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Preparation and Application of Intercalated Zinc Oxide Carbon Molecular Sieves

Mya Thuzar[1], Nyunt Wynn[2] and Khin Mar Tun[3]

Abstract

Synthetic carbon molecular sieves (CMS) have been prepared by pyrolysis of polyvinyl chloride (PVC) at different temperatures. Pyrolysis of PVC at different temperatures showed polymer derived carbon was formed. Only at the optimum temperature of 900°C, a thermally stable CMS with a yield of 3.03% was found to be produced. It was also characterized for its molecular sieves character by EDXRF, FT-IR, XRD, SEM, TGA and DSC (thermal analyses). The thermal stability of carbon molecular sieves was confirmed by TGA and DSC. FT-IR, XRD,SEM indicates the semi-crystallite structure (graphitic layer) and mesoporous nature of carbon molecular sieves. The prepared carbon molecular sieves at 600°C to 900°C were tested with iodine solution, methylene blue solution and phenol solution, three of the chemical sorption tests used to characterize the nature of carbon molecular sieves. Intercalated zinc oxide carbon molecular sieves (ZnO -CMS) has been prepared by using polyvinyl chloride (PVC) derived carbon molecular sieves (CMS) and zinc oxide at various temperatures of 300°C to 900°C. It was found to be most effective in the intercalation of zinc oxide particularly at 600°C and 18.09 ± 1 % of zinc (22.5 ±1% of ZnO) was intercalated in the CMS matrix. Only at these temperatures intercalation of zinc oxide was observed to take place because of the thermal stability of CMS, particularly at 900°C. Intercalative nature of zinc oxide in the graphitic CMS was characterized by using EDXRF, XRD, SEM, TGA and DSC (thermal analyses). The intercalation of zinc oxide was revealed by XRD, SEM studies of ZnO-CMS morphology before and after acid and base treatments on the intercalated sample. The catalytic activity performances of prepared intercalation zinc oxide carbon molecular sieves (ZnO-CMS) were used in the specific and lean air catalytic oxidation of methanol to formaldehyde. The liquid product was confirmed by organic qualitative test and FT-IR spectrum. The formaldehyde content was determined by iodimetric method. It was found that 12.16% strength of formaldehyde was achieved. The use of the intercalated compound as catalyst in this organic conversion shows that the zinc oxide carbon molecular sieves as an efficient and active catalyst.

Key words: Carbon molecular sieves (CMS); pyrolysis ; intercalated zinc oxide carbon molecular sieves (ZnO-CMS); catalytic activity; catalytic oxidation; organic conversion

1. Associate Professor, Department of Chemistry, Sittway University
2. Retired Professor, Department of Chemistry, Yangon University.
3. Retired Pro-rector, Yangon Distance University.

Introduction

Carbon molecular sieves (CMS) are a special class of active carbon, having small pore size, with a sharp distribution in the range of micro pores, as compared to other activated carbons (Mieville and Robinson, 1982). It depends upon the source, the heating rate, and temperature and operation techniques. Morphology of carbon molecular sieves is quite different from those of activated carbons. Different forms of activated carbons can be produced which can consisting of micropores, mesopores as well as marcopores, depending on the source of materials and the operating temperature, resistant temperature, their activation agent, such as air or other chemically treated special gases. However, molecular sieves depend only on the source material, usually plastic, their resistance, time of heating and specially their molecular sieves temperatures. (Inagaki, 2000)

The reported molecular sieves indicated channels or tube or pipe like interstitial structure of molecular sieves. This interstitial channel can hold other compounds known as intercalated compounds. They are infact, still-voids in the interstitial of the intercalated molecular sieves. However, the intercalated substance together with their molecular sieves as support can act as catalytic convectors. Common known graphite intercalation compound is a new class of electronic material that is classified as graphite-based of the host-guest systems. They have specific structural features based on the alternating stacking of graphite and guest intercalated sheets. The electronic structures showed two-dimensioned metallic properties with a large variety features including superconductivity. (Inagaki, 1989; Website)

Experimental

General: All the chemicals used were obtained from BDH unless otherwise stated. It is comprised of zinc oxide, sodium hydroxide, hydrochloric acid, BDH charcoal, polyvinyl chloride (Kento, Japan). The following instrument were used: Thermostatic shaker (Yamaha); Energy dispersive X-ray Fluorescence Spectrometer (EDXRF), Shimadsu, EDX-700, Japan; FT-IR spectrophotometer, Perkin Elmer 1600, Shimadzu model IR-408; X-ray Diffractometer (XRD), (Rigaku), RINT 2000/PC software, Cat.No.9240 J101, Japan; Electron Probe Micro Analyzer (SEM), Model Jeol-JSM-5610 LV, JEOL Ltd, Japan; Thermo analyzer, Model Universal V2-6D TA.

