast, as a consequence, its photocatalytic properties is limited.

There were many reports that the doping of various transition metals can effectively modify the phase transition from anatase to rutile phase. The crystallize size of doped catalyst may also decrease, then it has more effective properties as a consequence [1]. This research studies the effect of doping Sm on the photocatalytic activities of TiO_2. Sm doped TiO_2 was prepared by sol-gel technique, which is a simple method. Prepared catalyst has high homogeneity, small particle size and high surface area. In addition, its low temperature treatment and low cost. Synthesized Sm doped TiO_2 catalyst was used to studies the photodegradation of PAHs such as Phenanthrene in visible light. In this work, we characterize and report the photocatalytic properties of various Sm doped TiO_2 catalyst. Include, compare theirs ability for photodegradation of Phenanthrene between undoped and doped catalyst with different percentage of Sm on doping.

Methodology: The Sol-gel synthesized TiO_2 doped Sm was prepared from Titanium(IV)bis (ethylacetoacetato) diisopropoxide (A.R.grade, Aldrich) and Samarium(III)acetylacetonate hydrate consist of deionized water and ethylene glycol under constant magnetic stirring until gel was formed. The gel was calcined at various temperatures from 400 to 600 ^{o}C for 1 hour to obtain the desired nanocatalyst.

To determine the crystal phase composition and structure, X-ray diffraction (XRD) was carried out at room temperature using a Philips PW 1830 diffractometer with $CuK\alpha_1$ radiation (k = 1.54056 A^{o}). To observe and confirm the crystal structure, Raman spectroscopy was involved using Renishaw Raman Imaging Microscope as a Raman spectrometer.

In general, the photodegradation experiment was carried out in a fixed bed type photocatalytic reactor. Irradiation was carried out using Xe arc lamp adjust at 90W. The incident visible radiation from this lamp was filtered to eliminated light in the UV and IR region using glass lens. Reaction was set up by adding 0.1g of catalyst into 125 ml of 20 ppm Phenanthrene solution. The solution was stirred in the dark for 1 hour after the addition of catalyst. After that the visible light was activated, 5 ml of sample was withdrawn every 30 min intervals for analysis of the undegraded Phenanthrene in the solution via UV-Vis spectrophotometer (Perkin Elmer Lamda35) at wavelength 251 nm.

Results, Discussion and Conclusion: Figure 1 shows the XRD patterns of TiO_2, Sm_xO_y and various Sm doped TiO_2 catalysts. The XRD peaks of pure TiO_2 at 2Θ = 25.17^{o}, 37.77^{o}, 48.03^{o}, 55.28^{o} and 62.56^{o} indicated the presence of TiO_2 in anatase phase. Sm doped TiO_2 also showed the same peaks indicated that TiO_2 was also in anatase phase. Additionally, comparison between doped and undoped TiO_2, the relative intensity of major peak at $2\Theta = 25.17^{o}$ decreased significantly in doped TiO_2, indicated that Sm doping inhibits the phase transformation from amorphous to anatase in solid structure, leading to higher thermal stability. The result also shows that the calcination temperature has effect on structure of the prepared catalyst. The catalysts which were calcined at temperature 400°C – 600°C were in anatase phase. The crystallinity of the catalyst was higher with the increasing in calcination temperature .

