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ADSORPTION STUDIES ON CARBON MOLECULAR SIEVES (CMS) PREPARED FROM METAL IMPREGNATED COCONUT CHAR

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1. INTRODUCTION

The climate protection and life support system of the planet earth demands a safe level of CO_2 composition in the atmosphere. Due to the increased consumption of fossil fuels in power stations and use of automobile worldwide, the airborne CO_2 level has gone up which needs a continuous removal of CO_2 at the source of emission. From a detailed literature survey, a clear void is seen in the production of an efficient and economical adsorbent for CO_2. Solid amines, ion exchange resins and metal oxides for CO_2 adsorption have limited application due to their high cost and intensive equipment requirement. Zeolites, which show a good adsorption capacity for CO_2, cannot be used for CO_2 adsorption at the waste gas stream containing moisture. Also due to high cost of production and regeneration of zeolites, CMS are emerging as an alternative and effective adsorbent for CO_2.

2. THEORETICAL CONSIDERATIONS

CMS are micro porous carbons with characteristic slit shaped pore openings. The difficulty in identifying the shape of pores in CMS is due to the lack of crystallinity. CMS structure can be visualized as an ensemble of carbon layers, which is formed during the carbonization and activation of the raw material. Coke deposition via cracking of the hydrocarbons at the pore mouths is used to narrow down the pores to molecular dimension. Metal impregnation is done to introduce active catalytic centers for hydrocarbon cracking.

The gas separation in CMS is mainly due to kinetically controlled diffusion. In the case of CO_2 and CH_4 separation on CMS, fast diffusion of CO_2 occurs and the separation of the molecules is caused by the selective adsorption due to the shape and size of the molecules.

3. EXPERIMENTAL INVESTIGATION

The search for a novel and cost effective adsorbent for CO_2 adsorption leads to the coal based materials, activated carbon and carbon molecular sieves (CMS). In this project, emphasis is given to preparation of CMS from carbon precursors from coconut shell. Coconut char was obtained from Philippines. The coconut char was ball milled and sieved to 150 μ m and was then mixed with 25% by weight coal tar pitch, extruded to pellets of 3mm dia and then were dried at 90 °C for 8h in an oven.

3.1 Metal Impregnation

The metal chosen for impregnation were magnesium and calcium from alkaline earth metal group, copper, cobalt and nickel from the transition metal group. An 1 % solution of these metals prepared from their nitrate salts were used for impregnation. The oven dried extrudes were soaked in the metal solution (1 g extrude: 2 cc solution) at room temperature for 72 hours with intermittent shaking. The extrudes were then filtered out and washed 8 to 10 times with distilled water. The washed samples

were then air dried for 24 hours at room temperature and then carbonized, activated and subjected to pore narrowing by benzene cracking.

3.2 Carbonization and activation

Carbonization of the pellets was done in presence of nitrogen at 800 ^oC for 30 min and activation with CO_2 at 800 ^oC for 30 min. In the case of metal impregnated samples the carbonization time was kept 60 minutes. A rotary kiln set with a very low temp program was used for this purpose. Pore mouth tailoring of the activated pellets was done using coke deposition via. benzene cracking at 600 ^oC. In all 18 CMS samples were prepared, the list of which with the respective benzene cracking time is shown in the Table 1. The CO_2, CH_4 and N_2 adsorption data on the samples were done using a volumetric adsorption setup at 14 psi. About 1 g of the sample was used for the adsorption studies. The samples were degassed for 3 h at 250 ^oC before any adsorption experiments.

Table 1 : Sample code and time of benzene cracking of the CMS prepared
Carbonization / Activation temperature : 800 ^oC ;
Carbonization / Activation time : 30 min. (60 min. for metal impregnated CMS)

Sample code	Benzene cracking time, (min)	Sample code	Benzene cracking time, (min)	Sample code	Benzene cracking time (min)
CCCO2	0	CCCaCO2	0	CCCoCO2	0
CC20	20	CCCa30	30	CCCo30	30
CC60	60	CCCa60	60	CCCo60	60
CCMgCO2	0	CCCuCO2	0	CCNiCO2	0
CCMg30	30	CCCu30	30	CCNi30	30
CCMg60	60	CCCu60	60	CCNi60	60

4. RESULTS AND DISCUSSION

The CO_2 and CH_4 adsorption of the samples were studied using the PCT setup. Kinetic adsorption of CO_2 on the samples prepared is shown in Fig.1 and 2(a),(b). The CMS prepared from metal impregnated coconut char shows a sharp increase in the CO_2 adsorption capacity than the sample prepared from non-impregnated char. The alkaline earth metals are found to be more advantageous for CO_2 adsorption. This can be mainly due to the presence of metal oxide on the surface and metal atoms at the pore mouth. The copper, cobalt or Nickel impregnated sample also showed an improved adsorption capacity compared to the CMS sample prepared from the original coconut char. The equilibrium CO_2 adsorption capacities of the various CMS sample are tabulated in Table 2. Fig.3 shows the comparison of adsorption of CO_2 and CH_4 on the CMS prepared in this work. CMS. The uptake ratio obtained for CO_2 and CH_4 along with the adsorption capacity at 5 min. of adsorption on few representative samples is given in Table 3.

