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Development of Carbon Dioxide Adsorbents using Carbon Materials Prepared from Coconut Shell

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Abstract−Coconut shell, being a good carbon precursor and having a regular porous structure, was chosen for production of carbonic materials in this work. Metal doping on the coconut char was used to develop catalytic centers for hydrocarbon cracking and thereby obtain a product with good microporosity. Magnesium, calcium, cobalt, copper and nickel doping on the coconut char was done by soaking the coconut char in the aqueous solutions of the respective metal salt and further calcining. The characterization of the product samples was done by the measurement of surface area, adsorption capacity of CO_2, N_2, CH_4, and SEM analysis. The micro pore area obtained by using CO_2 adsorption at 298 K was found to be >400 m^2/g for samples prepared from coconut char impregnated with metal. The adsorption capacity of magnesium-doped sample was found to be 98 mg/g, whereas that for a sample prepared from non-impregnated coconut char was 55 mg/g. SEM analysis was conducted to study the morphology and nature of the samples prepared.

Key words: Metal Loading, Diffusivity, Carbonic Material, Coconut Char, CMS

INTRODUCTION

Carbonic materials from solid waste are becoming the center of attraction for many researchers involved in the global problem of removal of carbon dioxide from industries and automobile flue gases. Raw materials chosen are numerous, ranging from coal to plant products. In order to have a product with reproducible ordered porous structure, selection of a raw material is very important. 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 automobiles worldwide, the airborne CO_2 level has gone up, which requires 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, an alternative and effective adsorbent for CO_2 is highly sought [Jee et al., 2004] Many researches have been already carried out to prepare carbonic molecular sieves (CMS) and sorbents from a wide range of raw materials [Oh and Park, 2002; Guo and Lua, 2000; Nakagawa et al., 2002; Marquez, 2002; Bae et al., 2004]. 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 [Kyotani, 2000]. Although a considerable amount of research towards the pore size tailoring of carbon precursors has been done, a confirmed process to develop desired microporosity in carbonaceous materials has not been arrived at [Kim et al., 2002]. In the present work, metal impregnation of coconut char is done to introduce active catalytic centers for hydrocarbon cracking and thereby pore - mouth narrowing by coke deposition [Prasetyo and Do, 1999; Justin et al., 1999]. The gas adsorption and further separation on CMS is mainly due to kinetically controlled diffusion [Prasetyo et al., 1998]. The adsorption characteristics of different adsorbate molecules very much depend on the size, shape and the electronic interactions of the molecules with the adsorbent [Ried et al., 1998, 1999]. Adsorption of CO_2, CH_4, N_2, and O_2 on CMS occurs in the micropores. The separation of the gas molecules is caused by the selective adsorption due to the shape and size of the molecules [Moreira et al., 2000; de la Casa-Lillo et al., 2002]. Data on adsorption of N_2 at 77 K and CO_2 at 273 K is used to calculate the surface area of the samples prepared.

EXPERIMENTAL

Coconut char (obtained from the Philippines), was ball milled and sieved to 150 µm. This powder was mixed with 25% by weight of coal tar pitch, extruded to 3 mm diameter, and then dried at 90 °C for 8 h in an oven.

1. Metal Impregnation

The metals chosen for impregnation were magnesium and calcium from the alkaline earth metal group, and copper, cobalt and nickel from the transition metal group. One-percent solution of these metals prepared from their nitrate salts was used for impregnation.

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The oven-dried extrudes were soaked in the metal solution (1 g extrude per 2 ml solution) at room temperature for 72 h with intermittent shaking. The extrudates were then filtered out and gently rinsed with distilled water to remove the excess solution on the surface of the sample.

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

2. Carbonization and Activation

Carbonization of the oven-dried extrudates was done in the presence of nitrogen at 800 °C for 60 min and activation with CO_2 at 800 °C for 30 min. A rotary kiln equipped with a multi-step temperature programmer was used for this purpose. The rate of increase of temperature from ambient to 800 °C was maintained at 2 °C/min. Isothermal heating for 60 min each was maintained at 200 °C, 450 °C and 600 °C in order to remove the volatile and other impurities from the coconut char and the coal-tar pitch used in the preparation of the extrudates. Further carbonization at 800 °C for 60 min was maintained so as to decompose and disperse the metal salts used, within the bulk of the samples. The controlled and slow heating rate during carbonization was found to be very important for retaining the shape and mechanical strength of the CMS samples.

