Gas-solid Interaction

V. Specific and Non-specific Interactions in the Adsorption of Hydrocarbons on Magnesium Oxide and other Ceramic Oxides [○, *]

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The heats of adsorption on magnesium oxide of six linear chain alkanes (C_4 to C_9), of the corresponding 1-mono-olefins and of the cyclic compounds cyclohexane, cyclohexene, 1.4-cyclohexadiene and benzene have been determined by gas-solid chromatography and extrapolated to zero surface coverage.

The values obtained with n-alkanes are linearly dependent on the carbon atom number. By comparison with previous results for alumina and silica-gel, it is seen that the dispersion-interaction adsorption potentials for the CH_3- and CH_2-groups take very close values on the three different oxides.

As for the cyclic molecules, a constant increment of about 1.40 kcal/mole in the heat of adsorption on MgO is observed when passing from cyclohexane to cyclohexene and from the latter to 1.4-cyclohexadiene, in full agreement with the rrsults for Al_2O_3.

The values for benzene are intermediate between those for cyclohexene and those for 1.4-cyclohexadiene. These results are interpreted in view of a specific interaction of electrostatic nature between surface hydroxyls and π-electron systems.

With linear 1-alkenes, the specific contribution becomes more apparent with increasing chain length, the difference in the heats of adsorption reaching a value of 1.50 kcal/mole for the pair 1-nonene n-nonane.

It was observed that the heats of adsorption of water on the surfaces of MgO (basic), Al_2O_3 and SiO_2 (acidic) take comparable values [1–3]. This might seem rather surprising, in view of some opposite features of the above oxides.

In first place the greater ionic character of the MgO surface as compared with the covalent SiO_2 should cause quite a different mechanism of water adsorption, this being definitely of a dissociative type for SiO_2, while no dissociation of sorbed water molecules should occur with MgO [1] (Al_2O_3 possibly representing an intermediate case).

Secondly, surface hydroxyls or surface cationic vacancies are postulated for the 1 : 2 and 2 : 3 type oxides in order to satisfy the stoichiometric requirements of the crystal co-ordination; obviously this is not necessary for the 1 : 1 MgO structure [1, 4, 5].

On the other hand, some preliminary comparisons [6] between measured systematic data of adsorption heats for saturated hydrocarbons on Al_2O_3 and other available data for SiO_2 and MgO seemed to point out that in the considered systems only the dispersion interactions are effective and that they are of similar magnitude on the three oxides. However, the scantiness and inhomogeneity (particularly for MgO) of the literature data employed in the comparison [7] did not allow to draw definitive conclusions. At least for the alkane adsorption on MgO a direct experimental investigation appeared desirable. In the meanwhile, data of the adsorption heats

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[6] M. SANESI and V. WAGNER, Z. Naturforsch. **23 a**, 979 [1968].

[7] See Ref. [6], Table 3.

of some linear and cyclic olefins on Al_2O_3 have become available[8], thus enabling to extend the comparison to the specific interaction field.

For these reasons we have planned a systematic measurement of adsorption heats for both saturated and unsaturated hydrocarbons on MgO. In this work the heats of adsorption determined by the GSC technique for six linear alkanes and the corresponding 1-mono-olefins (from C_4 to C_9) and the four cyclic compounds cyclohexane, cyclohexene, 1.4-cylohexadiene and benzene are reported.

Experimental

The adsorbent was a sample of MgO from C. Erba S. p. A. (Milan) of RP grade. From chemical and spectroscopical analysis it resulted practically free of water, with a CO_3^{--} content of ca. 0.5%, while alkali-, earth-alkali- and transition metals and halogens were contained in trace amounts. Before the measurements, the MgO was heated at 450 °C for 24 hours. After packing, the chromatographic columns were flushed by a stream of carrier gas for 6 hours at 120 °C.

