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Investigations on the Energetic Heterogeneity of Thermally Pretreated Magnesia and Magnesite

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Abstract

The distribution of the adsorption energy on heterogeneous surfaces of thermally pretreated MgO and $MgCO_3$ was evaluated using a gas chromatographic method. The influence of the kind of adsorbate on the course of the differential distribution of adsorption energy on the surface of this adsorbent has been investigated. The correlation between the shapes of the functions of the adsorption energy distribution of compounds tested and the topography of the active adsorption centers has been proposed. The influence of the energetic heterogeneity of MgO and $MgCO_3$ on their resolution ability as gas-solid chromatography packings is briefly discussed.

INTRODUCTION

Activated magnesia and magnesite have been used for many years as adsorbents in liquid-solid adsorption chromatography. Their use as adsorbents in gas adsorption chromatography has not been widespread (1). The results obtained in our previous work (2) indicated that thermally pretreated MgO and $MgCO_3$ can be used as stationary phases in gas-solid chromatography of a hydrocarbon mixture. It was concluded that thermal activation leads to changes in the surface area and porous structure of these adsorbents and influences their selectivity. However, examination of the separation abilities of adsorbents in gas-solid chromatography are interesting and justified when the surface energy heterogeneity is taken into account (3-6). The present paper discusses the results of introductory investigations of the changes in surface heterogeneity of MgO and $MgCO_3$ by gas chromatography. The aim of these investigations is to determine the optimum

conditions for the preparation of these adsorbents of certain preset surface properties.

EXPERIMENTAL

The adsorbents investigated by us were irregularly shaped magnesia and magnesite from the Institute of Fertilizers, Puławy, Poland. Specific surface area S_{BET} from the adsorption and desorption of nitrogen and distribution of the pore volume according to their radius dV/dr were examined on all the adsorbents presented in Table 1, using sorptiomatic Model 1800 (Carlo Erba, Italy), with numerical calculation on a Odra 1204 computer (Elwro, Wrocław, Poland).

The chromatographic measurements were carried out on a Model GCHF 18.3 gas chromatograph (Chromatron, Berlin, East Germany) equipped with a flame-ionization detector. Nitrogen, purified by the use of a filter containing molecular sieve 5A, was used as the carrier gas at a flow rate of 60–80 cm³/min. A stainless steel column of 1 m × 4 mm i.d. containing the adsorbent was used. The measurements were made at 120 ± 0.1°C. The above conditions were chosen to eliminate the dynamic effects as far as possible. The experimental retention volume $V_{N,t}(p)$ versus p data were obtained by the peak-maxima elution method (7). The solutes (hexane, cyclohexane, benzene, and carbon tetrachloride) were obtained from different suppliers and were all of analytical reagent grade. A method based on an analytical solution of an integral equation for retention volume was used to calculate the energy distribution function for each solute (8):

$$\mathcal{X}(e) = - \left(\frac{F}{N_{\infty}} \right) \left(\frac{p}{RT} \right)^2 \left(\frac{\partial V_N}{\partial p} \right)_T$$

TABLE 1
Characteristic Values of the Adsorbents Studied

No.	Adsorbent	Particle size d_p (mm)	Temperature of activation t (°C)	Specific surface area S_{BET} (m ² /g)	Mean pore radius r_{dom} (nm)	$\frac{dV}{dr} \times 10^{-4}$ (cm ³ · g ⁻¹ · nm ⁻¹)
1	MgO	0.15–0.20	280	68.0	17	0.55
2	MgO	0.15–0.20	900	30.0	30	0.40
3	MgCO ₃	0.12–0.43	180	27.0	7	5.80

