



Trade Science Inc.

Organic CHEMISTRY

*An Indian Journal**Full Paper*

OCAIJ, 9(3), 2013 [92-96]

Study on the catalytic behaviors of expandible graphite in the synthesis of acetic ester and propionic ester

Rui-Nian Lin, Xiu-Yan Pang*, Ming-Yan Xu, Xiaoli Hu, Xin Su, Jin-Huan Liu

College of Chemistry and Environmental Science, Hebei University, Baoding 071002 People Republic of, (CHINA)

E-mail: pxy833@163.com

ABSTRACT

The catalytic activity of the prepared expandable graphite was studied taking the synthesis of acetic ester and propionic ester as probe reaction. Expandable graphite was prepared with KMnO_4 as oxidant, H_2SO_4 as inserting reagent. And it was analyzed with expanded volume, X-ray diffraction, Energy dispersion spectrum and thermal gravimetric mass spectrum analysis. Experimental results show: expandable graphite shows better catalytic activity for the synthesis of propyl acetate, butyl acetate, ethyl propionate, propyl propionate and butyl propionate, all the ester yields are above 95%. As for acetic ether, the yield is only 50%. The ester yield increases with the increase of alcohol molecular weight and the reaction temperature. When expandable graphite is repeatedly used, its catalytic activity decreases due to the increase of mass transfer resistance, but its expansion performance is not affected. The catalysis mechanism is discussed, and expandable graphite is a good solid acid catalyst.

© 2012 Trade Science Inc. - INDIA

KEYWORDS

Expandable graphite;
Acetic ester;
Propionic ester;
Catalytic activity;
Reuse.

INTRODUCTION

Expandable graphite is a kind of new material which is prepared through intercalation reaction of non-carbon substance such as H_2SO_4 under the condition of chemical or electric chemistry oxidation^[1,2]. It is normally used as sealing material and adsorbent of organic molecules such as oil, dyes after expansion under high temperature^[3,4]. At the same time, expandable graphite can be used as solid super acid catalyst^[5]. Li prepared a kind of expandable graphite with 32 mesh natural graphite as material under the mass ratio C : KMnO_4 : H_2SO_4 : HNO_3 of 1.0 : 0.12 : 5.0 : 1.0, and studied its catalytic activity in the synthesis of ethyl acetate^[6]. A 30% ethyl acetate was reported under the condition of:

mole ratio of acetic acid to ethanol 1.0 : 1.5, mass of expandable graphite 6.0 g, reaction time 50 min, reaction temperature 50 °C. Zhou prepared an expandable graphite under the mass ratio C : KMnO_4 : H_2SO_4 of 1.0 : 0.08 : 4.0, and studied its catalytic activity in the synthesis of butyl acetate^[7]. A 98.0% butyl acetate can be gained under the condition of n (butanol) : n (acetic acid) equaled 1.0 : 1.15, mass of expandable graphite 5.59% of the total amount of reactants, reaction time 55 min. In the preparation of propionic ester, many kinds of catalysts such as cation resin^[8,9], enzyme^[10,11], molecular sieve supported organophosphonic acid (PA/NaY)^[12] have been reported. With $\text{SO}_4^{2-}/\text{TiO}_2\text{-La}_2\text{O}_3$ as heterogeneous catalyst^[13], Lv synthesized ethyl propionate, propyl propionate, butyl propionate, isobutyl

propionate, amyl propionate and isoamyl propionate with the yield of 20.9%, 64.9%, 83.6%, 69.7%, 87.5%, 83.3%, respectively.

Expandable graphite can be prepared with simple material under gentle reaction temperature, vitriol can be loaded in one step reaction, and this catalyst can easily disperse and recycle in catalyzing reaction. At same time, it has showed different catalytic activity in the preparation of acetic ester, and there is no report on application for synthesis of propionic ester. Base on this reason, in this experiment, expandable graphite was prepared with KMnO_4 as oxidant and H_2SO_4 as inserting reagent, and then its structure characteristics are detected. With the synthesis of acetic ester and propionic ester as probe reaction, its catalysis for esterification between acetic acid with alcohol, propanol, butanol and propionic acid with alcohol, propanol, butanol was studied. The influences of reaction temperature, materials ratio, polar or molecular weight of reactant on ester yields were investigated, and possible catalytic mechanism was discussed.

