

Enthalpies of sorption of linear hydrocarbons (C₂–C₈) and chloroderivatives of methane and ethylene on the surface of hydrotalcite

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Abstract Differential molar adsorption enthalpies (DMAE) were determined by gas chromatographic measurements of specific retention volume of vapors on the surface of two forms of Mg–Al hydrotalcite. A linear dependence of the DMAE on the number of the carbon atoms in hydrocarbons was observed for both form of hydrotalcite. The dependence of the differential molar adsorption enthalpies on the number of chlorine atoms in organic molecules is discussed. A linear dependence of DMAE on the molecular weight of chloroderivatives of methane and ethylene on the basic form in an order monochloromethane < dichloromethane < trichloromethane or vinylidene chloride < 1,1-dichloroethylene < trichloroethylene was found.

Keywords Adsorption · Differential molar adsorption enthalpy · Gas chromatography · Mg–Al hydrotalcite

Introduction

Hydrotalcite is a natural mineral of relatively rare occurrence belonging to a class of anionic clays (layered double hydroxides). The structure of hydrotalcite is similar to the layered structure of magnesium hydroxide (brucite), where

each Mg²⁺ ion is octahedrally surrounded by six OH[−] ions. The octahedral groupings share edges to form infinite sheets. In hydrotalcite, some Mg²⁺ ions in the hydroxide layers are isomorphously replaced by Al³⁺ cations and the originally electroneutral hydroxide layers acquire a positive charge. The structure of hydrotalcite consists of alternating positively charged brucite-like [Mg_{1−x}Al_x(OH)₂]^{x+} layers and [(CO₃)_{x/2}·nH₂O]^{x−} layers composed of anions and crystal water molecules. Hydrotalcite has relatively good adsorption properties [1].

Behavior of Mg–Al hydrotalcite on heating depends on the Mg/Al ratio and on the kind of anions in the interlayer space [2]. On heating, hydrotalcite releases its interlayer water at 150–200 °C, but the crystalline structure is retained. During the subsequent heating at 350–600 °C, the hydroxyl and carbonate groups are simultaneously transformed into water and carbon dioxide. Heating also results in increase in surface area and pore volume [3, 4]. The layered crystal structure of hydrotalcite collapses to form a predominantly amorphous mixture of Mg and Al oxides. Further increase in temperature up to 900 °C results in crystallization of MgAl₂O₄ [1].

Hydrotalcite can be used as a sorbent for a number of compounds, such as amines, oils, dyes, phenols, ammonia, mercaptans, hydrogen sulfide, sulfur oxides and nitrogen oxides. Hydrotalcite can also be used to remove large anionic contaminants such as Cr₂O₇^{2−}, SeO₃^{2−}, trichlorophenol and radioactive pollutants TcO₄[−], ReO₄[−] and I[−] from solutions [5]. Hydrotalcite is used as an additive in some washing and cleaning agents. Owing to its basicity, hydrotalcite can be employed to remove some substances, such as heavy metal cations from solutions. Hydrotalcite can also be used as a precursor in the production of heterogeneous catalysts [6]. Much work concerns the adsorption of CO₂ on hydrotalcite [7, 8].

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The differential molar adsorption enthalpy (DMAE) [9] or ‘heat of adsorption’ [7], the enthalpy change for adsorption of compounds on the surface of hydrotalcite can be used for quantification of adsorption properties. DMAE can also serve as a criterion of ability to take part in intercalation reactions [9].

DMAE can be determined by gas chromatography. The differential molar enthalpy can be obtained from the relation [9]:

$$\ln V_g = \Delta H/RT + C \quad (1)$$

where V_g is the specific retention volume (mL/g), ΔH the differential molar enthalpy (J/mol), R is the universal gas constant ($R = 8.314$ J/K/mol), T is the thermodynamic temperature (K) and C is a constant. The dependence of $\ln V_g$ on $1/T$ is linear with the slope equal to $\Delta H/R$.

The specific retention volume can be calculated from retention times by the relation [9]:

$$V_g = 3T_0 F_c [(p_i/p_o)^2 - 1] [(t_r - t_m)] / [2T_c W] [(p_i/p_o)^3 - 1] \quad (2)$$

where $T_0 = 273.15$ K, T_c (K) is the column temperature, F_c (mL/s) is the mobile phase flow rate at the column temperature, p_i and p_o are the absolute pressures at the inlet and outlet of the chromatographic column, respectively, t_r (s) is a total retention time and t_m (s) is a retention time of a nonretained compound. W (g) is the weight of the solid adsorbent. Methane was used for nonretained compound.

