Asian Journal of Chemistry Vol. 11, No. 4 (1999), 1343–1347

Characterization of the Chemical Grafted Bentonite Supports by Gas Chromatography

A.A. RAMADAN, S. ANTAKLI* and A. ALHAJ SAKUR†
Department of Chemistry, Faculty of Science
Aleppo University, Aleppo, Syria

Gas chromatographic analysis technique was used for characterization of the gas chromatographic supports, which prepared from siliceous or natural origin. We studied the bentonite to be used as gas chromatographic support, which consists of aluminosilicate oxides mixture with some other metallic oxides. It possesses a porous structure, which permits its use in gas chromatography. The bentonite was thermally treated at 650°C to obtain firm granules, and acid washed by 6N-HCl to remove the soluble metallic oxides especially iron oxide, till white granules with mesh range 100–120, were obtained. The specific surface area of the support was measured to be 5.4 m^2/g. The superficial structure of the grafted bentonite by silicone SE-52 and dimethylchlorosilane was studied by "inverse gas chromatographic method" using dichloromethane as auxiliary solute plotting $\log V_s = f(1/T)$. We carried out many separations for different mixtures as cyclic and aromatic compounds and normal hydrocarbons. The grafted bentonite supports permit to obtain analytical results characterized with complete and good resolution with high efficiency and reproducibility for all studied columns packed with silicone SE-52 and dimethylchlorosilane grafted bentonite, compared with packed columns with bare bentonite.

INTRODUCTION

Silica represents the major constituent of clay, in addition to several amounts of other metallic oxides. The bentonite constituents were determined. It consisted of 47% SiO_2, 14.4% Al_2O_3 and some other oxides as Fe_2O_3, MgO, CaO and Na_2O, represent the remainder ratio[1]. The thermal treatment causes a decrease of bentonite specific surface area with increase in the temperature of thermal treatment[2].

A prolonged washing of bentonite by 6 N HCl removes all soluble oxides and about 67% of total iron oxide from the adsorbent, causing decrease of specific surface area and hydrolysis of siloxane groups on the surface of the support to yield more silanol groups[3–8].

Modification of the support surface by reaction with silanol groups was carried out by means of chlorosilane compounds as reactants[9, 10], or by condensation of a suitable polymer as PEG-20M, Se-30 and OV-101[8, 11–15]

EXPERIMENTAL

General preparation of the support: Bentonite granules of mesh 120–100 were treated at 650°C and washed with 6 N HCl at boiling point temperature, until no yellow hue could be detected in a fresh charge of 6N HCl, till white granules were obtaion. The bentonite was then washed with distilled water to neutrality. Finally, this support possesses a specific surface area 5.4 m^2/g.

---

†Department of Chemistry. Faculty of Pharmacy, Aleppo University, Aleppo, Syria.

Grafting

Silanization: The bentonite granules were reacted with dimethylchlorosilane in the vapor phase at 120°C in presence of a stream of dry pure nitrogen *(in situ* method) then the yield grafted support was washed by chloroform to remove the residual of reagent.

Polymer condensation: A suitable amount of bentonite granules was coated by rotary evaporation technique with 3% of silicone SE-52 and heated under a slow flow of dry pure nitrogen at 280°C, for 24 h, then extracted with chloroform in a Soxhlet apparatus for 48 h; the extracted material was dried at 100°C before being packed into chromatographic column, the gas chromatographic characteristics of packing were evaluated using inverse gas chromatographic method and plotting the relationship between variation of the logarithm of retention volume of CH_2Cl_2 as an auxiliary solute, with the reciprocal of the absolute temperature in the range 35–100°C.

Gas chromatographic analysis: We used the obtaned packings in separation of several mixtures of cyclic and aromatic compounds and normal hydrocarbon compounds.

RESULTS AND DISCUSSION

By conclusion, we found by studying the changes in superficial structure of grafted bentonite in the two above mentioned cases by using "inverse gas chromatographic method" in the range 35–100°C, using CH_2Cl_2 as auxiliary solute and plotting the relationship $\log V_s = f(1/T)$. We found differences between retention volumes for CH_2Cl_2 for three columns (50 cm × 4 mm), the first one packed with bare bentonite 5.4 m^2/g, (Fig. 1), the second packed with silicone SE-52 grafted bentonite (Fig. 2), the third packed with dimethylchlorosilane