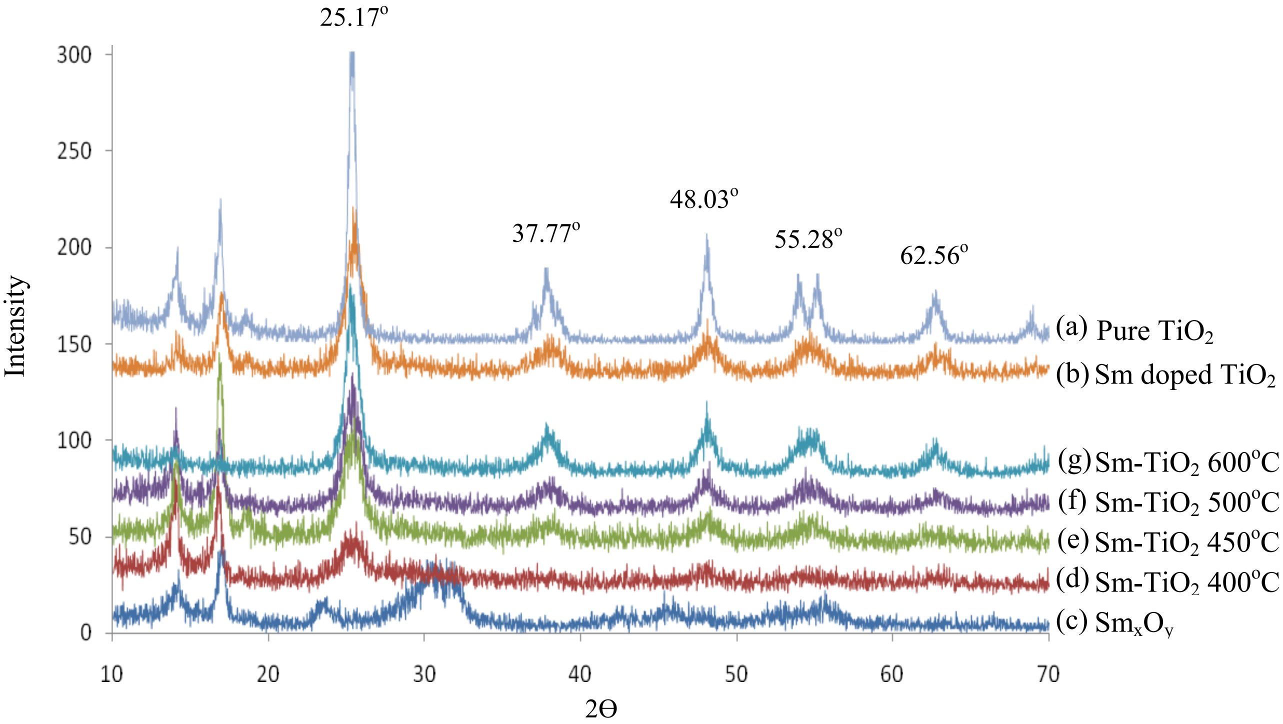

Figure 1 X-ray diffractogram of (a) undoped TiO_2, (b) Sm doped TiO_2, (c) Sm_xO_y, (d) Sm doped TiO_2 calcined at 400°C, (e) Sm doped TiO_2 calcined at 450°C, (f) Sm doped TiO_2 calcined at 500°C and (g) Sm doped TiO_2 calcined at 600°C.

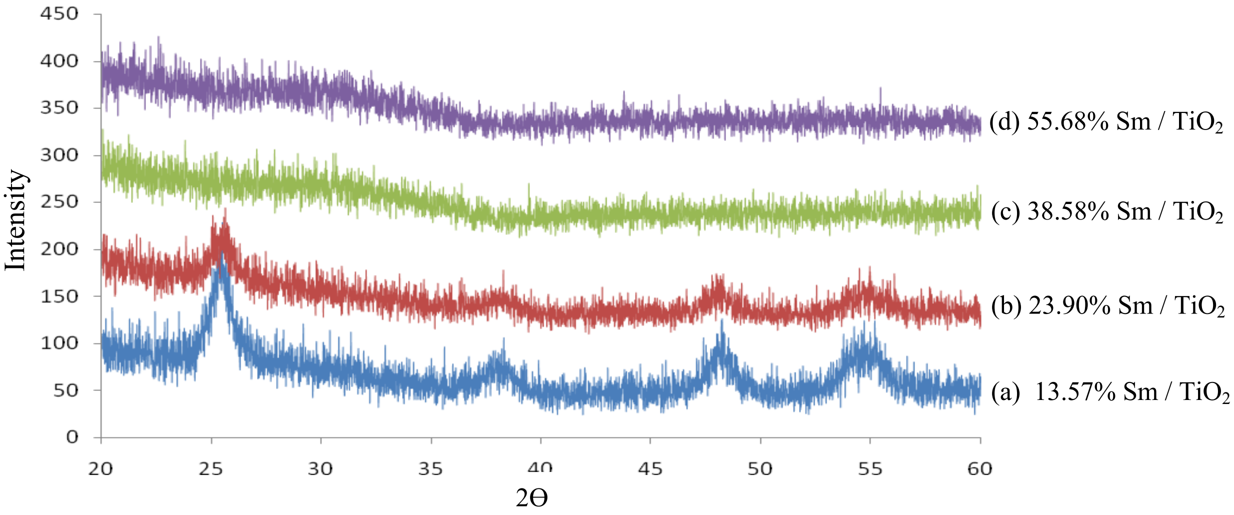

Figure 2 X-ray diffractogram of TiO_2 dope with various amount of %wt Sm loaded. (a) 13.57% Sm, (b) 23.90% Sm, (c) 38.58% Sm and (d) 55.68% Sm, all catalysts were calcined at 500°C in the same preparing condition.

