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Adsorption properties of surface iron oxide modified with stearic acid and octadecylamine

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Abstract. The adsorptive properties of iron oxide modified with stearic acid and octadecylamine have been studied by gas chromatography. Henry's constants of acetonitile, alcohols, aromatic hydrocarbons, ethers, ketones, n-alkanes and nitromethane have been determined. Kovats indices and the values of initial differential adsorption heats have been calculated. The modification of γ-iron oxide surface causes a decrease of adsorptive activity with respect to the substances molecules of which are characterized by high electronic density.

INTRODUCTION

The broad study of modified iron oxides has been caused by wide application of them in the production of magnetic memory carriers for the computers and also of pigments for varnish-and-paint industry. Since the purpose of γ-iron oxide modification is the preparation of materials with stable properties, a modifier layer is need strongly to bound up with the surface. As a results of the chemical modification we may obtain the materials with the specified properties of surface. The structure of modifying layer has an essential effect on the surface properties namely on homogeneity, polarity and accessibility of a surface for binder molecules. In this work we studied the adsorption properties of γ-iron oxide surface, modified with stearic acid (SA) and octadecylamine (ODA).We used method of gas chromatography. Adsorption characteristics of various organic substances gave a possibility to determine the surface affinity to various adsorbates, to estimate the degree of surface heterogeneity and to trace the influence of chemical structure of adsrptive molecules on the interaction with γ-Fe_2O_3 surface.

EXPERIMENTAL

Samples. The commercial γ-iron oxide sample (F) was characterized by specific surface area 20 m^2/g. Before the chromatography experiments it was heated at 300°C in helium flow during 4 hours.The sample SAF was obtained by liquid phase adsorption of SA from toluene solution on F oxide. Maximum adsorption value of SA was 10 mg/g. The sample ODAF was prepared in result of ODA adsorption from CCl_4 solution on F surface. Adsorption amount of ODA was consisted 70 mg/g. The preparation and colloid properties of SAF and ODAF samples were described in /1/.

Apparatus. The experimental study was carried by gas chromatograph TSVET-162 (MPO Khimavtomatika, Russia) with flame ionization detector. The gas-carrier (helium) flow rate was 30 cm^3/min.We used glass columns 500x5 mm, sample masses in the column were to 0.5 g (fractions 0.25-0.50 mm). Preliminary the samples were heated in He flow at 100°C.

RESULTS AND DISCUSSION

1. Hydrocarbons

The retention volumes V of small doses of adsorbates with various polar functional groups give a possibility to estimate the completeness of the modification, and the polarity of residual adsorption active centres of iron oxide surface and the structure of modifying layer. Chromatographical peaks obtained for all studied substances were narrow and symmetrical ones. The table1 contains the values of retention volumes V and initial differential heats $-\delta U$ for adsorption of n-alkanes and benzene on modified ODAF and SAF samples and on initial iron oxide for comparison.

Table 1. Values of retention volumes V, and differential adsorption heats $-\delta U$ of hydrocarbons on initial (F) and modified γ-Fe_2O_3 samples

ADSORBAT	V, cm^3/g, 100 °C			$-\delta U$, kJ/mole		
	ODAF	SAF	F	ODAF	SAF	F
n-Hexane	1.1	2.8	16.8	31	34	41
n-Heptane	2.9	5.2	50.1	36	40	46
n-Octane	5.6	11.0	155.0	39	43	49
n-Nonane	11.4	24.2	465.0	42	51	54
Benzene	1.8	4.4	108.2	33	42	38