3. Pore Mouth Narrowing

Pore mouth tailoring of the activated pellets was done by using coke deposition via. benzene cracking at 650 °C [Freitas and Figueiredo, 2001]. After activation of the samples, the temperature of the reactor was brought down to 650 °C and the sample was baked for 30 min at that temperature. Nitrogen at the rate of 100 ml/min was bubbled through a bubbler containing benzene, and then passed through the sample in the reactor kept at 650 °C, for a fixed duration of time, for coke deposition at the pore mouths of the sample. The benzene bubbler was then disconnected and the sample was kept at 650 °C for 30 min and then cooled to 200 °C in N_2 atmosphere. The list of samples thus prepared with different metal doping on coconut char along with the respective benzene cracking time is shown in Table 1.

4. Characterization of CMS

Characterization of the CMS samples was mainly done in terms of adsorption of gases. A volumetric setup was used for this purpose. Adsorption of CO_2, CH_4, N_2 and O_2 was conducted in the volumetric setup, where both kinetic as well as equilibrium adsorption of gases can be studied at a fixed temperature. The specific surface area of few representative samples was determined by using a Micromeritics ASAP-2010 with N_2 adsorption at 77 K. The CO_2 adsorption data was used to calculate the micropore area (S_{DA}) using the Dubinin-Astakhov equation. The SEM images of the samples were taken on a Philips make XL30 machine to study the morphology of the samples.

RESULTS AND DISCUSSION

1. Adsorption Isotherm

The adsorption isotherm is a very important data for the characterization of CMS. The adsorption isotherm on N_2 adsorption at 77 K on the CMS samples was used to calculate the micropore area as well as micropore volume using the BET system, ASAP-2010. The data for adsorption isotherms for CO_2 and CH_4 at ambient temperature on selected CMS samples were collected by using the volumetric set-up, for pressures ranging 1 to 7 bars. Most of the CMS samples showed 70% of the total adsorption of CO_2 at pressure 1 bar, beyond which, the adsorption curve levels to a virtual plateau. The Co loaded CMS samples showed a continuous increase in adsorption with increase in pressure, with both CO_2 and CH_4. The isotherm plot is shown in the Fig. 1. When the pore size was narrowed down to molecular dimension level of the adsorbing molecules, it was found that the adsorption capacity was constantly increasing with increasing pressure [Stoeckli et al., 2002]. This is because the

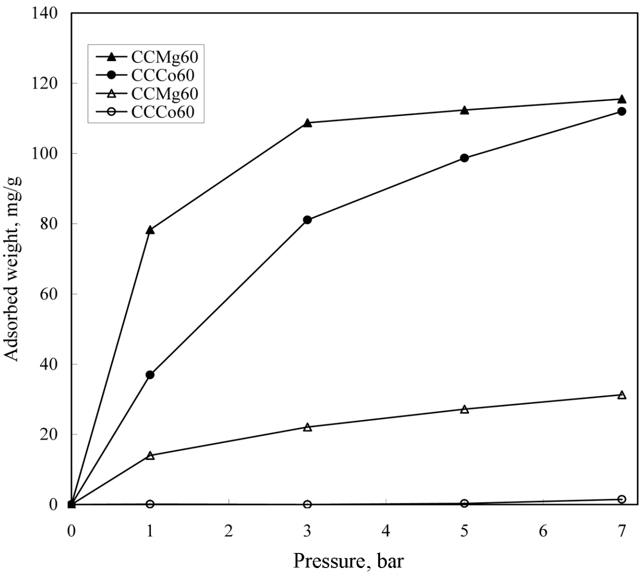


Fig. 1. Adsorption isotherms CO_2 and CH_4 on CCMg60 and CCCo60.

Table 1. List of samples along with the sample code and the respective time of benzene cracking

Sample code	Benzene cracking time (min)	Sample code	Benzene cracking time (min)	Sample code	Benzene cracking time (min)
CCA	0	CCCaA	0	CCCoA	0
CC20	20	CCCa30	30	CCCo30	30
CC60	60	CCCa60	60	CCCo60	60
CCMgA	0	CCCuA	0	CCNiA	0
CCMg30	30	CCCu30	30	CCNi30	30
CCMg60	60	CCCu60	60	CCNi60	60

Carbonization/Activation temperature : 800 °C; Carbonization time : 60 min; Activation time : 30 min.

adsorbing molecules pick up sufficient activation energy for adsorption as the pressure increases.