The aim of this work was to determine DMAE of hydrocarbons and chloroderivatives of methane and ethylene on hydrotalcite prepared by precipitation from sulphates. This preparation method is used less than the industrial production from chlorides [10]. The product prepared from chlorides usually has better crystallinity and purity, because chlorides have smaller ability to be absorbed into molecules of hydrotalcite than sulfates. Hydrocarbons and derivatives of methane and ethylene were chosen to determine the influence of the structure and bonds in adsorbates on adsorption ability of hydrotalcite. Gas chromatography was used for determination of DMAE.

Experimental

Preparation of hydrotalcite from sulfates

Eight-hundred milliliter of an aqueous solution containing magnesium sulfate (165 g $MgSO_4 \cdot 7 H_2O$, 0.667 mol) and aluminum sulfate (110 g $Al_2(SO_4)_3 \cdot 18 H_2O$, 0.165 mol)

was added with vigorous stirring into 800 mL of a solution containing 132 g of Na_2CO_3 and 40 g of NaOH. The addition took about 1 h. During the synthesis the temperature was maintained at 70 °C. After precipitation the product was washed twice with a water solution of Na_2CO_3 (5 g of Na_2CO_3 per 1 L) and seven times with distilled water. Volume of each wash solution was 1 L. The product was dried at 105 °C. The product prepared from sulfates contains 20.0 wt.% Mg, 10.5 wt.% Al, the content of sulfates was 1.0 wt.%. This compound is further denoted as a basic form. A part of the product was dehydrated by heating to 225 °C for 6 h in nitrogen atmosphere. This sample is denoted as a dehydrated form. For these two forms some authors [2] use terms Phase I and Phase II, respectively.

Preparation of hydrotalcite from chlorides

Thousand milliliter of an aqueous solution containing magnesium chloride (135 g of $MgCl_2 \cdot 6 H_2O$, 0.667 mol) and aluminum chloride (80 g of $AlCl_3 \cdot 6 H_2O$, 0.333 mol) was added with vigorous stirring into 1,000 mL of a solution containing 132 g of Na_2CO_3 and 60 g of NaOH. The addition took about 1 h. During the synthesis the temperature was maintained at 70 °C. After precipitation the product was washed three times with distilled water. Volume of each wash solution was 1 L. The product was dried at 105 °C. The product prepared from chlorides contains 20.5 wt.% Mg, 10.7 wt.% Al, This product was prepared for a comparison of some chemical properties of the product prepared from sulphates and the product prepared from chlorides whose properties are very often published [1–4].

Thermal measurements

Thermogravimetric analysis was carried out in nitrogen with an Auto TGA 2950 analyzer (TA Instruments, USA) with a heating rate of 10 K/min and flow rate of 10 mL/min. The weight of the sample was about 20 mg. Measurements were carried out on two samples of hydrotalcite—one of them prepared from chlorides and the other from sulfates. The aim is to compare thermal behavior of these two samples and also to find a temperature range in which these forms of hydrotalcite are stable.

Powder X-ray diffraction

Powder data were obtained with a D8-Advance diffractometer (Bruker AXE, Germany) with $CuK\alpha$ radiation with

secondary graphite monochromator. Diffraction angles were measured from 10° to 70° (2θ).

Surface area determination

Surface areas were determined with a BET equation on one-point N_2 gas adsorption isotherms. The samples were degassed at 100°C (the basic form) and 250°C (the dehydrated form) for 1 h. A MICROMERITICS RAPID SURFACE AREA ANALYZER 2200A (USA) was used to determine the surface area at temperatures below -196°C and 0°C using N_2 as the adsorbate.

DMAE measurements

The differential molar adsorption enthalpies were measured for two forms of hydrotalcite prepared from sulphates—the basic form that is stable up to 120°C , and the dehydrated form created by the release of interlayer water. The retention times were measured by gas chromatography with a CHROM 4 chromatograph, where the glass column of the gas chromatograph was filled with hydrotalcite. The length of the column was 120 cm, the diameter 3 mm. The total weight of hydrotalcite in the column was 3.71 g. Before starting the measurement, the chromatographic column was heated to 130°C (the basic form) or 225°C (the dehydrated form) in a nitrogen flow for 6 h. The carrier gas was also nitrogen. The flow rate of the carrier gas was 70 mL/min and was kept constant in each series of measurements. The adsorbates were injected in the form of liquids or gases. The injection volume was $0.1\ \mu\text{L}$ in the case of the liquids and $10\ \mu\text{L}$ in the case of gases. The temperature of the injection chamber was 160°C . The flame ionization detector was used for the detection of the species in the outlet. The retention times of various adsorbates were measured at 73 – 135°C for the basic form and 150 – 225°C for the dehydrated form. DMAE was determined from the linear dependence of logarithm of the retention volume on the reciprocal value of thermodynamic temperature—Eq. (1). The retention volume was calculated from Eq. (2). Measurements were conducted in Henry's region.