EXPERIMENTAL

Instruments

SX3-4-13 Muffle furnace (Tientsin, precision of temperature $\pm 0.1\%$ - 0.4% °C), WAY refractor (Shanghai, China), Y-4Q X-ray diffractometer (Dandong, China), Energy dispersive spectrum instrument EDS (Thermo NORAN Vantage DIS), NETZSCH TG209 F3 TG/MS (Germany) and FTS-40 Fourier transform infra-red spectrometer (America Biorad) were used in this experiment.

Materials and reagents

Natural graphite (C, 5092) was provided by Action Carbon CO. LTD, Baoding, China. Acetic acid, propionic acid, ethanol, propyl alcohol, butanol, H_2SO_4 (98%), KMnO_4 , Na_2CO_3 , CaCl_2 , NaCl are all analytical reagents.

Methods

(a) Preparation of expandable graphite EG

EG is prepared with 50 mesh natural graphite C, oxidant KMnO_4 and intercalation compound vitriol^[14]. The mass ratio of C to 98% vitriol and KMnO_4 is con-

trolled as 1.0 : 5.0 : 0.15. Vitriol is diluted to 75% before reaction, and the reaction lasts 30 min at room temperature. After reaction, solid sample is washed until waste-water pH reaching to 6.0-7.0. It is dipped in de-ionized water for 2.0 h, then filtrated and dried at 75~80 °C, EG product is obtained.

(b) Preparation of acetic ester and propionic ester

With a definite mole ratio, acetic acid (or propionic acid) and alcohol are added into the reactor appending stirrer and water segregator. Reaction lasts a certain time at boiling point with EG as catalyst, then the solid liquid reactant is filtrated under vacuum. Wash the filtrate with saturated solution of Na_2CO_3 , CaCl_2 , NaCl , respectively, collect the upper layer solution and distill under air pressure. The distillates are analyzed with refractor and IR, respectively. Yield of ester is calculated according to equation (1).

$$\text{Yield}\% = \left(\frac{m_{\text{ester obtained in experiment}}}{m_{\text{ester obtained in theory}}} \right) * 100\% \quad (1)$$

RESULTS AND DISCUSSION

Character of the prepared EG

(a) Expanded volume of EG

Expanded volume is an important factor to judge of the intercalation reaction of H_2SO_4 into natural graphite. A 0.300 g EG is expanded instantly at 900 °C in Muffle furnace, it turns into expanded graphite. Expanded volume is defined as the volume of expanded graphite corresponding to 1.0 gram of EG, written as mL/g. Volume of expanded graphite is detected with a measuring cup, and expanded volume of the prepared EG is detected as about 400 mL/g.

(b) X-ray spectrum of material graphite and EG

Analysis of XRD for natural graphite and EG are carried out. Two characteristic diffractive peaks with interplanar crystal spacing of 0.334 nm and 0.167 nm are observed in the spectrum of natural graphite (Figure 1). In the XRD analysis of EG (Figure 2), the interplanar crystal spacing changes to 0.342 nm and 0.172 nm, respectively. The increasing layer spaces testify new substances have inserted into graphene planes, and the intercalation molecule size is smaller than nanometer size. The lager expanded volume expandable

Full Paper

graphite possesses, the higher dosage of H_2SO_4 it holds.