Adsorbate	Temperature range [°C]	Flow rate [ml/min]	Pressure drop range [atm]
n-butane	80—130	30	0.69—0.83
n-pentane	120—170	30	0.79—0.92
n-hexane	130—180	50	1.35—1.50
n-heptane	150—200	50	1.59—1.87
n-octane	170—220	50	1.47—1.66
n-nonane	190—230	50	1.51—1.68
1-butene	90—140	30	0.72—0.84
1-pentene	120—170	40	1.06—1.35
1-hexene	140—190	50	1.48—1.66
1-heptene	170—210	50	1.49—1.67
1-octene	180—220	50	1.56—1.75
1-nonene	190—230	50	1.66—1.88
cyclo-hexane	120—180	50	1.37—1.66
cyclo-hexene	140—200	50	1.31—1.54
benzene	160—210	50	1.48—1.57
1.4-cyclohexadiene	150—200	50	1.32—1.49

Table 1. Gas-chromatographic conditions.
Carrier gas: hydrogen.
Column: stainless steel, length 1 m, i. d. 0.6 cm.

The adsorbate hydrocarbons were the same employed in both previous papers[6, 8].

The heats of adsorption of the considered compounds on MgO, have been determined by a gas chromatographic method, according to the procedure previously described[6]. The experimental conditions are summarized in Table 1.

n-butane	μmole	1.06	2.12	4.24	10.61	21.22	
	Q_a	6.65	6.55	6.48	6.28	6.00	
	S_Q	0.22	0.18	0.15	0.14	0.17	
n-pentane	μmole	0.89	2.68	4.47	6.26	8.94	17.88
	Q_a	7.59	7.58	7.57	7.54	7.30	6.86
	S_Q	0.08	0.04	0.14	0.10	0.10	0.03
n-hexane	μmole	0.77	2.30	3.83	5.36	7.65	15.30
	Q_a	9.03	8.53	8.39	8.35	8.19	7.98
	S_Q	0.17	0.17	0.13	0.14	0.18	0.10
n-heptane	μmole	0.70	2.09	3.40	4.87	6.96	13.92
	Q_a	9.89	9.17	8.82	8.67	8.52	8.42
	S_Q	0.47	0.36	0.25	0.25	0.28	0.31
n-octane	μmole	0.63	1.88	3.13	4.38	6.25	12.50
	Q_a	11.07	10.70	10.63	10.57	10.39	9.97
	S_Q	0.06	0.19	0.16	0.16	0.18	0.22
n-nonane	μmole	0.57	1.70	2.84	3.98	5.68	11.36
	Q_a	12.44	12.42	12.20	12.02	11.97	11.82
	S_Q	0.19	0.14	0.25	0.18	0.14	0.22
1-butene	μmole	1.32	2.64	5.28	13.19	26.38	
	Q_a	6.62	6.56	6.46	6.22	5.78	
	S_Q	0.12	0.17	0.16	0.19	0.19	
1-pentene	μmole	0.92	2.76	4.60	6.45	9.21	18.42
	Q_a	7.87	7.84	7.78	7.67	7.44	7.13
	S_Q	0.18	0.11	0.13	0.12	0.15	0.07
1-hexene	μmole	0.80	2.40	4.00	5.60	8.00	16.00
	Q_a	9.60	9.39	9.25	8.95	8.86	8.51
	S_Q	0.36	0.27	0.39	0.18	0.12	0.08
1-heptene	μmole	0.72	2.17	3.62	5.07	7.24	14.48
	Q_a	10.96	10.78	10.75	10.61	10.43	9.94
	S_Q	0.24	0.14	0.22	0.17	0.11	0.22
1-octene	μmole	0.64	1.91	3.19	4.47	6.38	12.76
	Q_a	12.25	12.09	11.91	11.75	11.78	11.71
	S_Q	0.61	0.31	0.25	0.27	0.27	0.38
1-nonene	μmole	0.59	1.76	2.93	4.10	5.86	11.72
	Q_a	13.85	13.64	13.16	12.96	12.76	12.66
	S_Q	0.22	0.19	0.05	0.23	0.25	0.42
cyclo-hexane	μmole	0.92	2.77	4.62	9.25	18.50	
	Q_a	8.55	8.51	8.27	7.83	7.60	
	S_Q	0.22	0.27	0.15	0.27	0.25	
cyclo-hexene	μmole	0.99	2.96	4.93	6.91	9.87	19.74
	Q_a	10.01	9.61	9.53	9.45	9.26	9.02
	S_Q	0.33	0.30	0.29	0.32	0.28	0.25
benzene	μmole	1.12	3.37	5.62	7.87	11.25	22.50
	Q_a	10.77	10.86	10.36	10.27	9.98	9.75
	S_Q	0.10	0.26	0.21	0.19	0.08	0.15
1.4-cyclo-hexa-diene	μmole	3.17	5.28	7.40	10.58	21.14	
	Q_a	11.08	10.61	10.21	9.93	9.22	
	S_Q	0.16	0.13	0.11	0.16	0.15	