It is seen from the table, that values V are less for samples of SAF and ODAF than ones for the initial one. The modification of γ-iron oxide surface decrease adsorption energy of n-alkanes, which are capable only to dispersion interaction with both the iron oxide surface and with grafted chains of modifier. However the $-\delta U$ values indicated in Table 1 give a possibility to make additional suppositions on the modifying layer structure and namely the decrease of V values indicate a considerable decrease of adsorption centres with the quantity on oxide surface. Adsorption of benzene molecules which are able to the specific interaction with modified samples remains higher than that of n-hexane. But the modification of γ-oxide surface with SA and ODA causes the convergence of Henry's constants of benzene and n-hexane comparing with the initial sample, which shows a decrease the specificity of iron oxide surface. The decrease of benzene adsorption is, probably, related with the alterations of the surface chemistry with the and character of interaction with sample modified with SA and ODA.The substitution and the screening of accepter centres of surface γ-iron oxide with grafted alkyl radicals causes a decrease of contribution of specific interaction in case of benzene adsorption. The sensitivity tests for residual inhomogeneity of γ-iron oxide surface are the substances with polar functional groups in molecules namely alcohols, diethylether, ketones, nitroalkanes and others. These molecules are capable of strong specific interaction with active centres of γ-Fe_2O_3 surface.

2. Polar compounds

Early it was shown /2-5/ for dehydroxylated γ-iron oxide it was observed activated reversible chemisorption of organic molecules of which have free electron pairs near heteroatoms of oxygen, nitrogen, such and as diethylether, triethylamine and acetonitrile. We can difference two types of adsorption interactions with oxide surface modified with ODA and SA: specific interaction with residual accepter centres on γ-iron oxide surface and nonspecific interaction with grafted hydrocarbon chains of modifier molecules.The retention values

Table 2. Values V, I, -δU and δ(-δU) for polar molecules on γ-Fe_2O_3, modified with ODA and SA.

ADSORBAT	V, 100 °C		I, 100 °C		-δU		δ(-δU)	
	ODAF	SAF	ODAF	SAF	ODAF	SAF	ODAF	SAF
Benzene	1.8	4.4	649	690	33	42	5	12
Toluene	4.4	8.3	762	791	37	45	5	8
Ethylbenzene	8.3	18.6	853	891	41	48	5	5
Diethylether	0.5	2.8	563	652	24	36	0	24
Acetone	1.3	12.5	612	842	22	37	3	21
MEK	2.1	22.1	666	911	33	43	10	20
Nitrometane	4.3	10.0	759	814	34	42	20	28
Nitropropane	6.6	29.5	823	-	40	52	17	21
Methanol	62.9	-	1108	-	18	-	6	-
Ethanol	34.8	-	1027	-	30	-	18	-
Acetonitrile	2.5	-	685	-	45	-	19	-

for all test substances for the sample modified with SA are higher than those for the sample modified with ODA (Table 2).

The retention volumes V of n-alkanes (Table 1) have shown that the ODAF sample surface is coated with more dense layer of modifier. In results of this the accessibility of ODAF surface for polar molecules is less than one of SAF surface. In this case small molecules with large dipole moment μ (nitrometane-μ=3,44, acetonitrile-μ=3,96) are adsorbed specifically on γ-iron oxide surface modified with ODA and SA. The comparison of retention volumes on SAF sample indicates that the quantity of accepter centres on the surface is higher, since the interaction of comparatively large molecules of methylethylketone, benzene, diethylether, is characterized by values V and I which was higher than those for ODAF sample.The contribution of the specific interaction to the adsorption energy is characterized by the Kovats indices calculated from the on the samples of ODAF and SAF. It should be noted, that the nature of residual accepter centres of ODAF and SAF surfaces is different what is seen from the comparison of retention values. Methylethylketone interacts strongly with he ODAF surface, but nitromethane molecules are ls strongly adsorbed on iron oxide surface, modified with SA. The comparison of adsorption values for ODAF and SAF samples in relation to the esters shows that active surface centers which are able to were screened by the modifier chains to a various degree. This considerable difference of ether adsorption on initial γ-iron oxide sample indicates the screening of unsaturated cations Fe(3+), irreversible specific adsorption of diethylether. Additional suppositions about the interaction of polar molecules with iron oxide surface, modified with SA and ODA can obtained from the differential of adsorption heats, calculated from the temperature dependence of retention volumes. For polar molecules the values -δU on SAF sample are higher, than ones on ODAF sample. Another order of -δU values is observed for ODAF sample ,which indicates the differences of surface properties of ODAF and SAF samples. The contribution of specific interaction energy to total adsorption energy was calculated as the difference of values -δU of polar molecules and hypothetic n-alkane relating to the same value polarizability α. It is seen from Table 2 that for diethylether the value δ(-δU) on the ODAF sample equel to zero. In case of adsorption on the sample modified with SA ethers molecules penetrate to surface of γ-iron oxide and interact specifically with cation Fe(3+), values δ(-δU) are equal to 12 kJ /mole.Benzene molecules practically interact with surface of iron oxide modified with OAF in the accordance with dispersion mechanism since the contribution of specific interaction energy less than 6 kJ /mole probably.

