Advanced Materials Research *Online: 2012-05-14*
ISSN: 1662-8985, Vols. 518-523, pp 579-583
doi:10.4028/www.scientific.net/AMR.518-523.579

Effect of Activated Time on the Properties of ZnO/AC Composites from Spent Catalysts

Wen JIN[1,2,4,a], Wenwen QU[1,2,3,b], Jinhui PENG[1,2,4,c], Xinhui DUAN[1,2,4,d]

[1]State Key Laboratory Breeding Base of Complex Nonferrous Metal Resources Cleaning Utilization in Yunnan Province，Kunming 650093，China

[2]Key Laboratory of Unconventional Metallurgy Education Ministry, Kunming 650093，China

[3]Faculty of Science，Kunming University of Science and Technology，Kunming 650093，China

[4]Engineering Laboratory of Applying Microwave Energy and Equipment Technology, Kunming 650093，China

[a]jinwen871212@163.com, [b]qwwen77@163.com, [c]jhpeng@kmust.edu.cn, [d]dxh1191984@yahoo.com.cn

Keywords: ZnO/AC composite materials, spent catalysts, activation time, microwave

Abstract. After being subjected to thermal treatment by microwave, a carbon-based spent catalyst from vinyl acetate synthesis has been proved to be a good precursor for the production of ZnO/activated carbon (AC) composites. Different operating activated times were found to have effect on the properties of the composites. As the activated time rises, the surface area of the activated carbon that is acting as the catalyst support increases due to the decomposition of the organic deposits that are clogging the porous structure. XRD was used to evaluate the transformation of zinc acetate to zinc oxide after thermal treatment. Both the iodine adsorption capacity and the yield of the resulting composites were calculated and SEM-EDX analysis was used to evaluate the changes in surface morphology.

Introduction

The material which is combined with carbon used as matrix and another material act as wild phase is called carbon matrix composite. The carbon matrix composite include features of three solid stuff which are metal, ceramic and organic polymer [1]. Apart from that, the carbon matrix composite also has some irreplaceable characteristics like high specific strength, high specific modulus, small density, high thermal conductivity and so on [2,3]. The carbon matrix composite has been applied to the aerospace domain, information technology, biotechnology and auto industry [4].

ZnO is one of a new wide-gap II-VI semiconductor material which is like TiO_2，CdS and SnO_2, because of high binding energy of free exciton, it can achieve laser-induced emission with high efficiency at room temperature. Therefore, ZnO is used as short wave long luminescence materials at emission of blu-ray and ultraviolet [5,6]. The application of ZnO is photodegradation of organic dye[7], photocatalytic sterilization[8] and to deal with heavy metal ions in the waste water[9]at present. However, the single zinc oxide's poor surface adsorption performance and low special surface area have reduced its photo catalytic performance.

According to the character of carbon matrix composite, if combined ZnO with activated carbon (activated carbon has tremendous surface area, pore structure and absorption of nonpolar, saturated bond and high molecular weight compound [10,11]), the composite materials will either improve photo catalytic performance of ZnO or have high chemical stability and light catalytic properties.

ZnO/AC composites may be prepared from spent catalysts used in the synthesis of vinyl acetate. The spent catalyst was attached to the zinc acetate at the surface which is known to be a good precursor for the preparation of ZnO, and the granular poriferous activated carbon used as the catalyst support. The abundance of this spent catalyst and its low cost are additional advantages that make the recycling of it an attractive alternative to its disposal by means of landfill or incineration.

This paper aimed at preparing ZnO/AC composite materials using conventional thermal treatment employ a carbon-based spent catalyst saturated with zinc acetate. The influence of different operating activation times on the adsorption capacity, yield and textural properties of the final photocatalyst was studied.

Materials and methods

Materials.

The spent catalysts containing zinc acetate were used for vinyl acetate production from the chemical plant in YunNan province of China. Table 1 is the chemical composition of the spent catalysts. Before experiment, all the samples were washed several times with distilled water until pH value is neutral, then dried in a drying cabinet at 150˚C until reaching a stable weight, and stored in a desiccator as standby.

Table 1 Chemical composition of the raw material

Element	C	Zn	O	Al	Si	Ca	P
Wt%	77.31	10.71	7.60	0.39	0.49	0.51	2.99

Preparation procedure.