where F = James-Martin compressibility factor,

N_{∞} = monolayer capacity

p = pressure of the adsorbate in the free gas phase at temperature T

T = column temperature

V_N = retention volume of the adsorbate

RESULTS AND DISCUSSION

Literature on the subject of magnesia and magnesite and substances adsorbed on their surfaces is not plentiful (9, 10). According to Anderson and co-workers (11), two types of hydroxyl groups exist on the surface of hydroxylated magnesium oxide: isolated (Type I) and bonded (Type II), which are perturbed by interaction with adjacent Type I groups on the surface. These groups are stable during thermal activation of MgO up to 600°C (10, 12) and these hydroxyl groups have a slight acidic property (10). Snyder (13) concluded that a decrease in the activity of magnesia in column chromatography with an increasing activation temperature suggests that surface hydroxyls are important adsorption sites. According to Packer (14), the solid, prepared by calcining precipitated magnesium hydroxide at 500°C, still contained 1.64% by weight of water. This is sufficient to cover 72% of the surface with hydroxyl groups, so that presumably the surface was heterogeneous. At temperatures above 150°C, surface hydroxyls react to form oxide groups which can form the third adsorption sites on the MgO surface (13). There is lack of data about the percentage concentration of each type of hydroxyl group on the MgO surface and the activity of these groups during adsorption. In order to describe the gas-solid interactions in the case of heterogeneous surfaces, the so-called differential energy distribution $\mathcal{X}(e)$ has been introduced. A method for evaluating this function from the pressure dependence of gas chromatographic retention data was developed (3, 8). It has been shown for many adsorbents (3, 5, 6) that the shape of the energy distribution function depends to a considerable extent on the structure of the surface layer of the adsorbent. Figures 1–4 present diagrams of the energy distribution functions for hexane, cyclohexane, benzene, and CCl_4 for the MgO adsorbents investigated. For MgO activated at 280°C, all the $\mathcal{X}(e)$ curves have three adsorption centers, with the energies for each adsorbate presented in Table 2. The main maxima seems to correspond to the interaction energy of the surface hydroxyl groups of MgO with the adsorbate. From Fig. 1 it can be deduced that nonspecific interactions occur between hexane molecules and Type II hydroxyl groups. This type of OH group can be divided on two parts which differ in their being surrounded by Type I OH groups on the MgO surface (15). In the case of cyclohexane (Fig. 2), the

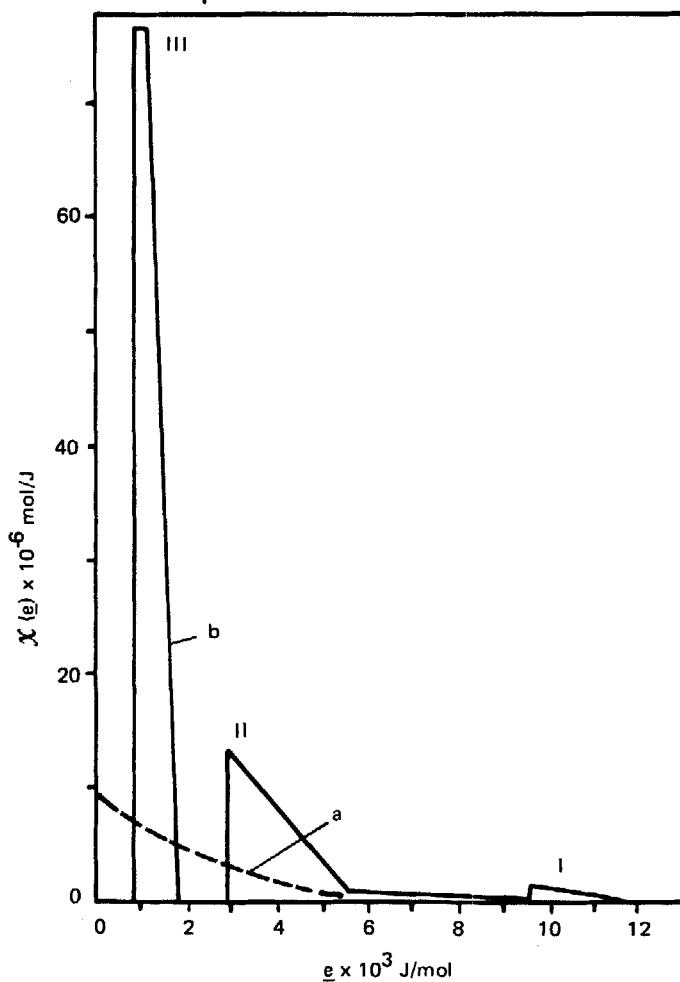


FIG. 1. Energy distribution functions for hexane on magnesia: (a) MgO activated at 900°C , (b) MgO activated at 280°C .