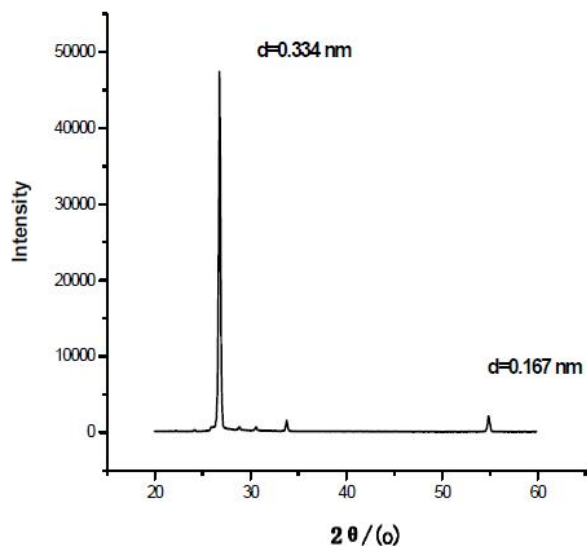


Figure 1 : XRD of natural graphite

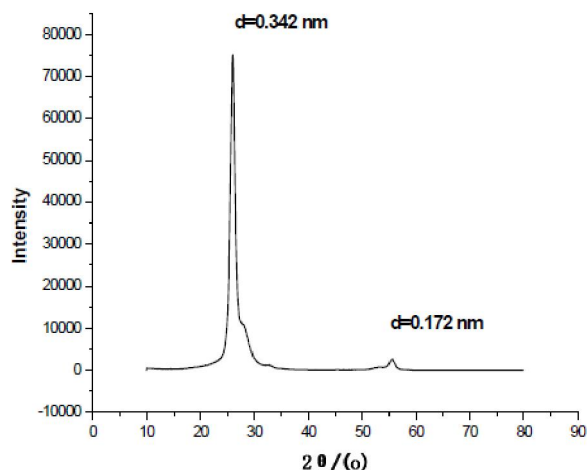
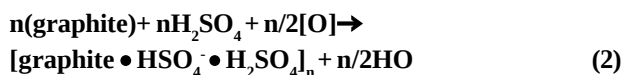


Figure 2 : XRD of EG

(c) TG-MS analysis

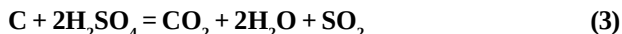
Graphite crystal has graphene planes structure. The force between graphene planes molecules is Van Der Waals force. So graphite can incorporate a wide range of intercalate guests between graphene sheets to form graphite intercalation compounds (GICs). When graphite is oxidized, it will form carbonic cation, and then accept anionic intercalates. When vitriol is used as intercalation substance, the reaction (2) might happen^[15].



[O] represents oxidant; $[\text{graphite} \cdot \text{HSO}_4^- \cdot \text{H}_2\text{SO}_4]_n$ represents graphite sulfate.

Duquesne *et al* studied weights lose and gas release during the thermal decomposition of EG^[15], and

give the reaction (3) according to experiment results.



In this experiment, TG-MS analysis is carried out for the prepared EG under the condition of N_2 ambience and a heating rate of 20.0 K/min. Through the results showed in Figure 3 we can conclude that there are SO_2 released when the temperature is above 400 °C, and another obvious lose of weight is at 700 °C. The detected results are consistent with equation (2) and (3), and it testifies that HSO_4^- or H_2SO_4 is loaded into graphene planes. Through oxidation and intercalation reaction, EG solid acid loaded with HSO_4^- or H_2SO_4 is simply synthesized.

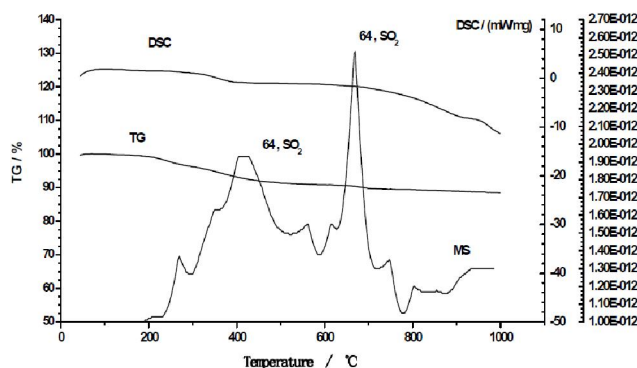


Figure 3 : TG-MS of EG

(d) Energy dispersion spectrum EDS analysis of EG

Figure 4 and 5 are results of EDS for natural graphite and the prepared EG. EG gives a relative higher intensity of S than that of natural graphite. The results indirectly testify the intercalation of HSO_4^- or H_2SO_4 .