A amount of spent catalyst (20g) was weighed and then placed inside a tube type microwave reactor cavity, and heated under N_2 atmosphere at a rate of 20˚C /min until the final temperature 800˚C was reached in each experiment. A 3000WMWat the frequency of 2450 MHz was used in this study. The residence time, at which the samples were kept at the certain operating temperature, was range 10 min from 40min. Once the thermal treatments completed, the final products were dried at 120˚C for 2h.

Analysis.

Adsorption capacity is the most important characteristic to judge pore structure of activated carbon. Iodine adsorption capacity provides an indication of the adsorption ability of activated carbon to small molecular compounds. Iodine adsorption capacity was tested for the prepared samples according to the National Standard Testing Methods of PR China (GB/T12496.8-1999).

The yield of products is an important parameter. The final product yield was calculated based on the following Eq.1:

$$\text{yield}\ (\%) = \frac{m}{m_0} \times 100\% \tag{1}$$

Where m and m_0 are the dry weight of new product (g) and dry weight of spent catalyst (g), respectively[12].

The resulting materials were identified by powder X-ray diffraction using a Japan D/max-3B Advance diffractometer equipped with Cu Kα radiation (40kV, 40mA). Before testing, the sample should be grinded to become a powdery form (200mesh sieve), then was placed into a sample holder. Once the diffraction data had been collected, the intensity of the diffraction peaks was compared amongst themselves. From the XRD patterns of the samples, the grain diameter, was calculated using Scherrer's equation[13] (Eq.2):

$$D = \frac{K\lambda}{(\beta_c - \beta_s)\cos\theta} \tag{2}$$

where D is the crystallite size of the catalyst, λ is the wavelength of X-ray diffraction, βc and βs are the FWHM of the catalyst and the standard, respectively. θ is the Bragg's angle and k is coefficient. When calculate crystal，k is 0.89 generally.

The microstructure of spent catalysts before the thermal process and ZnO/AC composites were measured by SEM-EDX (Holland XL30 ESEM-TMP).The specific surface areas and pore volume distributions of the catalysts were characterized by measuring the isothermal adsorption of N2 at 77K on a Quanta Autosorb-1.

Results and Discussion

Iodine adsorption capacity and yield.

Fig.1 shows the influence of activation time on iodine number and the yield of the ZnO/AC composites. It can be seen from the figure that in both cases an increase in activation time results in higher iodine numbers and lower yields. Along with the increase of activation time, more and more organic compounds and zinc acetate start to decompose, that in turn leads to a lower yield. Therefore, some of the blocked pores reopen, and the iodine adsorption capacity of the final composites increases gradually, which is in agreement with the relationship between the pore size distribution and the iodine number previously reported [14].

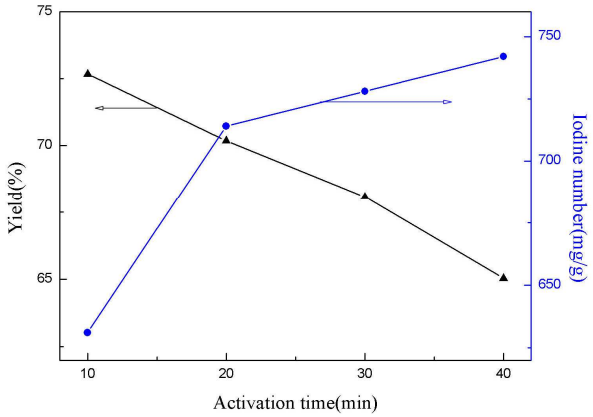


Fig.1 Effect of activation time on iodine adsorption capacity and yield

X-Ray Diffraction analysis.

XRD analyses were carried out in order to study the chemical composition of the samples. After thermal treatment with different activation times at 800˚C, the zinc acetate tends to be decomposed to produce ZnO increasingly. The XRD patterns of the ZnO/AC composites (Fig.2) show a series of zinc oxide diffraction peaks.