2. Surface Area and Textural Properties

Micropore area of CMS and the adsorption capacity of various gases reveal that 70% of the adsorption capacity in CMS is due to the micropores present in it [Pradhan and Sandle, 1999]. The N_2 adsorption at 77 K on any of the samples prepared was found to be very poor, and hence the surface area obtained from the Micromeritics ASAP-2010 was very low. The N_2 adsorption at 77 K is restricted due to the low activation energy of the N_2 molecules at that temperature owing to the quadrupolar interactions of N_2 with the adsorbent [Harnit et al., 1995]. This shows that the adsorption is mainly in the micropores. The micropore area of adsorbents is best calculated by using the Dubinin Astakhov (DA) equation. The equilibrium adsorption capacity of CO_2 on the samples, at different pressures was used in the DA equation for calculating the micropore area. The DA equation used was,

$$w=w_0\exp[-(A/E)^n] \tag{1}$$

Where 'W' is the amount adsorbed at relative pressure 'P/P_o', 'W_0' is the limiting micropore adsorption capacity, 'A' (Adsorption potential)=RT ln(P_0/P), 'R' is the gas constant, 'T' is the absolute temperature, 'E' is the characteristic energy of adsorption and 'n' is an integer representing the microporous nature of the adsorbent (equal to 3 in the case of the DA equation). The analysis of the N_2 and CO_2 isotherm is given in the Table 2. The micropore area (S_{DA}) of the sample after metal doping increased from 240 to 519 m^2/g. The metal loading on the CMS samples acts as catalyst centers for benzene cracking, thereby developing more micropores in the sample than in the CMS samples prepared from original coconut char. From closely examining the limiting micropore capacity of all the CMS samples, it is clear that the metal loading has catalyzed the coke deposition at the pore mouth and thereby assisted pore mouth tailoring. The value of 'n' was found to be approximately 3 for the metal doped samples, whereas the other samples prepared from original coconut char were found to be ~2.5. This confirms the credibility of the DA equation for finding the textural properties of the CMS samples prepared. The micropore size was estimated by using the empirical equation proposed by the Dubinin formulation for micropore half width. The Dubinin equation for calculating the micropore half width is, $x_0=k/E_0$, where the proportionality constant 'k' is 12 kJ·nm/mol. The CCCo60 sample showed a pore width of 0.8 nm, which supports the adsorption selectivity of the sample for CO_2 over CH_4.

Table 2. The micropore area and the textural properties of CMS samples

Sample code	W_o (g/g)	S_{DA} (m^2/g)	n	E_o (kJ/mol)	$X_{Dubinin}$ (nm)
CCCoA	0.12	484	2.8	19.6	0.6
CCCo60	0.14	434	3.0	25.2	0.4
CCMgA	0.15	519	2.7	19.2	0.6
CCMg60	0.12	415	2.8	19.8	0.6
CCCu60	0.12	415	2.8	19.8	0.6
CCA	0.08	277	2.4	16.4	0.7
CC60	0.05	242	2.5	17.6	0.7

Loading of Co showed a considerable amount of coke deposition leading to the pore narrowing during the benzene cracking on the sample. The micro pore surface area was very much comparable for the samples CCCoA and CCCo60 (484 and 434 m^2/g, respectively). Thus, it is clear that the coke deposition appears to be more at the pore mouth than inside the pores. Cobalt being a good catalyst for coke deposition by benzene cracking, the time, temperature and concentration of benzene in the N_2 stream have to be controlled to obtain a very effective pore narrowing. Detailed experimentation of coke deposition on Co loaded CMS sample would give a CMS sample with very much-desired pore narrowing for selective adsorption study.

