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IMPROVEMENT OF CO_2 PURIFYING SYSTEM BY PHOTOCATALYST FOR APPLICATION IN MICROALGAE CULTURE TECHNOLOGY

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ABSTRACT

By reactive grinding method Vanadium-doped rutile TiO_2 nanoparticle material was obtained with an average particle size of 20 - 40 nm, the Brunauer–Emmet–Teller (BET) specific surface area about 20 m^2g^{-1} and it absorbed strongly in the UV region and increased at the visible wavelength of 430 – 570 nm. This study focused on the improvement of exhaust gas treatment from coal-fired flue gas of the traditional adsorption-catalysis system (Modular System for Treating Flue Gas - MSTFG) by using the V_2O_5/TiO_2 Rutile as photocatalyst. The results showed that integrating both catalytic systems mentioned above increased the gas treatment efficiency: CO from 77 % to over 98 %, NO_x from 50 % to 93 %, SO_2 was absent as opposed to the input gas component. Also it showed that V_2O_5/TiO_2 Rutile integrated with MSTFG has got high efficiency of CO treatment, also secured the high obtained CO_2 concentration as a valuable carbon source for microagal mass culture as well as saving energy and simplifying devices.

Keywords: traditional adsorption-catalysis system, photocatalyst, integrating, coal-fired flue gas, carbon source.

1. INTRODUCTION

Process of burning coal can emit kinds of exhaust harmful gas out to atmosphere such as dust particles with minor sizes (PM), SO_x, NO_2, VOCs and a big volume of CO_2 gas, which participate in increase of the greenhouse effect, resulting in increase of the earth temperature leading to global climate change [1, 2].

Volume of CO_2 emitted in the exhaust gases was salvaged as material for different technological processes, which have been applied in many countries in the world. Eliminating

accompanied exhaust gas and isolation of CO_2 as a Carbon source for algae culture also included in the strategy mentioned above and is one of the advanced technologies in the going green of the century [3]. In Vietnam, we started using catalysts/absorbents able to convert harmful exhaust gases (NO_x, CO, C_xH_y, VOCs) into H_2O, N_2, CO_2 in order to improve cleanness of CO_2 used in *Spirulina* culture [3]. However, the catalytic system with the length of 60 cm and section of 25×25 cm^2 used in our previous study [3] showed that the exhaust gases generated from burning coal have been treated with no high efficiency: only more than 70 % CO, 90 % SO_x and 50 % NO_x at temperature of 310 – 320 °C. So, for reaching higher efficiency it is required to extend the catalytic system as with the length twofold. On the other hand, temperature for converting the harmful gases on catalyst at 320 °C consumes rather big amount of energy for operation. To overcome the two mentioned above drawbacks, we recommend the use of photocatalytic system connected in series with the current treatment system.

Photocatalyst can work in normal temperature under sun light. Thus, photocatalytic material is promising component in technology for air purifying [4], decreasing series of pollutants in water environment [5]. In the world, there were many publications on photocatalytic material having high ability of application [4, 5, 6, 7]. Results obtained in the study [5] showed that TiO_2 materials of Rutile type denatured by Vanadium able to work in visible light area with rather high efficiency: fabricated TiO_2/V_2O_5 not only well absorbs light in the ultraviolet light area but also rather highly absorbs the light with wave length of 400 – 600 nm; This material is also good catalyst for degrading methylene blue at normal light and room temperature. In this work, we fabricated TiO_2/V_2O_5 photocatalyst, tested for CO conversion reaction in order to replace the traditional catalytic system described in paper [3].

2. SUBJECT AND METHODOLOGY

2.1. Studied subject

Exhaust gases including CO_2, NO_x, SO_x, CO,...in which CO_2 generated from burning coal are removed from accompanied exhaust gases by catalytic – absorption technology.

V_2O_5/TiO_2 Rutile photocatalytic material.

2.2. Methodology and equipment

Exhaust gases were determined by equipment of MX6 and CA-6203, Testo 350-XL Emision Analyzer. Treating accompanied exhaust gases and cleaning CO_2 by traditional exhaust gas treatment modular system (EGTMS) were integrated with V_2O_5/TiO_2 photocatalytic material system.

Rutile TiO_2 was used as initial material with particle size bigger than 100 nm. Nano vanadi – doped rutile TiO_2 material was obtained by the reactive grinding method [5]. UV-Vis Absorption spectra of TiO_2 and V_2O_5/TiO_2 samples were measured by CARRY 5000 UV-Vis-NIR equipment. Specific surface area of Brunauer-Emmett-Teller (BET) of samples was determined by nitrogen physical absorption method at 77 K. Size of particles was determined Scanning Electron Microscope (SEM). Concentration of CO was determined by Landcom II machine, U.K.