From the Fig.2, we can see that the prepared composite materials show ten Sharp diffraction peak, which correspond to the characteristic peak of (100), (002), (101), (102), (110), (103), (112), (201), (203), (211) of hexagonal wurtzite type ZnO (JCPDSNo.36-1451) respectively. The diffraction peaks gradually weaken with the reduction of activation time. When activation time reduces to 10min, the diffraction peaks of zinc oxide do not appear, indicating that the zinc acetates could not decompose timely. As the activating time increased from 10min to 40min, zinc oxide diffraction peaks become narrower and higher as a consequence of crystal growth.Larger sizes and better qualities of the ZnO crystals are formed. The average grain diameter of ZnO was measured by Scherrer's equation and it was found that their size increased from 32.9nm to 59.1nm with the increase of activating time.

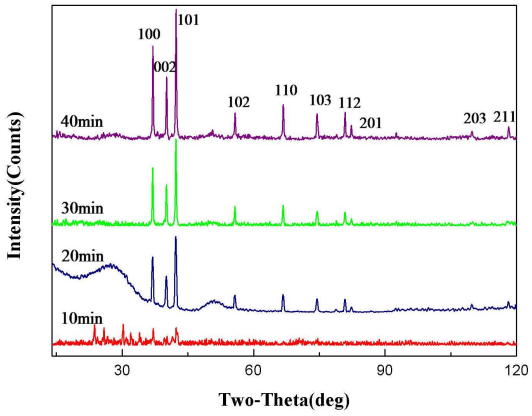


Fig. 2 XRD image of composite materials at 800˚C with different activation times

Surface area and pore size distribution.

The estimation of nitrogen adsorption isotherm is shown Fig.3. It can be seen from the figure that the N_2 adsorbed volume of the ZnO/AC composites with activation time ranging from 10 to 40min are higher than that of the spent catalyst. Moreover, the composites present a high adsorption capacity at relatively low pressures, which indicates the presence of a well-developed microporous structure. The specific surface area accessible to N_2 determined by the BET equation of ZnO/AC composites is from 566m^2/g to 914 m^2/g when activation time is from 10min to 40min. And the highest specific surface area of ZnO/AC composites is 4.1 times higher than the spent catalyst. The total pore volume of products with 40min activation time is 0.61 cc/g while the spent catalysts are 0.14cc/g. The explanation is that the block pores are gradually reopened along with more new pores formed as the activation time increasing.

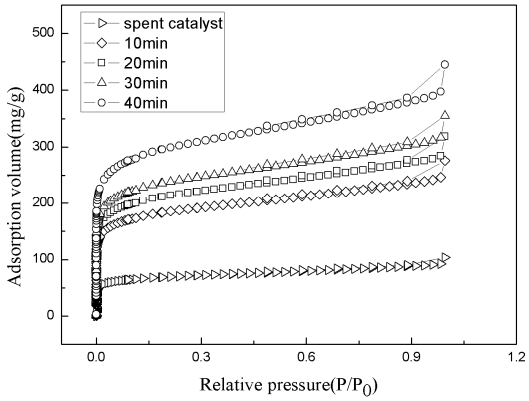
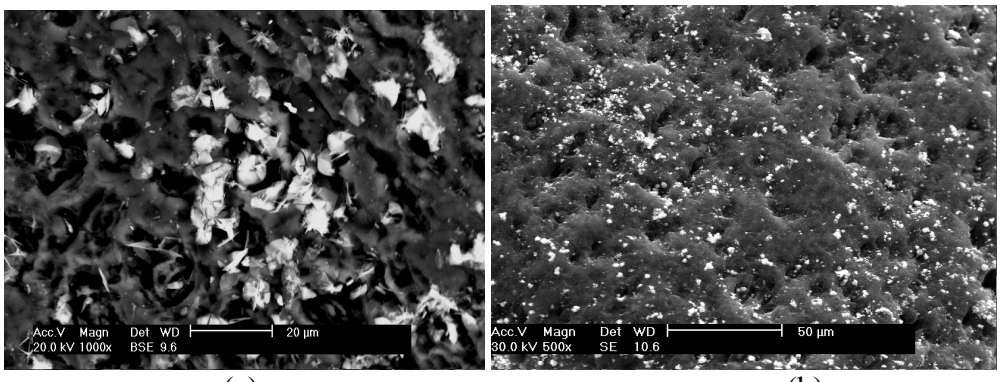


Fig. 3 Nitrogen adsorption isotherm of the spent catalysts and materials with different times

SEM-EDX analysis.