Preparation of Carbon Molecular Sieves (CMS): A representative sample about 20 g (mesh size no. 60- 250) was placed in a refractory porcelain cup and sealed. It was then pyrolyzed in the box furnace at 200°C. It was cooled in a desiccator and reweighed. Similarly, samples about 20 g in sealed porcelain cups were pyrolyzed at 400 °C, 500 °C, 600 °C, 700 °C,800 °C and 900 °C. It was stored in sealed bottles and coded as CMS-600°C, CMS-700°C, CMS-800°C, CMS-900°C with respect to related carbonization temperatures of 600°C, 700°C, 800°C, 900°C, respectively. Prepared carbon molecular sieves and PVC sample, there were necessary to analyses using conventional and instrumental methods. According to the characterization of PVC sample and CMS-600°C, CMS-700°C, CMS-800°C, CMS-900°C samples were determined by EDXRF, FT-IR, XRD, SEM, TGA and DSC.

Preparation of Intercalated Compound (ZnO-CMS): About 3g of prepared CMS-900°C and 1g of pure zinc oxide (BDH) were mixed uniformly in the carbon matrix. It was placed in a previously weighed refractory porcelain cup and sealed. The porcelain cup was then placed in the furnace and slowly heated at about 300°C ± 5°C for 10 minutes. It was cooled in a desiccator and reweighed. After cooling it was washed with 2% HCl solution and filtered. It was repeatedly washed with distilled water until all the acid has been removed. It was then placed in a drying oven and heated at 105°C for 10-15 minutes and coded as 300°C- ZnO-CMS. The compound mixture was stored in a sealed bottle. Similarly other compound mixtures coded as 400°C-ZnO-CMS, 500°C-ZnO-CMS, 600°C-ZnO-CMS were prepared at the respective temperatures. The prepared compound mixture were then stored in sealed bottles. Intercalative nature of zinc oxide in the graphitic CMS was characterized by using EDXRF, XRD, SEM, TGA and DSC (thermal analyses). The intercalation of zinc oxide was revealed by XRD, SEM studies of ZnO-CMS morphology before and after acid and base treatments on the intercalated sample.

Application of ZnO-CMS as Catalyst: The catalytic activity performances of prepared intercalation zinc oxide carbon molecular sieves (ZnO-CMS) were used in the specific and leán air catalytic oxidation of methanol to formaldehyde. The formaldehyde liquid product was confirmed by organic qualitative test and FT-IR spectrum. The formaldehyde content was determined by iodimetric method.

Results and Discussion

In the preparation of carbon molecular sieves (CMS), it was found that only at optimum temperature 900°C, CMS was achieved. On a macro furnace scale, primary CMS was formed at 600°C with the percent yield of 14.30 % and at 900°C significant CMS was formed with the percent yield of 3.03 %. From the result of thermal analysis (TGA) (Figure1), the pyrolysis of PVC sample was an unstable moiety because it undergoes loss in weight at three temperature; firstly, at 281°C with the loss of 0.32%, secondly, a loss in weight of 63.68% at 445°C and finally, a loss in weight of 90% at 590°C. From 590°C, the fixed carbon achieved becomes thermally stable. CMS-900°C did not show any significant TGA thermogram, relevant to endothermic and exothermic nature. It means to point out that the CMS-900°C was thermal stable even up to 800°C. This confirmation is supported by the data from DSC thermogram, which also shows thermal stability.