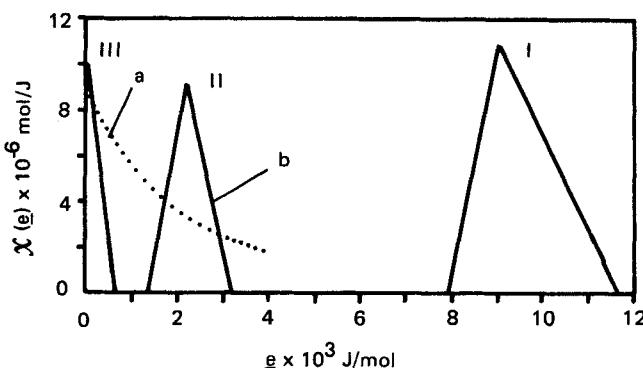


FIG. 2. Energy distribution functions for cyclohexane on magnesia: (a) MgO activated at 900°C , (b) MgO activated at 280°C .

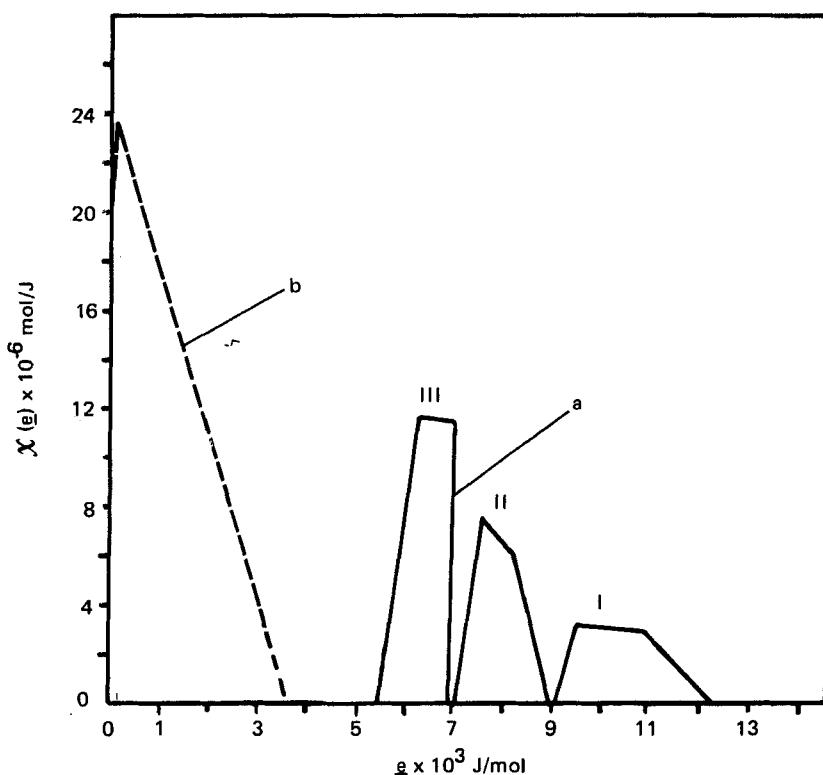


FIG. 3. Energy distribution functions for benzene on magnesia: (a) MgO activated at 280°C , (b) MgO activated at 900°C