3. Kinetic Adsorption Characteristics of the CMS Samples

The CMS samples prepared were further characterized by study-

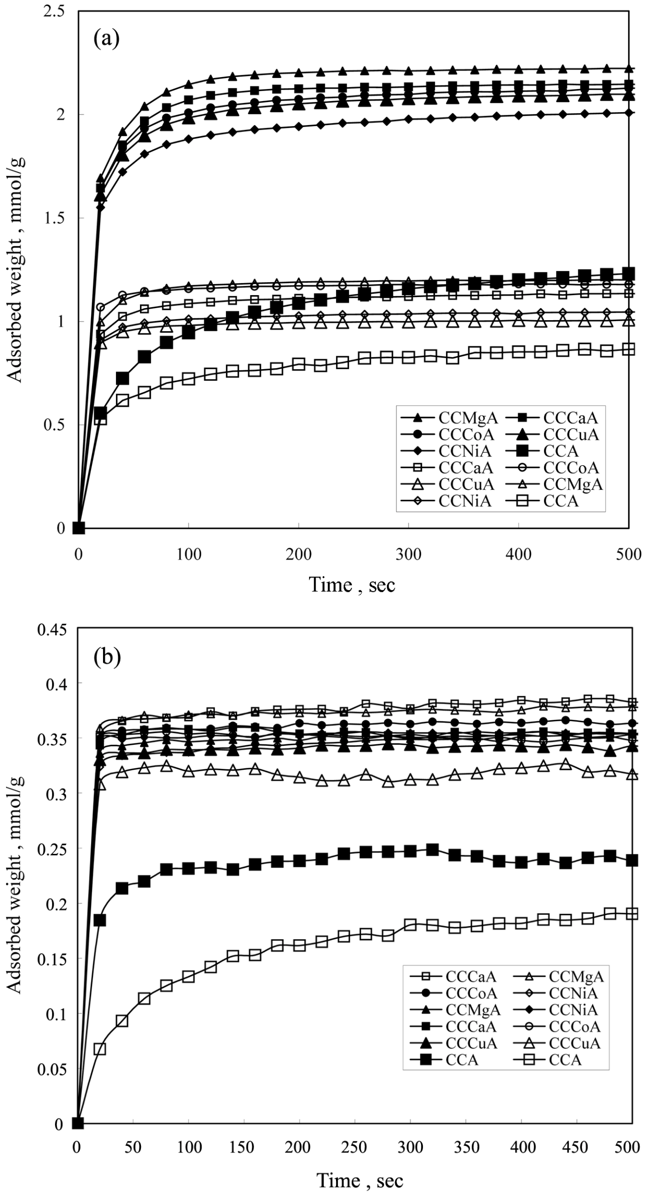


Fig. 2. (a) Kinetic adsorption of CO_2 and CH_4 on CMS samples. (b) Kinetic adsorption of N_2 and O_2 on the CMS samples prepared by CO_2 activation.

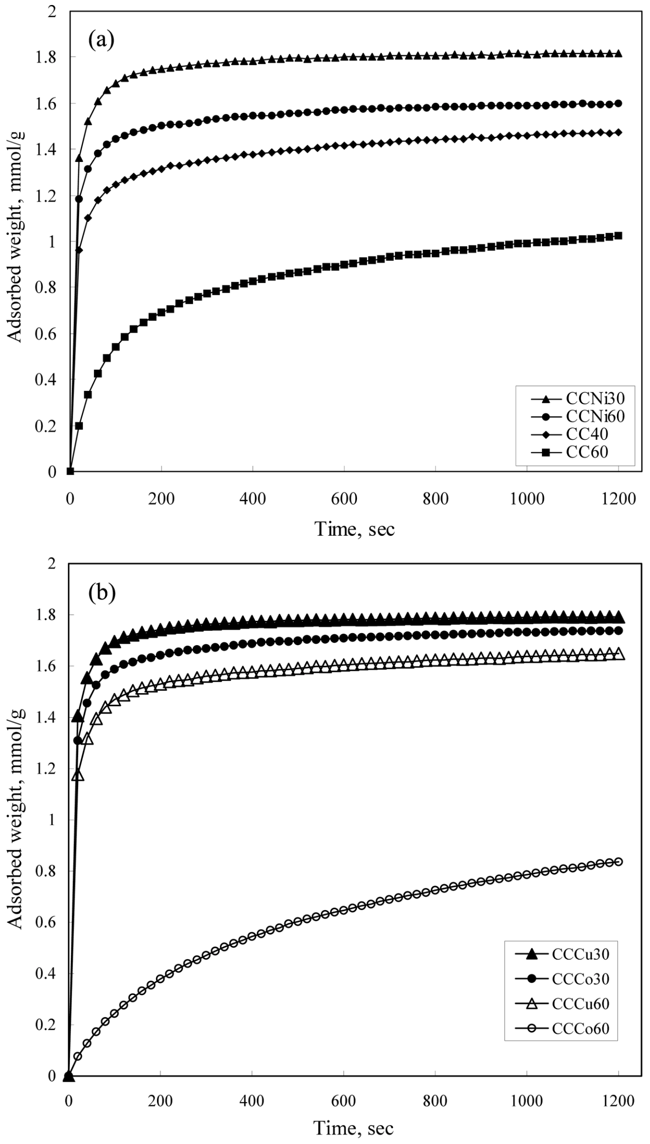


Fig. 3(a) and (b). Effect of benzene cracking on CO_2 adsorption.