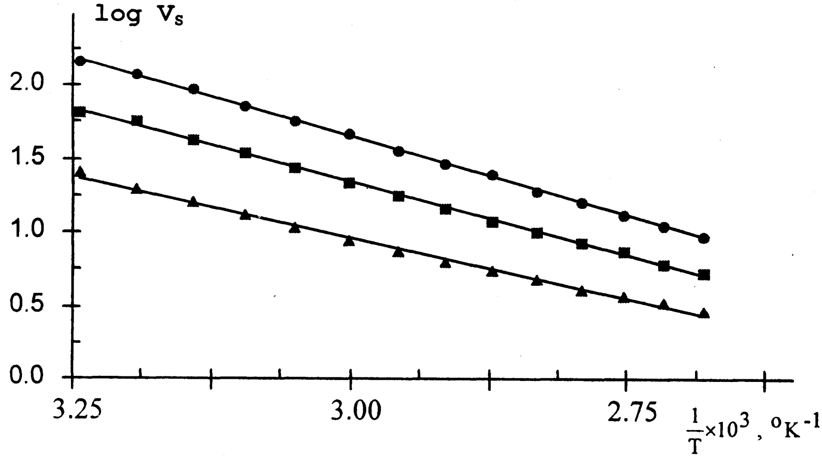
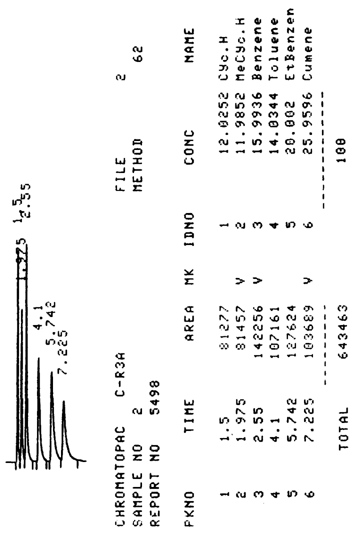


Figure (1)
Variation of log V_S with 1/T for CH_2Cl_2 as a test solute on (50cm x 4mm) packed columns :
1-● - with bare bentonite.
2-■ - with SE-52 grafted bentonite.
3-▲ - with DMC silanized bentonite.



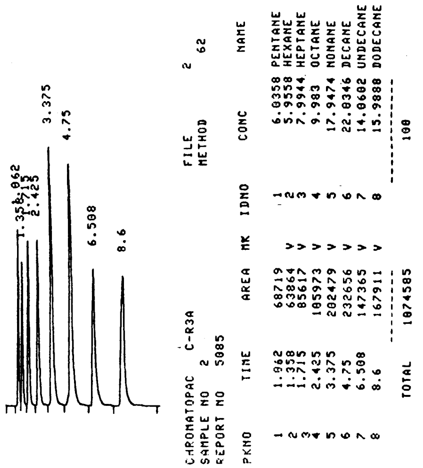
```
CHROMATOPAC   C-R3A                   FILE        2
SAMPLE NO   2                         METHOD       62
REPORT NO   5498

PKNO      TIME       AREA  MK  IDNO      CONC        NAME

  1       1.5        81277      1        12.0252 CYc.H
  2       1.975      81457  V   2        11.9852 MeCYc.H
  3       2.55      142256  V   3        15.9936 Benzene
  4       4.1       107161      4        14.0344 Toluene
  5       5.742     127624      5        20.002  EtBenzen
  6       7.225     103689  V   6        25.9596 Cumene
                 ---------           ------------
         TOTAL      643463                100
```

Figure (2)

Separation and determination mixture of cyclic and aromatic compounds on SE-52 grafted bentonite (250cm x 1.75mm), temperature program (135-170)°C,5°C/min., N_2 flow 35 ml/min, temperature inject port 250°C ..



```
CHROMATOPAC   C-R3A                  FILE        2
SAMPLE NO   2                        METHOD       62
REPORT NO   5085

PKNO      TIME       AREA  MK  IDNO      CONC      NAME

  1       1.962      68719      1       6.0358  PENTANE
  2       1.358      63864  V   2       5.9558  HEXANE
  3       1.715      85617  V   3       7.9944  HEPTANE
  4       2.425     105973  V   4       9.983   OCTANE
  5       3.375     202479  V   5      17.9474  NONANE
  6       4.75      232656  V   6      22.0346  DECANE
  7       6.508     147365  V   7      14.0602  UNDECANE
  8       8.6       167911  V   8      15.9888  DODECANE
                 ---------          -------------
         TOTAL     1074585               100
```

Figure (3)

Separation and determination mixture of normal hydrocarbons C_5-C_{12} on DMCS silanized bentonite (250cm x 1.75mm), temperature program (120-180)°C, 5°C/min., N_2 flow 38 ml/min, temperature inject port 250°C silanized bentonite (Fig. 3). We found differences in retention volumes between the bare bentonite and the grafted bentonite ones due to the new *superficial* structure of supports, (Fig. 1).

The packed column with SE-52 grafted bentonite was suited for separation mixture of cyclic and aromatic compounds: cyclohexane, methyl cyclohexane, benzene, toluene, ethylbenzene and cumene, with good symmetric peaks (Fig. 2). The packed column with DMCS silanized bentonite gave a very good separation for mixture of normal hydrocarbons C_5 to C_{12} with very sharp, symmetric peaks with very short retention times (Figure 3). In all separations, we obtained completely separated peaks, with a high sensitivity and reproducibility, (Table 1 and 2).