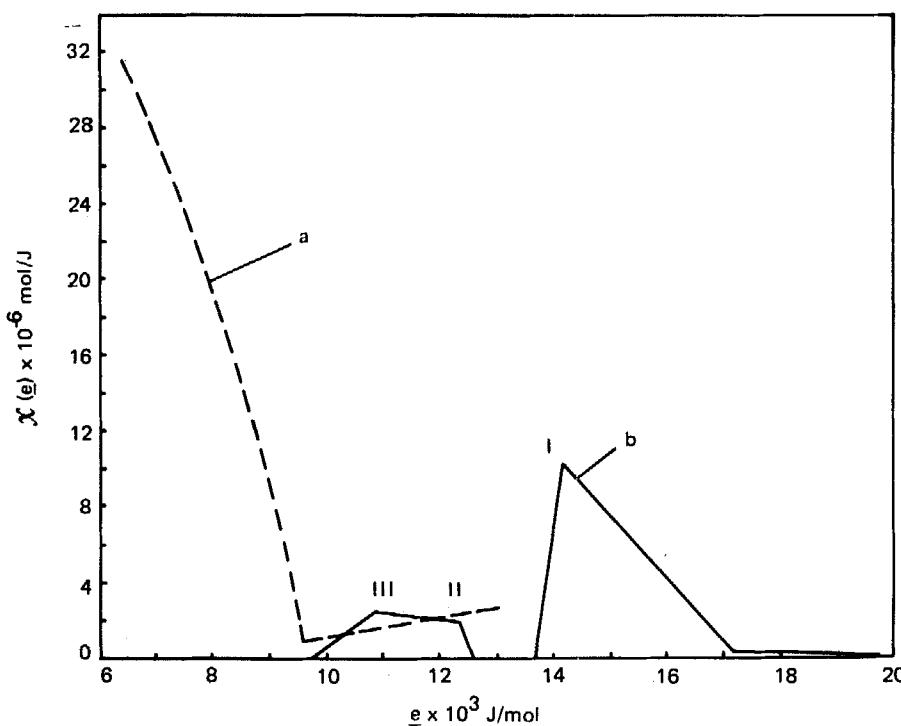


FIG. 4. Energy distribution functions for CCl_4 on magnesia: (a) MgO activated at 900°C , (b) MgO activated at 280°C .

TABLE 2

The Energies of the Appropriate Adsorption Areas and Their Percentage Contributions
Estimated from the $\mathcal{X}(e)$ Curves for Different Adsorbates on MgO Activated at 280°C

Adsorbate	Type of adsorption sites			Percentage contribution of sites			Average adsorption energy \bar{e} (kJ/mol)
	I	II	III	I	II	III	
Hexane	9.57	2.92	0.87	2.7	29.5	67.8	1.71
Cyclohexane	9.11	2.21	0.10	62.2	27.0	10.8	6.27
Benzene	10.10	7.62	6.32	23.53	34.73	41.74	7.66
CCl_4	14.10	12.37	10.87	77.54	6.74	15.72	13.61

nonspecific interactions between this molecule and all three types of OH groups are involved. However, we can suppose that free hydroxyl group Type I is mainly attached in this process. Specific interaction of the benzene molecule occurs with all three types of hydroxyl group (Fig. 3). Molecules of CCl_4 together with free hydroxyl groups on the MgO surface may form hydrogen bonds (16). This conclusion is supported by changes in the values of average adsorption energy \bar{e} (Table 2) calculated from an additive equation:

$$\bar{e} = \sum S_n \cdot e_n$$

where S_n denotes the fraction of the adsorbent surface occupied by the n th type of adsorption centers having an average energy e_n . The values of \bar{e} for the adsorbates on MgO activated at 280°C change as follows: $\bar{e}_{\text{CCl}_4} > \bar{e}_{\text{benzene}} > \bar{e}_{\text{cyclohexane}} > \bar{e}_{\text{hexane}}$. It is concluded that the energy of the hydrogen bond between the CCl_4 molecule and surface OH groups on MgO is greater than the energy of the specific interactions of these groups and the benzene molecule. This indicates that in the chromatographic process the whole geometric surface of the adsorbent is not reacting but only a part of it. The size of the active surface depends on the character of the adsorbate (the size of the molecules and their chemical nature).

In the case of MgO activated at 900°C , it is seen that the energy distribution is exponential and there is only one energetic patch with local heterogeneity. The adsorption centers on the dehydrated MgO surface are constituted mainly by Mg^{2+} ions or the $\text{Mg}—\text{O}$ "ion pair" (17). As seen from an infrared study of dehydrated MgO (17), different environments for this ion are possible, and might arise from different crystal planes exposed at the surface. Molecules of CCl_4 have a high polarizability and possess a dipole moment (16), and they interact with Mg^{2+} surface ions. This can be confirmed if we compare the areas of $\mathcal{X}(e)$ plots for each adsorbate investigated on MgO activated at 900°C . For hexane and cyclohexane these areas are nearly equal, and that means that these active sites are occupied by these molecules in the same way. However, for the CCl_4 molecule the adsorption energy is shifted to 6.5 kJ/mol which supports our previous conclusion that classical Coulomb interactions may contribute largely to the specific interaction energy between the MgO activated at 900°C and such adsorbates. For this adsorbent the overlap of the $\mathcal{X}(e)$ curves for hexane and cyclohexane is large and we propose that for these compounds separated the value of the selectivity coefficient k_c will be small when they are separated by the gas-solid chromatography process. This was confirmed by our experimental results (2). In the case of benzene and cyclohexane, no overlap of the $\mathcal{X}(e)$ curves was observed, and the values of the selectivity coefficient k_c for