Table 3. Uptake ratio of binary gas mixtures along with the adsorption capacity on the CMS samples prepared

Sample code	Adsorption capacity at 20 min (mg/g)				Uptake ratio at 20 min	
	CO_2	CH_4	N_2	O_2	CO_2/CH_4	CO_2/N_2
CCA	48	12.6	4.5	7.6	3.8	10.3
CC40	57.8	4	4.0	5.5	14.5	14.4
CCCuA	90.3	16	7.5	11	5.6	12.1
CCCu30	76.6	14	8.4	10	5.5	9.1
CCCu60	67.3	14	6.8	9	4.8	9.9
CCNiA	85.4	17	9.4	11	5.3	9.1
CCNi30	77	19.2	8.5	10	4	9.1
CCNi60	66	11	8.1	9	6	8.2
CCCoA	91.1	17.5	9.6	12	5.2	9.5
CCCo30	72.2	12.4	8.8	11	5.6	8.2
CCCo60	17	0.04	0.8	8	>400	22
CCMgA	97	18	10.7	11	5.4	9.1
CCMg60	73	12	8.7	9	6.1	8.4
CCCaA	93.5	18.7	10.5	11.5	5	8.9
CCCa60	70.8	12.4	7.7	9.5	5.7	9.2

ing the adsorption of gases like CO_2, CH_4, N_2 and O_2 on them by using a volumetric setup. The kinetic adsorption curves obtained for adsorption of these gases on selected CMS samples prepared by CO_2 activation are shown in Fig. 2(a & b). The pore narrowing of the CMS samples was achieved by the coke deposition by benzene cracking at the pore mouths. The effect of benzene cracking time on the CO_2 adsorption characteristics of various metal loaded samples is shown in Fig. 3(a & b). Table 3 gives the adsorption capacity of each gas at 5 min on the sample along with the uptake ratio of binary gas systems like CO_2-CH_4 and N_2-O_2. The CO_2 adsorption capacity of cobalt loaded sample dropped from 77 to 17 mg/g at ~1 bar adsorption pressure and 20 min adsorption time, when the benzene cracking time was increased from 30 to 60 min. In the case of copper, nickel, calcium or magnesium loaded CMS sample, the drop in adsorption capacity of CO_2 was ~11 to 20 mg/g at 20 min of adsorption time and 1 bar adsorption pressure. The CO_2 adsorption capacity of the metal loaded CMS samples was found to be, CCMg>CCCa>CCCo=CCCu>CCNi. Magnesium and calcium ions, due to lower melting point and more labile electronic property than the other metals used for doping, can give rise to good dispersion and distribution in the bulk of the sample during carbonization and activation. Also, MgO and CaO, which have an affinity for CO_2, also would be present on the surface of the sample. This can also contribute to the increased CO_2 adsorption capacity observed in the Mg and Ca doped samples. Table 3 also reveals that the Mg and Ca doped samples show a higher adsorption of CO_2 than the Cu, Co or Ni doped samples. The uptake ratio for CO_2/CH_4 was found to be in the range 4 to 6 and that for CO_2/N_2 was found to be between 8 to 12, for all the metal-doped CMS samples, excepting the sample CCCo60. The uptake ratio of the binary gas systems on the CCCo60 was found to be >400 for CO_2/CH_4 and 22 for CO_2/N_2. This is a clear indication of the pore narrowing of the sample to molecular dimension level, by the effective catalytic cracking of benzene followed by the coke deposition. The adsorption capacity of N_2 and O_2 on CMS samples prepared by CO_2 activation of Mg and Ca loaded coconut char was found to be low (10-11 mg/g. Further narrowing of the pores is required, for using these samples for N_2 separation from air. It is to be noted that the alkaline earth metals, Mg and Ca loaded CMS samples showed a high adsorption capacity for the various gas adsorption studied, but the catalytic activity for coke deposition from benzene was less compared to the transition metals studied in this work. The cobalt-doped CMS sample after benzene cracking showed a considerable decrease in adsorption capacity of CO_2, CH_4, N_2 and O_2. The enhanced benzene cracking and further coke deposition leading to pore-mouth narrowing was observed in these samples. A clear restriction of the adsorption of gas molecules larger than 3.6 Å was observed on the benzene cracked CCCo samples. The N_2 (3.64 Å) and CH_4 (3.46 Å) showed a very poor adsorption on CCCo60 sample. Fig. 4 shows the kinetic adsorption of CO_2, CH_4, N_2 and O_2 on CCCo60. The adsorption of CH_4 and N_2 was found to be very low in this sample.