Adsorbates

Ethane ($\geq 99.95\%$ (GC)), butane ($\geq 99.0\%$ (GC)), pentane ($\geq 95.0\%$ (GC)), heptane ($\geq 99.0\%$ (GC)), hexane ($\geq 97.0\%$ (GC)), octane ($\geq 95.0\%$ (GC)), methylchloride ($\geq 99.95\%$ (GC)), dichloromethane ($\geq 99.8\%$ (GC)), trichloromethane ($\geq 99.5\%$ (GC)), tetrachloromethane ($\geq 99.8\%$ (GC)), vinyl chloride ($\geq 99.95\%$ (GC)), 1,1-dichloroethylene ($\geq 99.5\%$ (GC)), cis-1,2-dichloroethylene ($\geq 97.0\%$), trans-1,2-dichloroethylene ($\geq 98.0\%$ (GC)), trichloroethylene ($\geq 99.5\%$ (GC)), tetra-

chloroethylene ($\geq 99.5\%$ (GC)) were purchased by SIGMA-ALDRICH and used as received.

Results and discussion

The TG curves of both samples are shown in Fig. 1. Hydrotalcite prepared from chlorides has better crystallinity (see powder X-ray diffractograms in Fig. 2) and is more thermally stable. This curve agrees with published curves [11]. Interlayer water of the sample prepared from sulphates begins to release at lower temperature. Owing to the small content of sulphates this sample has a greater basal spacing [8]. That is why it is easier to release the water molecules from the interlayer space. On heating to 120°C the weight of sample decreases only about 3 wt.% from water lost from pores and surface [12]. Next 12 wt.% of weight loss represents interlayer water released at 120 – 220°C . The layer structure is not destroyed but basal spacing is slightly decreased [2, 13]. The dehydration process may involve several stages: the breaking of bonds among brucite layers, anions and water molecules; the slight deformation of initial crystal lattice. The changes of the structure of hydrotalcite caused by the heating to about 200°C were confirmed by the determination of the surface area. The surface areas of the basic and dehydrated forms are $91\ \text{m}^2/\text{g}$ and $102\ \text{m}^2/\text{g}$, respectively.

Hydrotalcite has a tendency to adsorb moisture from the air; this moisture is very easily released during heating up to 60°C [12]. Adsorbed water affects the sorption behavior of hydrotalcite and reproducibility of the measurement of the retention volume. The dependence of the retention volume of dichloromethane on time is given in Fig. 3. Heating of the chromatographic column at 94°C in a nitrogen flow for about 6 h is sufficient to ensure the reproducibility of the measurement. The conditions of this

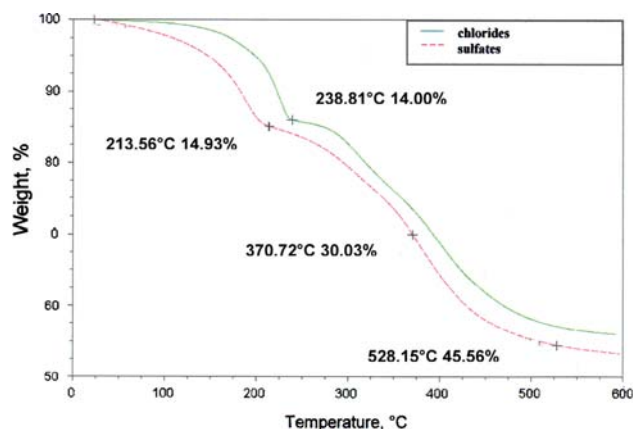


Fig. 1 TG curves of the hydrotalcite samples prepared from chlorides and sulfates