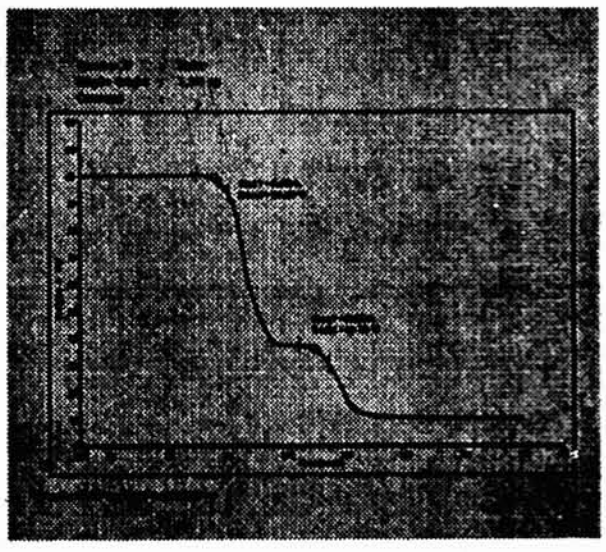

Figure 1. TGA thermograph of PVC

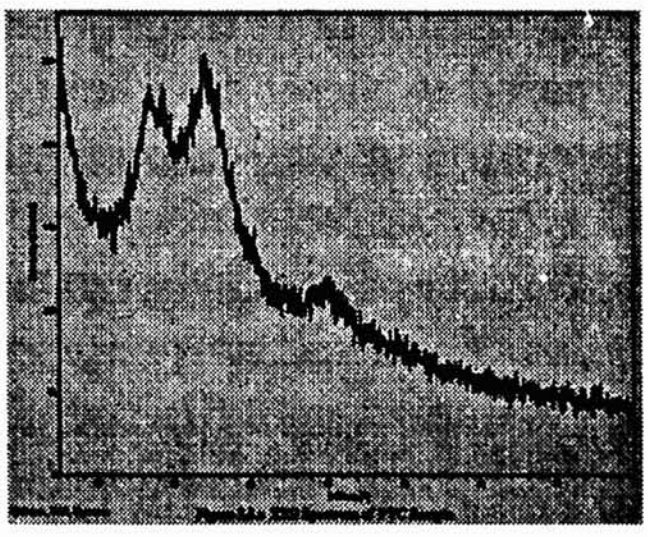

Figure 2. XRD spectrum of PVC

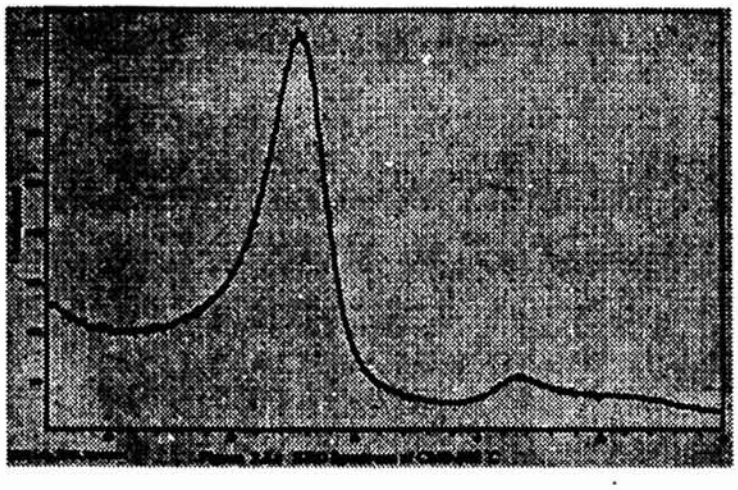

Figure 3. XRD Spectrum of CMS-900°C

From the result of XRD patterns (Figures 2and 3), the PVC sample shows the hump-like nature of XRD peak ($2\theta = 15$). It indicates the amorphous nature of carbon. The XRD patterns of CMS(s) includes a sharper peak at $2\theta = 25$, which indicated the semicrystallite nature or graphitic nature. From the result of SEM micrographs (Figure 4 and 5), in contrast, the PVC sample and the prepared CMS(s) revealed different surface morphology. The surface morphologies of CMS clearly indicate mesoporous nature of CMS. The diameter of CMS-900°C is estimated to be 5nm i.e., CMS-900°C had mesoporous nature of CMS. Therefore CMS-900°C was selected to be the represented sample in the preparation of intercalated compound.