4. Diffusivity of Various Gases on the CMS Samples

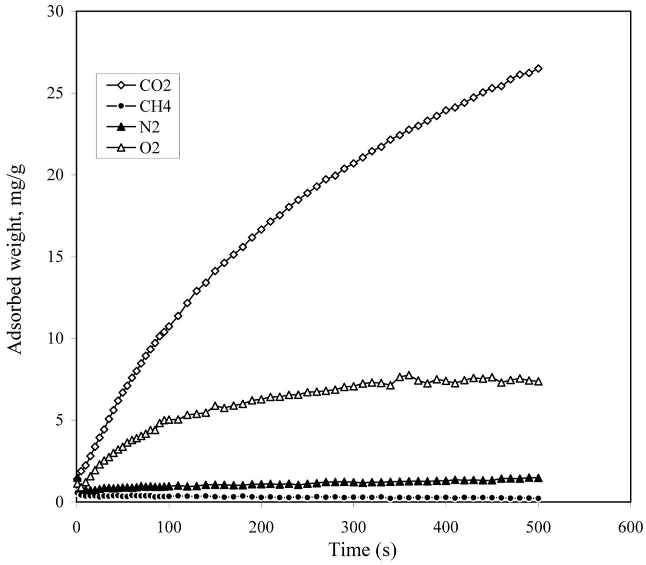


Fig. 4. Kinetic adsorption of CO_2, CH_4, N_2 and O_2 on CCCo60.

The empirical formula for kinetic diffusion for adsorbents (Eq. (2)) is used to see the credibility of diffusion of gases in the CMS sample prepared.

$$\frac{M_t}{M_\infty}=kt^n \qquad (2)$$

Where 'M_t' is the amount of gas adsorbed at time t seconds and 'M_∞' is that at equilibrium, 'n' is the diffusion exponent and 'k' is a constant. A plot of $\ln(M_t/M_\infty)$ against ln(t) was found to be a straight line (Fig. 5), the slope of which is below 0.5. Thus the diffusion mechanism of these samples can be considered to be obeying Fick's model. From the Fick's law for isothermal diffusion, it can be written for small adsorption time as (Eq. (3)),

$$\frac{M_t}{M_\infty}=\frac{6D^{1/2}t^{1/2}}{\pi^{1/2}a} \qquad (3)$$

Where 'D' is diffusivity constant and 'a' is the radius of the spherical entity where adsorption takes place.

A plot of M_t/M_∞ versus $t^{1/2}$ is found to be a straight line, the slope of which is, $\frac{6D^{1/2}t^{1/2}}{\pi^{1/2}a}$; the D/a^2 for different gases on the CCCo60 sample is shown in Table 4.

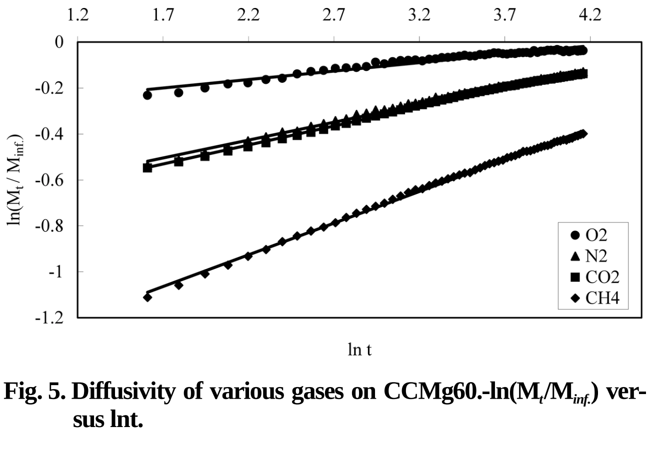


Fig. 5. Diffusivity of various gases on CCMg60.-$\ln(M_t/M_{inf.})$ versus lnt.