Table 2. Heats of adsorption, Q_a, and standard deviations, S_Q, (kcal/mole), measured for different sample amounts.

Strictly linear plots of log (retention time) vs. $1/T$, were always obtained, analogous to those reported in previous papers[6, 8]. The adsorption heats, Q_a, calculated for different injected amounts, are reported in Table 2, together with the standard deviations, S_Q. From the plots of these Q_a values vs. injected amounts (Fig. 1) the final Q_a values at zero coverage, reported in Table 3, were obtained by graphical extrapolation.

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[8] M. Sanesi and V. Wagner, Z. Naturforsch. **25 a**, 688 [1970].

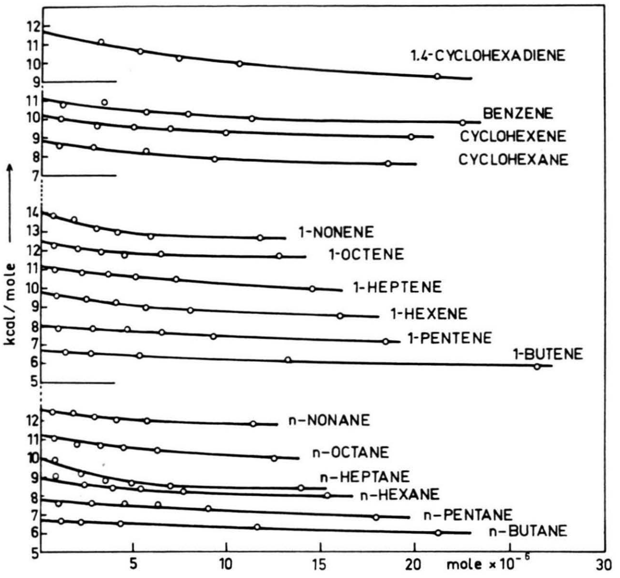

Fig. 1. Change of the chromatographic heat of adsorption with injected sample amount.

Adsorbate	Q_a (kcal/mole)	Adsorbate	Q_a (kcal/mole)	Adsorbate	Q_a (kcal/mole)
n-butane	6.60	1-butene	6.70	cyclohexane	8.80
n-pentane	7.70	1-pentene	8.00	cyclohexene	10.20
n-hexane	8.90	1-hexene	9.70	1.4-cyclo-hexadiene	11.60
n-heptane	10.00	1-heptene	11.10	benzene	11.10
n-octane	11.20	1-octene	12.40		
n-nonane	12.50	1-nonene	14.00		

Table 3. Heats of adsorption at zero coverages for hydrocarbons on MgO.