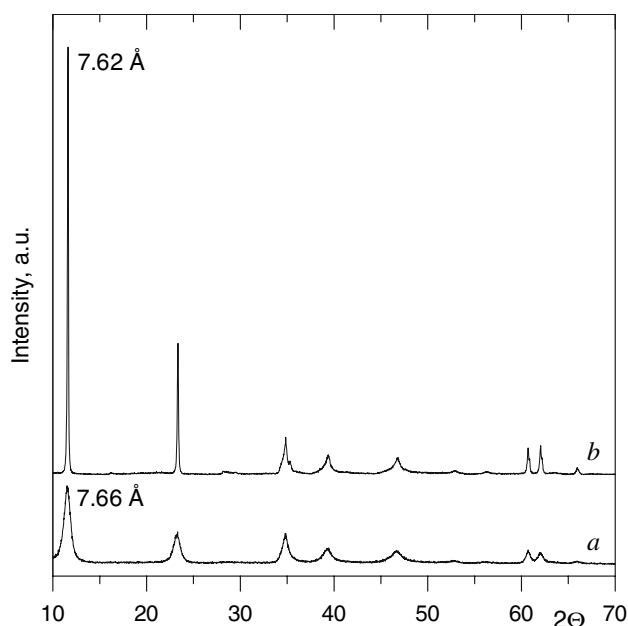


Fig. 2 Diffractograms of hydrotalcites prepared from sulfates (a) and chlorides (b)

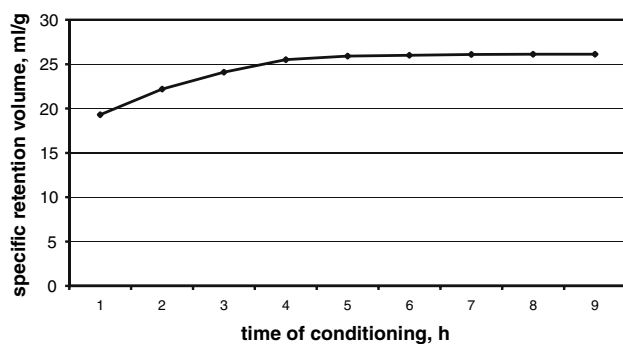


Fig. 3 Conditioning of the sample. The dependence of the retention volume of dichloromethane on the conditioning time at 94 °C

process should be sufficient [4] to release all water from the pores of hydrotalcite.

Measurements of differential molar adsorption enthalpy

The differential molar enthalpies (DMAE) of chloroderivatives of methane (monochloromethane, dichloromethane, trichloromethane, tetrachloromethane) and ethylene (vinylidene chloride, 1,1-dichloroethylene, cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, tetrachloroethylene, trichloroethylene) were determined. Unbranched hydrocarbons (C₂–C₈) were tested for comparison. Table 1 shows some parameters of the measurements and DMAE for individual adsorbates. The dependence of the logarithm

of the retention volume on reciprocal temperature is linear for all tested adsorbates and for both forms of hydrotalcite.

The dependence of DMAE of hydrocarbons on their molecular weight (m_w) is linear for both hydrotalcite forms: $\Delta H = 0.426m_w + 1.3$ ($R^2 = 0.9999$) for the basic form and $\Delta H = 0.589m_w - 4.3$ ($R^2 = 0.9997$) for the dehydrated form. The dependence of DMAE on the number of the carbon atoms in the molecule (n_c) is also linear, $\Delta H = 6.0n_c + 1.3$ ($R^2 = 0.9999$) for the basic form. Extension of the aliphatic chain by one methylene group increases the $-\Delta H$ value by about 6 kJ/mol. This result means that the molecules are anchored to the adsorbent only by van der Waals forces and adhere to the adsorbent surface by the whole lengths of the carbon backbones. The hydrogen atoms of hydrocarbons interact with the oxygen atoms on the surface of hydrotalcite. For the dehydrated form, the dependence of DMAE is described by $-\Delta H = 8.27n_c - 4.3$ ($R^2 = 0.9997$). Extension of the aliphatic chain by one methylene group increases $-\Delta H$ by about 8.3 kJ/mol. This value is higher than that for the basic form. The higher value of DMAE results from a larger surface area, greater density of positive charge on the surface, greater ability to polarize hydrocarbon chains, the lack of hydrogen bonds between oxygen atoms of the molecules of interlayer water and hydrogen atoms of brucite-like layers that causes higher ability of surface to interact with partially polarized molecules of hydrocarbons.