Table 4. Diffusivity constant for various gases on the CMS sample CCCo60

Sample code	D/a^2 (s^{-1})				Ratio of D/a^2	
	CO_2	CH_4	N_2	O_2	CO_2/CH_4	O_2/N_2
CCCo60	8.0×10^{-4}	0.9×10^{-4}	2.2×10^{-4}	4.4×10^{-4}	8.9	2

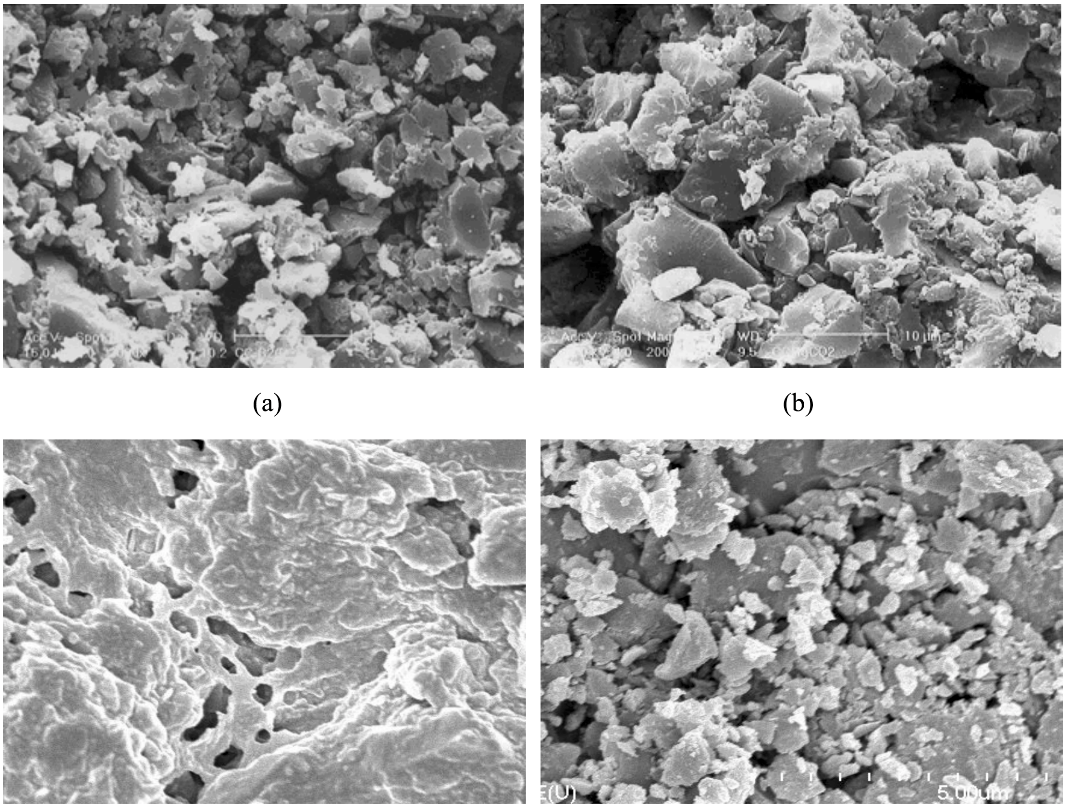
The micropores in the sample CCCo60 are observed to be of molecular dimension. The CO_2, being the smallest of the gas molecules chosen for adsorption (CO_2, CH_4, N_2 and O_2), was adsorbed the maximum. When the adsorption capacity as well as the adsorption rate of the gases is significantly low, a difficulty in arriving at the equilibrium uptake of these gases occurs. The diffusivity values calculated for such gases are expected to deviate from the actual value. Hence the ratio of the diffusivity values of different gases on these samples would be giving only a rough idea of the preferential adsorption of gases on it. The diffusivity ratios for CO_2-CH_4, as well as CO_2-N_2 thus calculated, gives an idea of the adsorption selectivity of the gases on the CMS samples prepared.