3. RESULTs AND DISCUSSION

3.1. Photocatalytic material fabrication

According to the paper [5] we carried out fabrication of TiO_2 mixed with vanadium by reactive grinding method via high-energy. The optimal time for grinding samples to synthesize V_2O_5/TiO_2 was selected to be 4 hours. TiO_2 rutile and V_2O_5 in ratio 95:5 were dried at 120 °C/2 hours then was grinded by high energy mill (Spex 8000 M). This machine used two balls, including one with Φ15 mm and the other with Φ5 mm made of WCx hard steel. Mixture of 9.5g TiO_2 and 0.5g V_2O_5 was put into a hard steel container with inner volume of 50 cm^3. The obtained material after 4 milling hours was examined in structure, size (by XRD method), morphology (by SEM photo), BET surface properties, light absorption capacity (by electronic absorption spectrometry) and accessed the activity on CO into CO_2 conversion reaction.

3.2. Determination of material structure by X-ray diffraction diagram X (XRD)

Figure 1 is X-ray diffraction diagram X of initial TiO_2 and vanadium mixture material after grinding. It can be seen from the diagram, typical peaks of TiO_2 appeared in form of rutile but peaks of V_2O_5 are absent (for ground material). Typical pics of initial TiO_2 samples were higher and narrower than that of V_2O_5/TiO_2 ground after 4 hours. Thus, it can be seen that ground V_2O_5/TiO_2 particles had significantly smaller sizes compared to initial TiO_2 material.

On X-ray diffraction diagram of V_2O_5/TiO_2 samples, there were not typical peaks of Vanadium Oxide appearing. Non appearance of typical Vanadium Oxide could be due to the fact that Vanadium Oxide content was below the detectable threshold of the method or Vanadium Oxide's even desperation in the system or vanadium's existence in other forms in the crystal system of titanium oxide. This result was similar to [5]. Accordingly, in spite of non appearance of Vanadium Oxide peaks on X-ray diffraction diagram, the XAS analysis result (X-ray absorption spectrometry) indicated the existence of state of V^{4+} replacing V^{5+}, that means vanadium displacing Ti^{4+} or lying at empty position of TiO_2 structure. So it can be said that a part of vanadium existed in form of V_2O_5 evenly dispersed and a part existed in form of V^{4+} lying in TiO_2 crystal network.

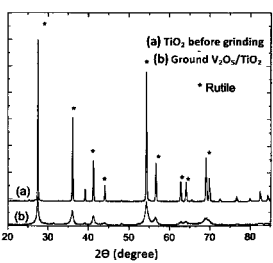
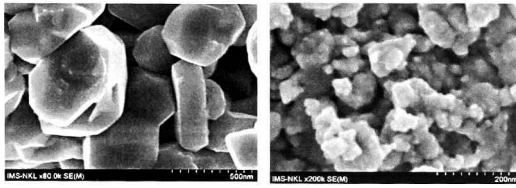


Figure 1 XRD patterns of Rutile TiO_2 before grinding (a) and ground V_2O_5/TiO_2 for 4 hours(b).

3.3. Determining morphology, particle size and the BET specific surface area

Figure 2 is SEM image of the material. We can see that TiO_2 before grinding (a) had size of 100 – 130 nm, after grinding and mixed with vanadium (b) had size of 20 - 40 nm. After determining specific surface area (BET) and comparing the typical features with the sample fabricated in paper [5] represented in Table 1, it is seen that the previously fabricated samples and the present one are rather similar. This also confirms the material fabrication process was stable.



(a) (b)

Figure 2. Scanning electron microscopy image (SEM) of Rutile TiO_2 before grinding (a) and (b) ground V_2O_5/TiO_2 for 4 hours.

Table 1. Particle size and the BET specific surface area of materials.

Samples	Grinding time (h)	Average particle size (nm)	BET (m^2/g)
TiO_2	0	100-130	1,19
V_2O_5/TiO_2	4	20-40	19,5
[5] V_2O_5/ TiO_2	4	22	20,80

3.4. UV-Vis absorption spectrum of V_2O_5/TiO_2 photocatalyst materials

Figure 3 is the light absorption spectrometry of unground TiO_2 rutile (a) and ground V_2O_5/TiO_2 after 4 hours (b). We can see that the unground TiO_2 sample absorbed light at wave length less than 420 nm, while the mixed and milled sample after 4 hours absorbed light at longer-wave length in 430 - 570 nm area. This result can be compared with some anatase TiO_2 and TiO_2 Rutile previously published of authors Anpo et. al [6] and Liu et. al [7]. Thus, obtained material had rather big nano size and specific surface area, at the same time was denatured by vanadium (be considered as the most brilliant value in the series of metals used as doping for TiO_2) promising a high activity of photo catalyst.

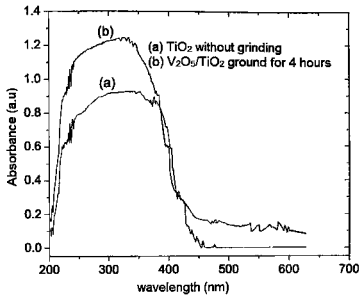


Figure 3. UV–Vis absorption spectra of Rutile TiO_2 before grinding (a) and (b) ground V_2O_5/TiO_2 for 4 hours.