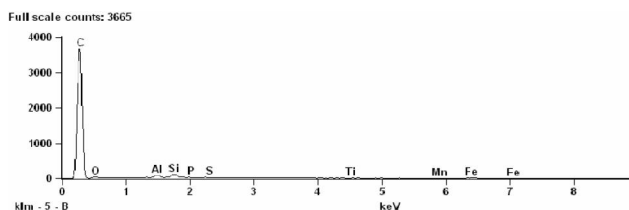


Figure 4 : EDS of natural graphite

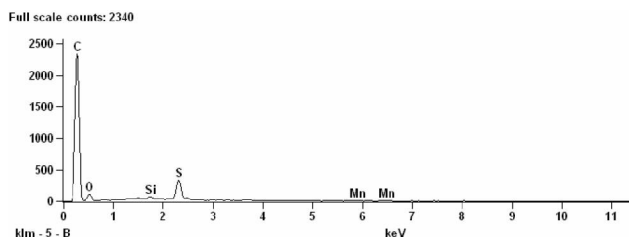


Figure 5 : EDS of EG

Optimizing of esterification reaction

To investigate the catalytic activity of the prepared EG, esterification reactions under different mole ratio of alcohol to acid, amount of EG, reaction temperature and reaction time are carried out. We gain the feasible conditions to synthesize acetic ester and propionic ester, and the results are listed in TABLE 1.

TABLE 1 : Results and condition of the synthesis of acetic ester and propionic ester

Ester	Alcohol : Acid mol/mol	EG dosage / %	Temperature / °C	Reaction time / h	Yield of ester %
Acetic ether	1.5:1.0	7.5	85	1.5	51.6
Propyl acetate	2.0:1.0	8.0	96	1.0	95.9
Butyl acetate	1.6:1.0	9.0	120	1.0	98.2
Ethyl propionate	2.2:1.0	8.0	98	0.75	97.6
Propyl propionate	2.0:1.0	8.0	101	1.0	97.2
Butyl propionate	2.0:1.0	9.0	102	0.9	96.1

Catalytic activity analysis of EG

Take the synthesis of acetic ester and propionic ester as probe reaction, the catalytic activity of EG can be analyzed according to the results listed in TABLE 1. Under the catalysis of EG, the yields of acetic ether, propyl acetate, butyl acetate, ethyl propionate, propyl propionate and butyl propionate are 51.5%, 95.9%, 98.2%, 97.6%, 97.2% and 96.1%, respectively. Except for acetic ether, yields of other acetic ester and propionic ester are all above 95%, which are obviously higher than the yields in the catalysis of $\text{SO}_4^{2-}/\text{TiO}_2\text{-La}_2\text{O}_3$ [13]. At the same time, mole ratios of alcohol to acid are above 1.5:1.0, the dosage of EG is in the range of 7.5%~9.0%, reaction temperatures are all above 95 °C (except for acetic ether), reaction times are less than 1.5 h. And the most important is that preparation method of EG is very simple, the used reactants are cheap, and the catalyst can be separated from reaction product with filtration.

About water-carrying reagent

Water-carrying reagent is in favor of ester yield due to separation and formation azeotrope with water produced in reaction. The normally used reagent is cyclohexane, the boiling point of azeotrope is 68.95 °C when it consists of 8.4% water and 91.6% of cyclohexane [16]. When reaction is kept at 68.95 °C, it would not only decrease reaction rate, but also consume a large amount

of heat energy during distillation owing to the addition of vast cyclohexane. In ester reaction with EG as catalyst, the feasible mole ratios of alcohol to acid are all above 1.5:1.0, the superfluous alcohol would play the role of carrying water. So no additional water-carrying reagent is needed.

Reuse of EG

EG shows better activity for the tested ester reaction, so its reuse is carried out under the mentioned reaction condition. Before reuse, the catalyst is treated with vacuum filtration and dryness at 75~80 °C. As showed in TABLE 2, these yields are all decrease with the increase of EG using frequency. The results illuminate catalytic activity of EG decreases evidently with using frequency, and this might be caused by the change of EG grain brim structure. The increasing solid phase mass transfer resistance causes the decrease of total reaction rate and ester yield corresponding to definite reaction time. But detection results of expanded volume of these reused EGs illuminate that EG expanded volume has no obvious change (The expanded volume is 400 mL/g before used in the reaction, it's 390~400 mL/g after the catalysis), and the catalytic reaction has no influence on expansion capacity of EG.