Table 2: CO_2 adsorption capacity of CMS samples from coconut char

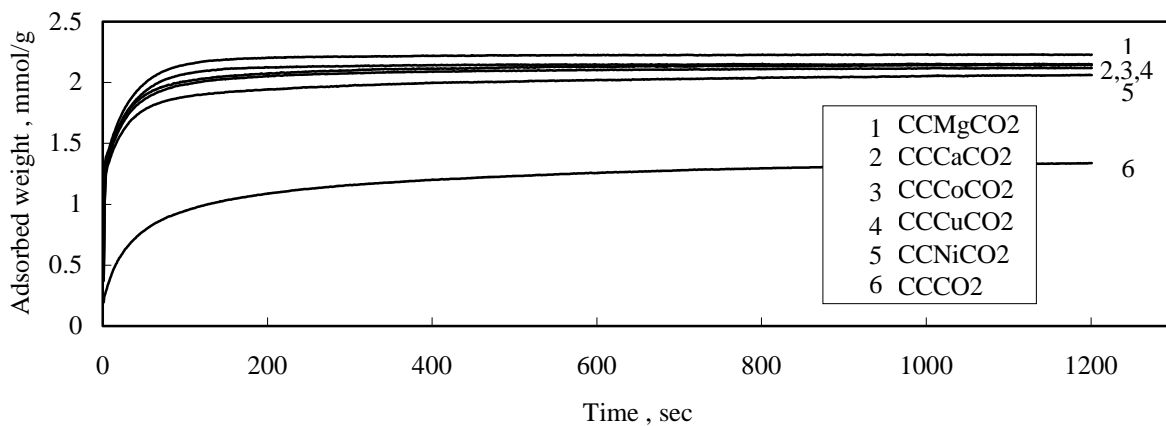| Sample code	CC60	CCMg60	CCCa60	CCCu60	CCNi60	CCCo60
Amount adsorbed (mmol/g)	43	79	74	73	70	37

Fig 1. Effect of metal impregnation on CO_2 adsorption
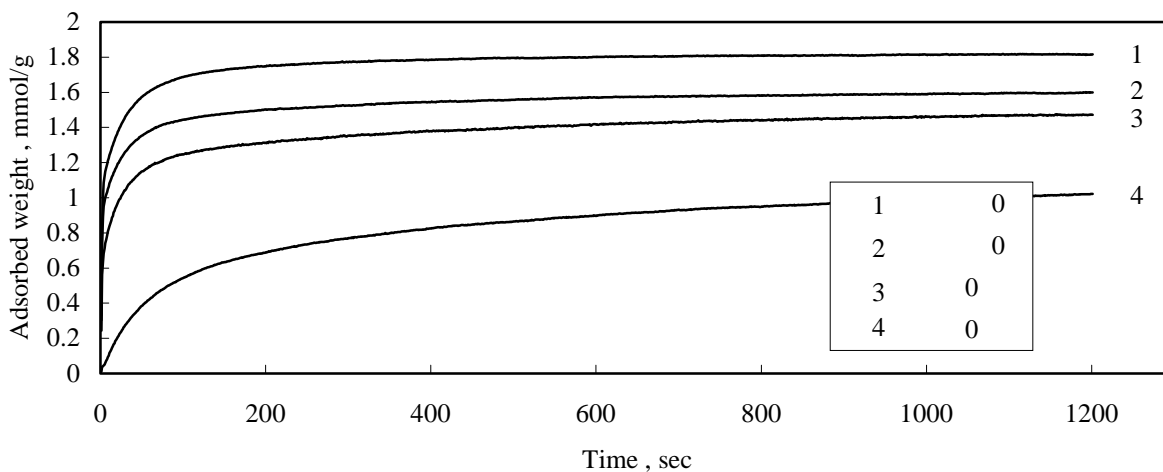