3.5. The test on application of V_2O_5/TiO_2 Rutile photocatalytic material in treating exhaust gas generated from burning coal in semi-pilot scale

We carried out the test on treating exhaust gas generated from burning coal in two stages (Figure 4): 1. Initial exhaust gas was treated for the first time via a traditional catalytic system (A) – exhaust gas treatment modular system – with dimensions of 60 × 25 × 25 cm^3, operating at temperature 320 °C. Exhaust gas after being treated by the traditional catalytic system has rather high temperature will be cooled to the room temperature system (B). 2. The volume of cooled gas was treated for the second time by photocatalytic material designed by 3 rock crystal modules, each had diameter of 0.7 cm containing 1g photocatalytic material (C). The exhaust gas after the two said treatment stages was collected into gas collector (D). Concentration of gas components after each stage was determined and served for calculating the treatment efficiency of each stage.

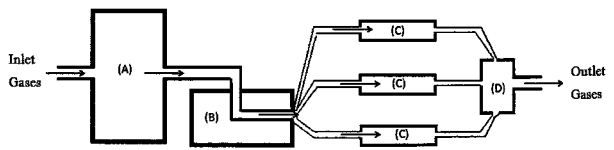


Figure 4. Diagram of the flue gas treatment from coal combustion. A: The traditional Modular system of Exhausted Gas Treatment; B: The gas cooling system at room temperature; C: Quartz tube; D: The purified gas storing system.

Table 2. Components of coal-fired flue gases inlet and oulet analysis

Components	Inlet of gases	The period after treating via traditional MEGT systems		The period after treating via photocatalyst systems	
		Concentration	Efficiency of reduction (%)	Concentration	Efficiency of reduction (%)
CO (ppm)	2000	454	77,3	38	98,1
SO_2 (ppm)	16 – 22	2	> 87,5	0	100
NO_x (ppm)	30 – 32	16	> 46,7	2	93
CO_2 (%)	4,64	6,03	-	6,47	-

Obtained results in table 2 showed that the exhaust gas generated from burning coal after going through Exhaust Gas Treatment Modular System with traditional catalyst integrated with V_2O_5/TiO_2 photocatalytic material system was very well treated: the converted CO was more than 98 %, SO_2 – 100 % and NOx – 93 %, respectively compared to the composition of the input exhaust gas. Volume of CO_2 obtained was rather high, from 4.54 % increased to more than 6.47 % quite good for microalgae culturing.

4. CONCLUSION

V_2O_5/TiO_2 photocatalytic material system was successfully fabricated with size 20 – 40 nm, BET specific surface area is of approximately 20 m^2/g. This material strongly absorbs light in both UV area and 430 – 570 nm wave length area.

V_2O_5/TiO_2 photocatalytic material was a good catalyst for CO, NO_x and SO_2 conversion process. The integration of a traditional catalytic system (A) – Exhaust Gas Treatment Modular System with V_2O_5/TiO_2 photocatalytic material system increased treatment efficiency of exhaust gases: CO from 77 % up to 98 %, NO_x from 50% up to 93 % and 100 % for SO_2 compared to the input exhaust gas composition. The rather high CO2 concentration- 6.47 %, is quite good carbon source for microalgae cultivation.

In the economical point of view, The EGTMS with traditional catalysts operating at comparatively high temperature 320 °C (Project KC08.08/11-15) intergrated with V_2O_5/TiO_2 photocatalytic material system operating at the room temperature will help to significantly reduce equipment size.

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TÓM TẮT

CẢI THIỆN HỆ THỐNG LÀM SẠCH CO_2 BẰNG XÚC TÁC QUANG NHẰM ỨNG DỤNG TRONG CÔNG NGHỆ NUÔI TẢO

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Bằng phương pháp nghiền phản ứng, vật liệu xúc tác quang Nano Vanadi – doped Rutile TiO_2 chế tạo được có kích thước 20 – 40 nm, diện tích bề mặt riêng BET gần 20 m^2/g, vật liệu hấp phụ mạnh trong vùng UV đồng thời tăng sang vùng bước sóng dài 430 – 570 nm. Bài báo này nghiên cứu khả năng cải thiện hiệu quả xử lí khí thải của Hệ Modun xử lí khí thải (HMĐXLKT) xúc tác truyền thống bằng việc kết nối thêm hệ modun sử dụng xúc tác quang V_2O_5/ TiO_2 Kết quả cho thấy việc tích hợp hai hệ xúc tác nói trên đã làm tăng hiệu quả xử lí khí CO từ 77 % lên trên 98 %, NO_x từ 50 % lên 93 % và làm sạch hoàn toàn SO_2 so với thành phần khí đầu vào. Điều này cho thấy hiệu quả của việc sử dụng hệ vật liệu xúc tác quang V_2O_5/ TiO_2 trong quá trình xử lí triệt để CO, đồng thời vẫn đảm bảo hàm lượng CO_2 thu được khá cao đáp ứng cho quá trình nuôi tảo như một nguồn cacbon giá trị, tiết kiệm được năng lượng và vận hành đơn giản.

Từ khóa: hệ thống xúc tác/ hấp phụ truyền thống, xúc tác quang, tích hợp, khí thải đốt than, nguồn cacbon.