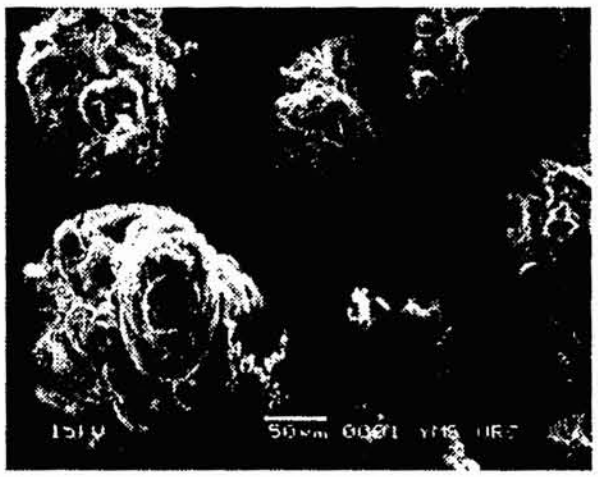

Figure 4. SEM micrograph of PVC

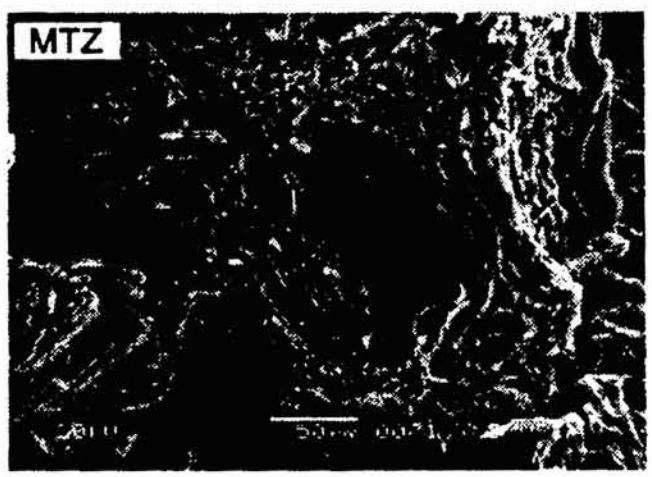

Figure 5. SEM micrograph of CMS-900°C

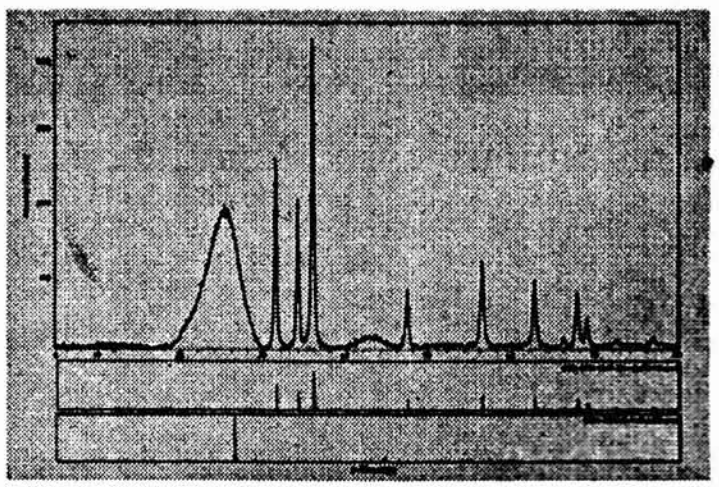

Figure 6. XRD Spectrum of 600°C-ZnO-CMS

Intercalated zinc oxide carbon molecular sieves (ZnO -CMS) has been prepared by using polyvinyl chloride (PVC) derived carbon molecular sieves (CMS) and zinc oxide at various temperatures of 300°C

to 900°C. It was found to be most effective in the intercalation of zinc oxide particularly at 600°C and 18.09 ± 1 % of zinc (22.5 ±1% of ZnO) was intercalated in the CMS matrix. Only at these temperatures intercalation of zinc oxide was observed to take place because of the thermal stability of CMS, particularly at 900°C. Furthermore, it's intercalation in CMS matrix was confirmed by XRD (Figure 6). The XRD diffractogram confirmed that ZnO was actually intercalated in the semicrystalline structure of CMS-900°C. The CMS micrograph clearly indicated porous nature whereas those of the ZnO-CMS photomicrograph (Figure 7) did not reveal the porous nature . It was possible that ZnO moieties had been intercalated in the pores of the CMS as well as being formed as layers in the semicrystalline layer of the CMS. After intercalation, the pores may have embedded in the pores. In the way, the pores may have become narrower or smaller. Intercalated ZnO in CMS-900°C were confirmed by treating with base. The SEM micrograph of 600°C-ZnO-CMS (Figure 8) showed the same morphology of the original CMS, i.e., the appearance of mesopores. The mesopores diameters of CMS are estimated to be less than10 nm.