TABLE 2 : The catalytic activity of EG in repeated use

Ester / Repeat time	1	2	3
Acetic ether	51.6	46.0	29.0
Propyl acetate	96.0	75.0	60.0
Butyl acetate	97.5	86.6	61.2
Ethyl propionate	97.6	76.5	52.4
Propyl propionate	97.2	78.7	54.6
Butyl propionate	96.1	77.7	51.6

Catalytic mechanism analysis

EG shows better catalytic activity in esterification reaction, yields of acetic ester and propionic ester are all above 95% except for acetic ether. Possible catalytic mechanism might be:

In the preparation of EG, graphite carbon cation will produce under oxidation of oxidant such as KMnO_4 , and then strong acid or its anion like H_2SO_4 or HSO_4^- will intercalate the graphene planes as showed in equation (2). H_2SO_4 or HSO_4^- is fixed and the acidity is enhanced due to the electrostatic effect. In reaction,

Full Paper

acid and alcohol diffuse into graphene planes from liquid phase, and esterification occurs under the catalysis of H_2SO_4 or HSO_4^- . Natural graphite and the prepared EG are lipophilic and with weak polarity, so organic molecules with large molecular weight will have stronger affinity than the smaller one, and the former can easily diffuse into graphene planes and give high ester yield. As for ethanol, high molecule polarity and low reaction temperature (85°C) with acetic acid cause the lower diffuse speed and yield than other alcohol. While, in the synthesis of ethyl propionate, the improved reaction temperature of 98°C intensifies the esterification between ethanol and propionic acid, and then increases the yield. EG grain brim structure will change gradually in reaction, and it will increase solid phase mass transfer resistance then cause the decrease of ester yield.

CONCLUSIONS

Feasible conditions to prepare acetic ester and propionic ester with the prepared EG as catalyst are gained. EG shows better catalytic activity for these ester reaction, and its catalytic activity increases with the increase of alcohol molecular weight and reaction temperature. When it is repeatedly used, the catalytic activity lowers significantly, but the expansion performance is not affected. The main influence factors of EG catalytic activity are alcohol molecular weight, reaction temperature and reuse frequency.

ACKNOWLEDGEMENTS

This study was supported by Lab Opening Fund Project of Hebei University (2012018) and Doctor Foundation of Hebei province Education Office (China, No.B2004402). We gratefully acknowledge their support during the study.

REFERENCES

- [1] M.L.Xue, Y.L.Yu, Z.H.Ren, J.S.Zhang; *Fine Chem.*, **19**, 567 (2002).
- [2] X.L.Chen, K.M.Song, J.H.Li; *Chinese Carbon*, **34**, 1599 (1996).
- [3] F.Y.Kang, Y.P.Zhang, H.Zhao, H.L.Wang, L.L.Wang, W.C.Shen, M.Inagaki; *New Carbon Mater.*, **18**, 161 (2003).
- [4] X.Y.Pang, R.N.Lin; *Asian J.Chem.*, **22**, 4469 (2010).
- [5] T.S.Jin, Y.R.Ma, T.S.Li; *Indian J.Chem.*, **B38**, 109 (1999).
- [6] Y.F.Li, Z.Y.Wang, Q.Lai, G.Q.Liu; *Ind.Catal.*, **15**, 24 (2007).
- [7] Y.C.Zhou, X.J.Liu, L.K.Meng; *Chem.Prod. Technol.*, **10**, 21 (2003).
- [8] S.H.Ali, A.Tarakmah, S.Q.Merchant, T.Al-Sahhaf; *Chem.Eng.Sci.*, **62**, 3197 (2007).
- [9] E.Ameri, A.Moheb, S.Roodpeyma; *Chem.Eng.J.*, **162**, 355 (2010).
- [10] Q.Wu, M.Wang, Z.C.Chen, D.S.Lu, X.F.Lin; *Enzyme and Micro.Technol.*, **39**, 1258 (2006).
- [11] R.B.Salah, H.Ghamghui, N.Miled, H.Mejdoub, Y.Gargouri; *J.Biosci.Bioeng.*, **103**, 368 (2007).
- [12] Z.H.Zhao; *J.Molecular Catal.A: Chem.*, **154**, 131 (2000).
- [13] B.L.Lv, W.L.Tong; *Fragrance Flavor and Cosmetic*, **4**, 16 (2004).
- [14] X.Y.Pang, J.H.Liu; *Asian J.Chem.*, **22**, 3014 (2010).
- [15] S.Duquesne, M.L.Bras, S.Bourbigot; *Fire and Mater.*, **27**, 103 (2003).
- [16] L.X.Cheng; *Solvent handbook*, 3rd Edition, Chemical Industry Publishing House; Beijing, (2002).