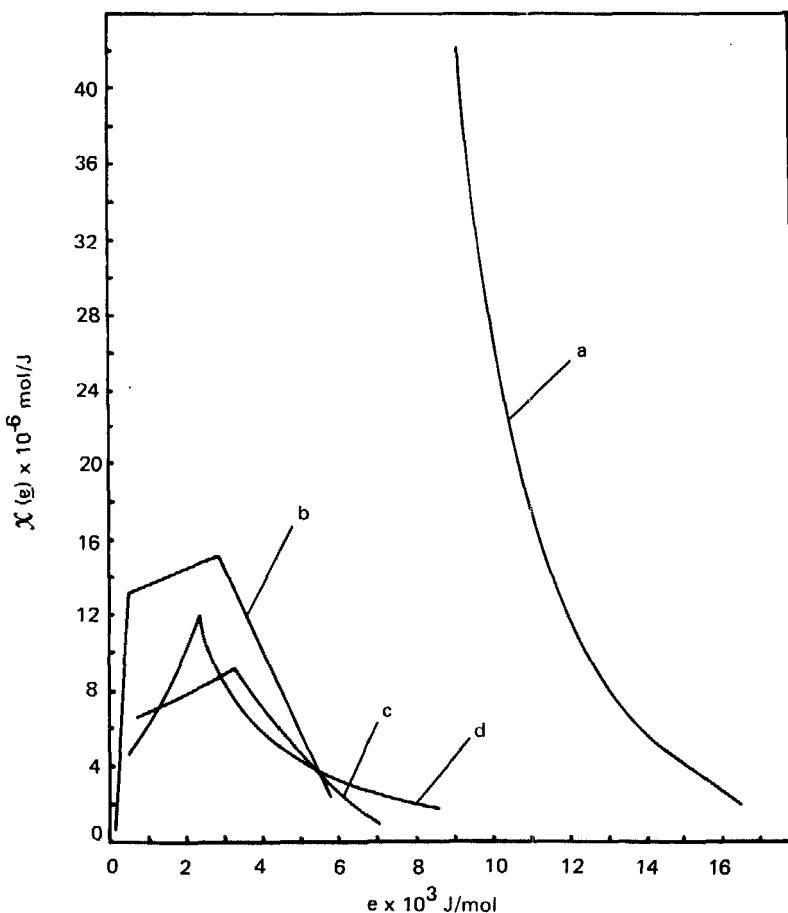


FIG. 5. Energy distribution functions on magnesite activated at 180°C: (a) CCl_4 , (b) cyclohexane, (c) hexane, (d) benzene

these compounds is extremely good (2). These results confirm a previous theoretical study (18).

In Fig. 5, $\chi(e)$ curves for MgCO_3 activated at 180°C are presented. For all adsorbates only one maxima is observed, and we can believe that the MgCO_3 surface is more energetically homogeneous than MgO activated at 280°C. However, the selectivity of MgCO_3 used as a gas-solid chromatography packing is poorer than MgO (2). This phenomenon is caused by the large pore volume of MgCO_3 compared to MgO (Table 1). For MgCO_3 the quasi-Gaussian energy distribution can be matched by a Dubinin-Radush-

kevich isotherm (19, 20). In this case the selectivity coefficient k_c will depend on the B parameter in the DR isotherm which is directly associated with the porous structure of the adsorbent. This conclusion was also predicted theoretically (18).

CONCLUSION

Hydroxyl groups present on the MgO surface have a negative influence on the kinetics of the adsorption-desorption process occurring on this adsorbent when used as gas-solid chromatography packing. The hydroxyl group, especially Type II, disturbs the relationship between the individual types of adsorption centers and their adsorption energy, which leads to a decrease of MgO selectivity. During thermal activation of MgO not only are a better porous structure and a smaller surface area achieved, but also the homogeneous surface is more energetic, which leads to an increase in selectivity for this kind of adsorbent in gas-solid chromatography. A further study of these support materials is desirable in order to evaluate critically the influence of their porous structure on the shape of the energy distribution function.

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