TABLE-1
QUANTITATIVE DETERMINATION OF SEVERAL MIXTURES OF NORMAL HYDROCARBONS C_5–C_{12} ON DMCS SILANIZED BENTONITE COLUMN
[(250 cm × 1.75 mm), temperature program (120–180)°C, 5°C/min., N_2 FLOW RATE 38 mL/min, temperature inject port 250°C.]

No.	Compound	Amount V%		RSD %
		taken C	determined $\overline{C}$	
1	pentane	4	4.00	3.20
	hexane	8	8.00	2.96
	heptane	10	9.97	2.90
	octane	6	6.04	3.04
	nonane	12	11.99	2.64
	decane	18	18.01	2.33
	undecane	22	21.96	2.01
	dodecane	20	20.03	2.21
2	pentane	6	6.03	3.03
	hexane	6	5.96	2.91
	heptane	8	7.99	2.85
	octane	10	9.98	2.80
	nonane	18	17.94	2.48
	decane	22	22.03	2.11
	undecane	14	14.06	2.49
	dodecane	16	15.99	2.69
3	pentane	10	9.98	2.69
	hexane	4	4.05	3.16
	heptane	6	6.04	2.96
	octane	12	11.97	2.61
	nonane	16	16.02	2.48
	decane	14	13.99	2.55
	undecane	16	15.99	2.42
	dodecane	22	21.96	2.09

TABLE-2

QUANTITATIVE DETERMINATION OF SEVERAL MIXTURES OF CYCLIC AND AROMATIC COMPOUNDS ON SE-52 GRAFTED BENTONITE COLUMN

[(250 cm × 1.75 mm), temperature program (135–170)°C, 5°C/min., N_2 flow rate 35 mL/min, temperature inject port 250°C]

No.	Compound	Amount V%		RSD %
		taken C	determined $\bar{C}$	
1	cyclohexane	8	8.05	3.61
	methylcyclohexane	16	16.03	2.86
	benzene	20	19.97	2.66
	toluene	22	21.99	2.52
	ethylbenzene	14	14.02	3.04
	cumene	20	19.94	2.78
2	cyclohexane	12	12.03	3.06
	methylcyclohexane	12	11.95	3.11
	benzene	16	15.96	2.81
	toluene	14	14.04	2.93
	ethylbenzene	20	19.97	2.61
	cumene	26	26.05	2.36
3	cyclohexane	16	15.97	2.88
	methylcyclohexane	8	8.06	3.68
	benzene	10	10.00	3.26
	toluene	10	9.99	3.12
	ethylbenzene	24	24.01	2.41
	cumene	32	31.97	2.19

REFERENCES

1. A.A. Ramadan, A.R. Kourini and M. Lahmik, M.Sc. Chem. Thesis, Aleppo University, Aleppo, Syria (1987).
2. A.A. Ramadan, S. Antalkli and M. Martini, M.Sc. Chem. Thesis, Aleppo University, Aleppo, Syria (1992).
3. D. Carrol and H.C. Starkey, *Clays Clay Miner.*, **19**, 321 (1971).
4. X. Chin and J. Huang, *Kuangchan Zonghe Liyonge*, **3**, 28 (1993).
5. P. Komadel, J. Stucki and B. Cicel, *Geol. Grapathica-Clays*, **1**, 11 (1993).
6. V.M. Russu, N.T. Okopanaya, G.V. Stratulat and V.M. Ropot, *Inst. Khim.*, 257 (1979).
7. Y. Takayama and K. Bunseki, *J. Chromatogr.*, **28**, 579 (1979).
8. C.R. Vogt and W.A. Aue, *J. Chromatogr. Sci.*, **16**, 268 (1978).
9. Y. Ono and E. Suzuki, Nippon Shokubai Co., Ltd., *Jpn. Kokai Tokyo JP04*, **92**, 338, 393 (1992).
10. E. Suzuki, M. Okamoto and Y. Ono, *Sekiyu Gakkaishi*, **37**, 103 (1994).
11. W. Cheng, Y. Miao, P. Fan and Q. Zhao, *Huaxue Yu Nianhe*, **3**, 170 and 183 (1992).
12. M.M. Daniewski and W.A. Aue, *J. Chromatogr.*, **147**, 119 (1978).
13. A.A. Ramadan, S. Antakli and A. Alhaj Sakur, M.Sc. Chem. Thesis, Aleppo University, Aleppo, Syria (1995).
14. B.D. Skrbic and J. Dj. Cvejanov, *Chromatographia*, **37**, 215 (1993).
15. S.A. Volkov, V. Zelvenskii and G.A. Smolyantov, *Zh. Anal. Khim.*, **47**, 1442 (1992).

(*Received*: 30 March 1999; *Accepted*: 17 July 1999) AJC–1794