Table 1 Crystal parameters data of pure TiO_2 and Sm doped TiO_2 with various % loaded of Sm calcined at 400-600 °C for 2 hrs.

Catalyst	**Calcination Temp °C**	**%wt of Sm doped**	**$\%X_A$***	**$\%X_R$***	**Diffraction Angle 2Θ**	**Crystallize size * nm**
Ti	500	0	98.30	1.70	25.31	16.3368
Ti + Sm	400	13.57	51.31	48.69	25.59	8.4772
Ti + Sm	450	13.57	79.54	20.46	25.99	8.5059
Ti + Sm	500	13.57	85.36	14.64	25.35	8.7987
Ti + Sm	600	13.57	86.71	13.28	25.19	10.4609
Ti + Sm	500	13.57	70.96	29.04	25.46	9.9813
Ti + Sm	500	23.90	67.40	32.60	25.14	8.5596

* $\%X_A$ calculate from equation $\% X_A = 100 / (1+1.265\, I_R/I_A)$

I_A is intensity of anatase peak at $2\Theta = 25.25$

I_R is intensity of rutile peak at $2\Theta = 27.42$

* Crystallize size calculate from Scherrer formula $L = K\lambda / \beta\cos\Theta$

($K = 0.9$ $\lambda = 0.1542$ nm β = the linewidth at half-maximum height)

Figure 2 shows the XRD patterns of Sm doped TiO_2 with various amount of Sm loaded. The XRD results of 13.57% and 23.90% Sm doped show that catalysts presence in anatase phase. Higher amount of %Sm shows broad peaks of Samaria indicated that these catalysts were amorphous and Sm species dispersed on their surface.

Table 1 shows that crystallize size of prepared Sm doped TiO_2 was smaller than undoped. And also showed the ratio of anatase to rutile of prepared catalyst can be calculated following by Liqiang's equation [4]. Amount of Sm doped also effect to crystallize size and ratio of anatase to rutile in catalyst structure. More amount of Sm doped gave smaller crystallize size and decrease in percentage of anatase. This indicates that Sm ion could hinder the increase of crystallize size during calcinations. Additionally, at the calcination temperature of 500°C gave higher percentage of anatase than lower temperature. And as increasing temperature the crystallize size is slightly increase. It means that the suitable temperature for calcinations should not be lower than 500°C and should not be too higher than this temperature. Unless the crystallize size would be greater and phase transform to rutile would be occur. Decrease the activity of catalyst, as a result.

The Raman spectrum (Fig. 3) of pure TiO_2 shows characteristic peak at 386.94, 508.54 and 632.92 cm^{-1} which can be assigned to the anatase phase. The spectrum of Sm doped TiO_2 which calcined at temperature lower than 500°C gave the broad spectrum, indicated that catalyst could be amorphous solid. However, the spectra of Sm doped TiO_2 which calcined at 500 °C and 600 °C similar to pure anatase TiO_2 but slightly shifted as a result of crystal structure modification via doping [1]. Additionally, we can also indicated that Sm may incorporated into the TiO_2 structure and should be in anatase hole which can makes Ti-O bond contracted. Because there were characteristic peaks that fit to reference spectrum of TiO_2 and the slightly shifted on the anatase Ti-O peaks (386.94, 508.54 cm^{-1}) to higher frequency indicated that the Ti-O bond was shorter and stronger due to bond contraction. And there was not Sm-O peak occur in these spetra. Because the size of Sm atom was much larger than Ti atom, then Sm could not be formed bond to O atom in TiO_2 but should be incorporated into the interstitial site of the catalyst.

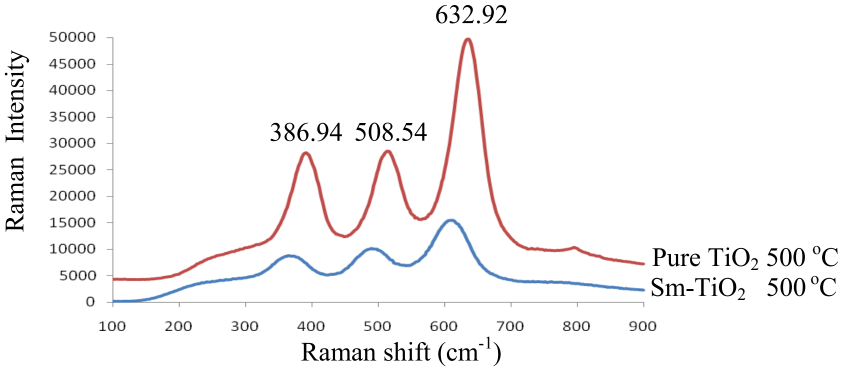

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Figure 3 Raman spectra of undoped and Sm doped TiO_2 catalyst calcined at 500°C for 2 hrs.