5. Scanning Electron Microgroscopic (SEM) Analysis of the Metal Doped Samples

Surface images of a few representative CMS samples prepared in the present work were taken on the SEM apparatus (Philips XL30) at electron energy 20 kV. The degassed sample was carefully cut to get an even cross section and was fixed onto the microscopy holder and sputtered with gold in plasma; the cross-sectional images of the samples were micro-graphed at a magnification 2,000× (Figs. 6a, 2b & 2c). The CMS sample prepared from coconut shell char without loading metal was found to have a uniform grain size and grain distribution. The metal-doped sample has many of the grains shielded by a layer and appears to be bigger grains. This may be a film or mask formed by the metal in the bulk of the sample. These metal centers provide catalytic sites for benzene cracking and thereby help in narrowing of pores by coke deposition. The SEM photographs of CC20, CCMgA, CCCoA and CCCo60 are shown in Figs. 6 a to 6d. Depletion of the film on the cross section of the sample CCCoA (Fig. 6c) was observed in the sample CCCo60 (Fig. 6d). The microporosity of the sample cannot be micrographed by using the SEM technique. The SEM-EDAX analysis (Figs. 7a and 7b) also confirms the presence of Co on the CCCoA and CCCo60 sample. The Co content is observed to be less in the CCCo60 (C: 90.41 weight%, Co: 9.59 weight%) sample than that in CCCoA (C: 64.36 weight%, Co: 35.64 weight%) sample. Many Co atoms in CCCo60 sample must have gotten completely masked with coke deposition.

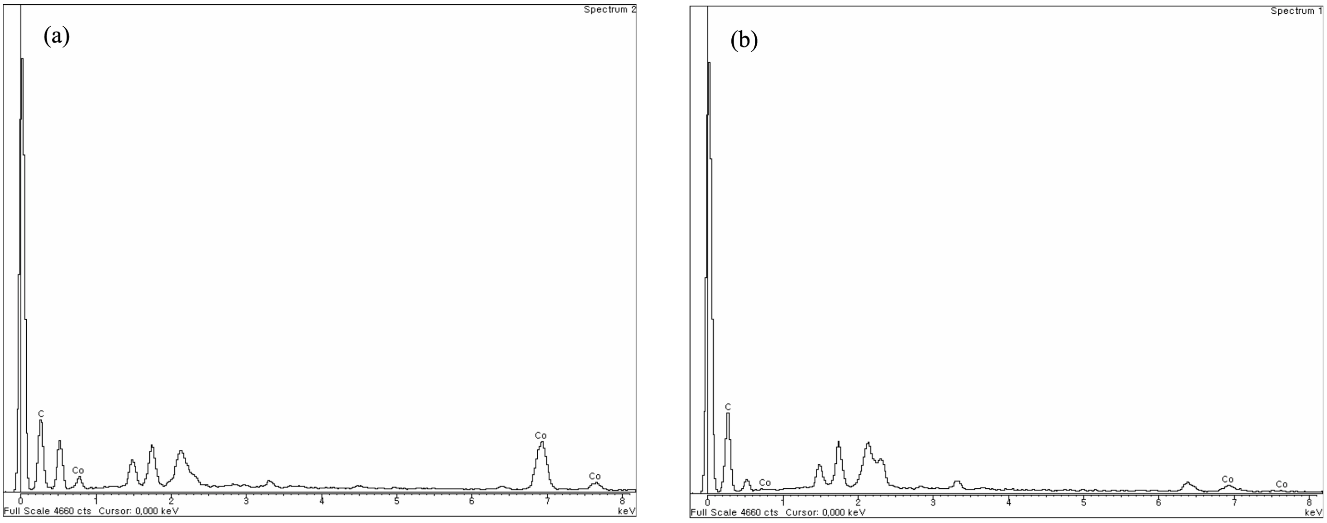
CONCLUSIONS

Carbon molecular sieves were prepared from coconut shell char from the Philippines by metal impregnation followed by carbon dioxide activation and coke deposition via benzene cracking. Alkaline earth metals as well as transition metals show a favorable effect for benzene cracking. The CMS samples prepared from Mg loaded coconut char showed a very high adsorption capacity for CO_2. Cobalt loading improved the pore narrowing by coke deposition. Out of the five metals chosen (Mg, Ca, Cu, Co and Ni), cobalt was found



(a) (b) (c) (d)

Fig. 6(a), (b), (c) and (d). SEM images of CC20, CCMgA, CCCo and CCCo60 respectively.



C : 64.36 weight%, Co : 35.64 weight%

C : 90.41 weight%, Co : 9.59 weight%

Fig. 7(a). SEM-EDAX of CCCoA sample. (b) SEM-EDAX of CCCo60 sample.

to be the best catalyst for benzene cracking and coke deposition. The CMS sample with Co loading showed an uptake ratio more than 100 at adsorption pressures 1 to 7 bar for CO_2/CH_4 and ~20 for CO_2/N_2. The micropore area of the CMS sample increased from 72 to 450 m^2/g when the carbon precursor was loaded with metals. Cobalt metal loading and controlled benzene cracking on the sample can be used to produce CMS sample that can be used for N_2 separation from air.

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