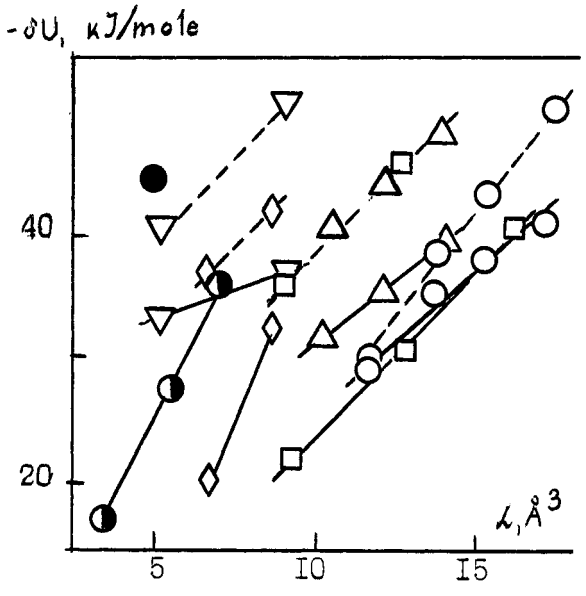

Fig.1

Dependence of differential energy of adsorption -δU upon of molecules polarizability on γ-iron oxide, modified with ODA (solid line) and SA (broken line). ○ n-alkanes, △ alkylbenzene, □ ethers, ▽ nitroalkanes, ◇ ketones, ◑ alcohols ● acetonitrile.

Molecules acetonitrile, ethanol and nitromethane penetrate through a ODA layer to surface active centers of γ-iron oxide and form strength adsorption complexes with summary energy of 45, 40 and 34 kJ/ mole respectively.The contributions of specific interaction energy are 19, 18 and 20 kJ /mole respectively.Iron oxide, modified withmoleculesSA shows the ability to specific interaction with benzene, ethylbenzene and toluene molecules with δ(δ-U) energy which are equal to 12, 5 and 8 kJ /mole respectively. Molecules of acetone, diethylether and nitromethane interact specifically with γ-iron oxide surface modified with SAF. The values δ(-δU) are to equal 24, 21 and 28 kJ/mole respectively. The obtained results give a possibility to characterize quantitatively the alteration of adsorption properties of iron oxide surface after the modification with molecules of SA and ODA.

CONCLUSION

Thus on the basis of the results of chromatoraphic studies it is possible to say that in case of modification of γ-iron oxide surface with long chain ODA and SA molecules the active centers with strongly expressed electron-acceptor properties are screened by the formation of surface modifier layer.The residual centres are considerably weakened and almost unaccessible for the interaction with polar molecules.In an result on what adsorption of diethylether, acetonitrile, ketones, nitroalkanes has the reversible character in the comparison with one on initial γ-iron oxide.

REFERENCES

1. S.A. Sosnina, G.S. Matrosova, S.N. Tolstaya, Lakokrasochnye materialy, 4, 28-31, (1989).
2. N.V. Kovaleva, E.F. Levina, YU.S. Nikitin, I.S. Protonina, Zh. Fiz. Khim.,63, 2667-2671, (1989).
3. E.V. Zagorevskaya, N.V. Kovaleva, N.S. Kulikova, Yu.S Nikitin, I.S. Protonina, B.V. Scherbinin, Zh .Fiz. Khim., 63, 3289-3291, (1989).
4. B.V Kuznetsov, Yu.S. Nikitin, T.A. Rakhmanova, E.A. Simanovich Zh. Fiz. Khim., 64, 1761-1765, (1990).
5. Modificirovannye kremnezemy v sorbcii, katalize i khromatographii, (Ed. Lisichkin), Moskva, Khimia, (1986), (in Russian)