The values of DMAE of chloroderivatives of methane are about four times higher than DMAE of ethane. There is not only a weak physisorption, but also stronger interaction because of dipole moments on the molecules of derivatives. The dependence of ΔH on the molecular weight is linear for the adsorption on the basic form and replacement of one hydrogen atom by a chlorine atom increases ΔH by about 8.5 kJ/mol in an order monochloromethane < dichloromethane < trichloromethane. ΔH of tetrachloromethane is lower than extrapolated from the linear dependence. It can be presumed that the molecules of the derivatives adhere to the adsorbent surface by the plane of the tetrahedron and an increase of the number of the chlorine atoms in this plane increases the density of a partial negative charge of this plane and also increases affinity of the molecule to adsorb itself on the surface. In case of tetrachloromethane, the fourth chlorine atom does not increase the number of the chlorine atoms in the plane and decreases the dipole moment of the molecule and thus decreases the force for adsorption. In the case of the adsorption on the dehydrated form, the values of DMAE are similar for all tested chloroderivatives. They are higher than those for the adsorption on the basic form with exception of trichloromethane. The reasons for higher DMAE on dehydrated form than basic form are similar to those for hydrocarbons. In this case the

Table 1 Differential molar adsorption enthalpy (DMAE) and the temperature ranges of measurement

			Basic form	Dehydrated form
	Boiling point (°C)	Molecular weight (g/mol)	DMAE (kJ/mol)	DMAE (kJ/mol)
Chloromethane	–24	50.49	32.3 ± 0.4	45.0 ± 0.5
Dichloromethane	40	84.93	41.0 ± 0.4	45.2 ± 0.6
Trichloromethane	61	119.38	49.5 ± 0.6	45.1 ± 0.4
Tetrachloromethane	77	153.82	41.9 ± 0.4	45.2 ± 0.5
Vinylidene chloride	–14	62.50	30.5 ± 0.2	46.2 ± 0.2
1,1-dichloroethylene	60–61	96.94	36.6 ± 0.6	45.7 ± 0.8
Trans-1,2-dichloroethylene	47–49	96.94	39.7 ± 0.6	47.9 ± 0.3
Cis-1,2-dichloroethylene	30–32	96.94	51.8 ± 0.5	49.8 ± 0.8
Trichloroethylene	86–88	131.39	42.4 ± 0.5	47.7 ± 0.5
Tetrachloroethylene	121	165.83	41.9 ± 1.0	50.6 ± 0.8
Ethane	–88.6	30.07	14.0 ± 0.5	13.4 ± 0.5
Propane	–42.2	44.10	20.2 ± 0.4	21.8 ± 0.8
Butane	–0.5	58.12	26.2 ± 0.5	29.6 ± 0.9
Pentane	36.1	72.15	31.8 ± 0.7	38.6 ± 0.9
Hexane	68.7	86.18	38.0 ± 0.3	46.0 ± 0.8
Heptane	98.4	100.20	44.1 ± 0.9	55.0 ± 0.5
Octane	126	114.23	–	63.0 ± 0.6

higher density of positive charge on the hydrotalcite surface is more important than the fact that dehydrated form has larger surface area.

The values of DMAE of chloroderivatives of ethylene are similar to DMAE of chloroderivatives of methane for the adsorption on both forms of hydrotalcite (see Table 1). The presence of the double bond has not a great influence on DMAE. This is reasonable, because Mg–Al hydrotalcite does not contain a metal with suitable free orbitals for interaction with π electrons from the double bond of the ethylene derivatives. There is obviously only a small influence of these π electrons to the other chlorine atoms that reduces their ability to interact with the positively charged surface of the adsorbent and that is why the DMAE values of chloroderivatives of ethylene are only about 2 kJ/mol lower than DMAE of chloroderivatives of methane. The dependence of DMAE on the number of the chlorine atoms is linear and a replacement of hydrogen by a chlorine atom increases ΔH by about 6 kJ/mol in an order vinylidene chloride < 1,1-dichloroethylene < trichloroethylene. It may confirm that the molecules of chloroderivatives of ethylene adhere by the plane of the whole molecule on the surface of the adsorbent and all chlorine atoms interact with the surface of hydrotalcite.

In the case of adsorption on the dehydrated form of hydrotalcite, the DMAE are about by 10 kJ/mol higher than those of the basic form with the exception of cis-1,2-dichloroethylene. The reasons of this are similar to chloroderivatives of methane. Nevertheless, a linear dependence of ΔH on the number of the chlorine atoms

was not observed. The adsorbed molecules are not adhered in the same way as in the case of the basic form. Influences like polarizability of the molecule and changes in dipole moment are more important than number of chlorine atoms or orientation of planar molecule of derivatives to the surface.

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