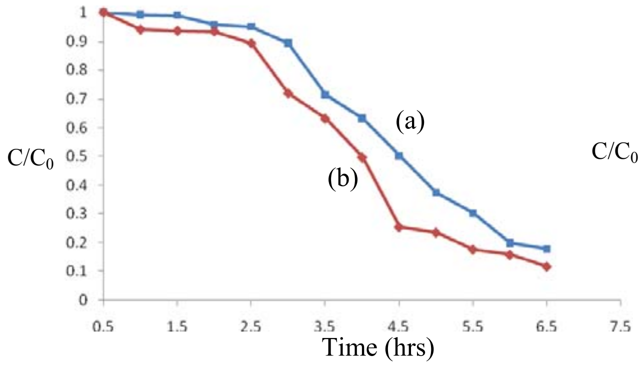

Figure 4-1 (a) Pure TiO_2 (b) Sm doped TiO_2 All samples were calcined at 500°C.

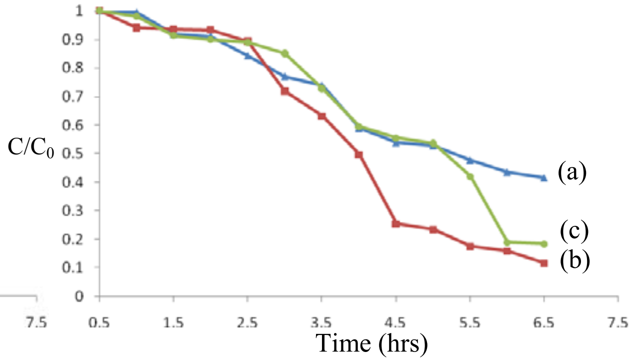

Figure 4-2 Calcination temp. (a) 450°C, (b) 500°C (c) 600°C All samples doped with 13.57% of Sm.

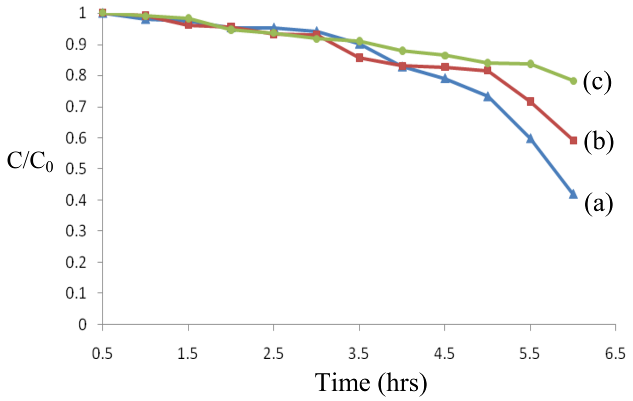

Figure 4-3 (a) 10.58% Sm/TiO_2, (b) 13.57% Sm/TiO_2 and (c) 55.68% Sm/TiO_2. All samples were calcined at 500°C.

Figure 4 Photodegradation of Phenanthrene via preparing undoped and various Sm doped TiO_2 catalyst under visible light.

The photodegradation results show in Fig. 4. The result from Fig. 4-1 indicated that Sm doped TiO_2 catalyst is more effective for degradation of Phenanthrene in optimized condition than the undoped catalyst. In case of Sm doped catalyst, the degradation rate of Phenanthrene is faster than the undoped. Propose that the rate of degradation is first order reaction. Different calcination temperatures gave different results (Fig.4-2), catalyst which calcined at 500°C is the most effective catalyst compared with calcined at 450°C and 600°C in the same amount of Sm doping. Also the different percentages of Sm loading (Fig.4-3), gave different results. As increasing amount of Sm on doping, the degradation rate was decrease. This due to exceeding of Sm loaded on catalyst, as a consequence, the catalyst was amorphous solid or Sm species dispersed on anatase surface reduce the activity of catalyst.

TiO_2 doped Sm catalyst prepared by sol-gel technique could be improved activity in photocatalysis degradation of Phenanthrene over pure TiO_2. With smaller crystallize size, higher surface area as a consequence and extended photoresponse to visible light improved as more efficient photocatalyst.

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