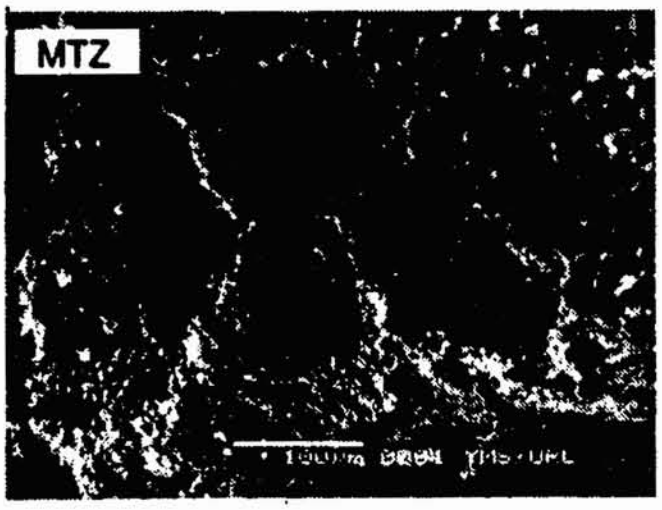

Figure 7. SEM micrograph of 600°C-ZnO-CMS treated with HCl soln.

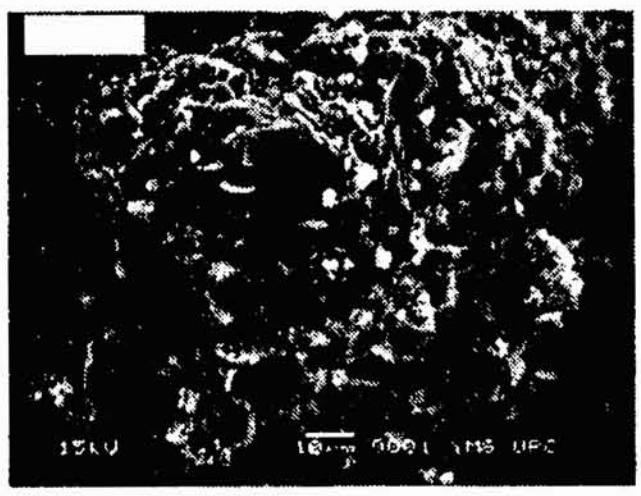

Figure 8. SEM micrograph of 600°C-ZnO-CMS treated with NaOH soln.

The prepared intercalated compound (600°C-ZnO-CMS) is used in the specific and lean air catalytic oxidation of methanol to formaldehyde. It was found that 12.16% strength of formaldehyde was achieved (Walker, 1953). In this research work, catalytic oxidation of primary alcohol to aldehyde gives a good yield.

Conclusion

The results of the investigation showed that a CMS can be prepared by pyrolysis of polyvinyl chloride (PVC) at 900 °C. Only at the optimum temperature at 900°C, significant CMS was formed with a yield of 3.03%. And then intercalated zinc oxide carbon molecular sieve (ZnO -CMS) have been prepared by using CMS-900°C and zinc oxide at temperature of 600°C. It was found to be most effective in the intercalation of zinc oxide particularly at 600°C and 18.09 ± 1 % of zinc (22.5 ± 1% of ZnO) was intercalated in the CMS matrix. The use of the prepared intercalated compound as catalyst in the specific and lean air catalytic oxidation of methanol to formaldehyde showed that the intercalated zinc oxide carbon molecular sieves as an efficient and active catalyst.

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References

Inagaki, M., (1989), Application of Graphite Intercalation Compounds, *J. Mater. Res*, 4(6), 1560

Inagaki, M., (2000), New Carbon Control of Structure and Functions, Elsevier, publishing Ltd., UK, 1-14626

Mieville, R.L., and Robinson, Ken. K., (1982), Carbon Molecular Sieves and Other Carbons, Synthesis and Applications, Mega-Carbon Company

Walker, J.F., (1953), Formaldehyde, 2nd Ed, American Chemical Society Monograph Series, New York

Website, http://www.ias.au.in/sadhana/pdf,2003Apr/Re1070, Porous Carbon, 2003