Fig. 4 show the SEM images of spent catalyst (a) and the ZnO/AC composites treated at 800℃ with activation time of 40min (b). It can be seen that before thermal treatment, the hole of the spent activated carbon has been blocked by many white substance which may includes some organic deposits and zinc acetate. After thermal heating, the organic deposits and zinc acetate were decomposed. ZnO particles well adhered and more uniformly dispersed on the surface of AC. And as the activating time increases, the amount of white ZnO particles coating on the AC also increases. EDX analysis of the composite activating 40min (Fig.5) further proved that the white particles really correspond to zinc and oxygen element.



(a) (b)

Fig.4 SEM image of spent catalysts (a) and ZnO/AC composite activating 40min(b)

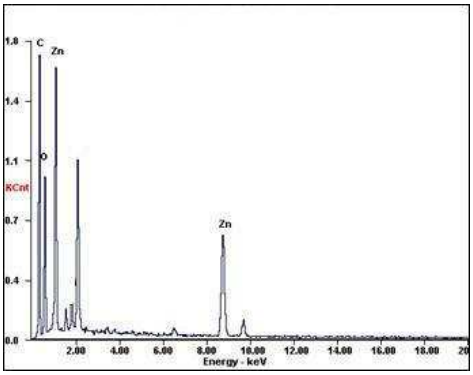


Fig.5 The EDS image of Fig.4(b)

Conclusion

In this paper, a spent catalyst from vinyl acetate synthesis subjected to microwave thermal treatment under N_2 atmosphere, has been demonstrated to be a good precursor for the production of ZnO/AC composites. After the thermal treatment, the zinc acetate present in the spent catalyst is decomposed into ZnO, which is known as a good photocatalyst as TiO_2. The influence of activation time was also studied and was shown to have obvious effects on the properties of final materials. As the activation time of the thermal treatment rises, the product presents a higher surface area as a result of the increased porosity. The excellent adsorption properties make them suitable as potential adsorbents to the removal of various toxic pollutants.

Acknowledgements

This work was financially supported by the National Science Foundation of China (No. 51004059) and the Natural Science Fund in YunNan province of China (No. 14051157).

References

[1] Z. Qian: *Carbon technology* (Metallurgical technology press, Beijing 1996).

[2] L.J. Guo, H.J. Li, H. Xue, Z.H. Shi, K.Z. Li: New Carbon Materials. Vol. 19 (2004), p.119.In Chinese

[3] J.D.Buckley : Am Ceram Soc Bull. Vol. 67 (1988), p. 364

[4] F. He, M.Z.Wang: *Carbon fibers and composites* (Science press, Beijing 1995)

[5] M. Bär, J. Reichardt, A. Grimm, I. Kötschau, I. Lauermann, K. Rahne: Journal of Applied Physics. Vol. 98 (2005), p. 053702-1

[6] Z.C. Jin ,I. Hamberg and C.G. Granqvist : Journal of Applied Physics. Vol. 64 (1988), p.5117

[7] N. Sobana, M. Swaminathan: Solar Energy Materials&Solar Cells. Vol. 91 (2007), p.727

[8] J.Sawai , H.Igarashi, A.Hashimoto: Journal of chemical engineering of Japan.Vol. 28 (1995), p.288

[9] Y. Kikuchi ,Q.R. Qian and M. Machida: Carbon. Vol. 44 (2006), p.195

[10] Z.F. Dou, B.Y. Yao: Fuel Processing Technology. Vol.92(2011), p.394. In Chinese

[11] D.E. Bleiker, G. Farquhar, E. Mcbean: Waste Management &Research. Vol.13 (1995), p.533

[12] Z.Y. Zhang, H. Niu, Y. Fernández, J.A. Menéndez, J.H. Peng, Z.B. Zhang, L.B. Zhang, X.H.Duan: Journal of the Taiwan Institute of Chemical Engineers.Vol.41(2010), p.617

[13] N. Sobana, M. Muruganadham, M. Swaminathan: Journal of Molecular Catalysis A: Chemical. Vol. 258(2006), p.124

[14] X.H. Duan, C. Srinivasakannan, J.H. Peng, L.B. Zhang, Z.Y. Zhang: Fuel Processing Technology.Vol.92 (2011), p.394