Fig 2 (a). Effect of benzene cracking on CO_2 adsorption

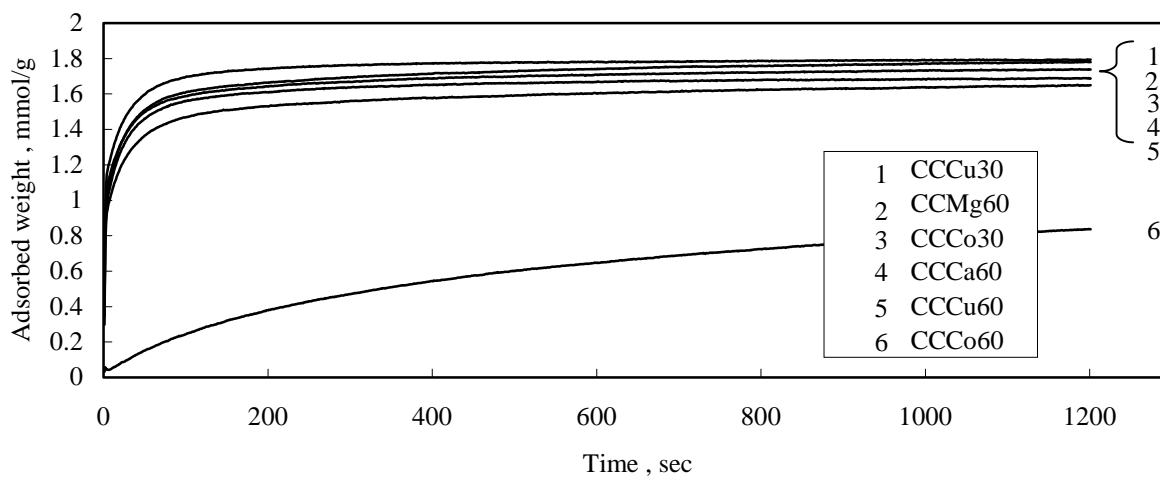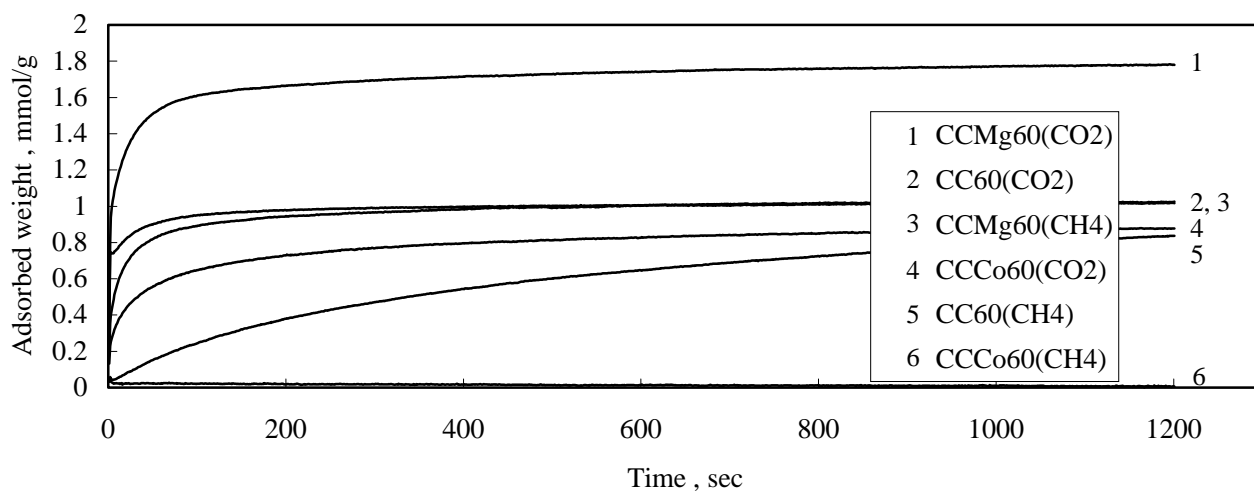Fig 2 (b). Effect of benzene cracking on CO_2 adsorption

Fig 3. Adsorption of CO_2 and CH_4 on CMS samples

Table:3 Uptake ratios for CO_2 and CH_4 on the CMS samples

Adsorption pressure 0.92 atm ; Adsorption temperature 25 ^{o}C

Sample code	CO_2 adsorbed at 5 min. (mg/g)	CH_4 adsorbed at 5 min. (mg/g)	Uptake ratio
CCMg60	78.3	14.0	5.6
CCCa60	74.3	12.9	5.8
CCCu60	72.5	14.0	5.2
CCCo60	36.8	0.1	368
CCNi60	70.4	12.5	5.6

5. CONCLUSION

1. The metal impregnation increases the CO_2 adsorption capacity. Metal oxide formation on the surface or pores can enhance the CO_2 adsorption. Co is a better cracking catalyst compared to the other metals used in this work.

2. The CO_2 adsorption on CMS prepared from non-treated coconut char is found to be 1.2 mmol/g, whereas the one from Mg treated char showed 2.3 mmol/g.

6. REFERENCE

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