Discussion

In Fig. 2, the Q_a values for the systems of alkanes with MgO, Al_2O_3 [6] and SiO_2 [9] are intercompared as functions of the carbon atom number n_C. A straightforward analogy between the considered systems is apparent. The straight-line equation for the MgO systems is:

$$Q_a = 1.85 + 1.17\, n_C \qquad (4 \leqq n_C \leqq 9) \qquad (1)$$

while for Al_2O_3 [6] and SiO_2 [9] the equations respectively are:

$$Q_a = 2.12 + 1.21\, n_C \qquad (4 \leqq n_C \leqq 9) \qquad (2)$$

$$Q_a = 1.50 + 1.24\, n_C\,. \qquad (3)$$

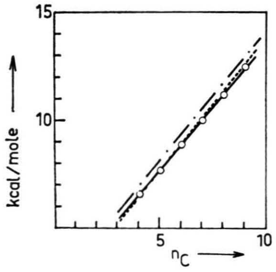

Fig. 2. Dependance of the heat of adsorption on the carbon atoms number for n-alkanes on: —o— MgO; —•— Al_2O_3; ------ SiO_2.

For all three systems the linear dependance of Q_a on n_C previously suggested [6] is fully verified and can be expressed by Eq. (3) of the previous paper [8], which is:

$$Q_a = 2\,D(\alpha_{CH_3} - \alpha_{CH_2}) + R\,T + n_C\,D\,\alpha_{CH_2}. \qquad (4)$$

By comparison of the slopes of the straight-lines (1), (2) and (3), it is apparent that the average dispersion potential per CH_2-group, $P_{ads,\,CH_2} \equiv D\,\alpha_{CH_2}$, takes very close values on these three different oxides, the difference amounting to $\sim 4-5\%$ only.

From the numerical values of the intercepts of Eqs. (1), (2) and (3), corresponding to the quantity $[2\,D(\alpha_{CH_3} - \alpha_{CH_2}) + R\,T]$, the average dispersion potential per each CH_3-group can also be evaluated. Taking into account for our measurements on MgO and Al_2O_3 a mean temperature of 450 °K, while Kiselev's measurements on SiO_2 [9] refer to room temperature (~ 300 °K), the following values are obtained for $P_{ads,\,CH_3}$ on MgO, Al_2O_3 and SiO_2 respectively: 1.64, 1.82, and 1.69 kcal/mole. These values are also satisfactorily comparable, the differences being of the order of 10%.

Since, for a generic group i,

$$P_{ads,\,i} = A\,\alpha_i/(B + C) \qquad (5)$$

where $A = (3/10)\,\pi\,r_e^{-4}\,\varrho\,6\,m\,c^2$, with ϱ = specific number of interacting centers on the surface, r_e = equilibrium distance, m = mass of the electron, c = velocity of light; $B = \alpha_s/\chi_s$ and $C = \alpha_i/\chi_i$, i. e. the ratios of the electronic polarizability to the magnetic susceptibility of the surface interacting centers and of group i, respectively, it follows that

$$A_{MgO}/(B_{MgO} + C) \cong \qquad (6)$$

$$\cong A_{Al_2O_3}/(B_{Al_2O_3} + C) \cong A_{SiO_2}/(B_{SiO_2} + C)\,.$$

If compensation effects between A and B are excluded, the relations (6) could be a consequence of the close correspondence in the adsorption con-

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[9] A. V. Kiselev, Proc. 2nd Int. Congr. Surface Activity (see Ref. [2]), p. 179.

ditions, i. e. for the center number[10] and for the equilibrium distance, as well as for the structural parameter of the solid oxide surface α_s/χ_s [11].

Further insigths about the previous conclusions should be drawn considering other actual factors affecting the surface, e. g. the energetic heterogeneity (particularly the pore spectra) and the hydration degree. Both factors, generally making adsorbent surfaces to differentiate from one another, apparently do not play a significant role in the present case, as it can be judged from the plots Q_a vs. injected amount (i. e. vs. surface coverage) for MgO and Al_2O_3, which actually show very similar trends (Fig. 3), despite the chemical and structural differences. Moreover, depending on the mild activation conditions here employed, the MgO and Al_2O_3 surfaces can be supposed as nearly completely covered by a layer of hydroxyls. In such conditions, the possible occurrence of specific interactions for each of three considered oxides can be uniquely due to the existence of hydroxylic protons. Consequently, not only the non-specific dispersion interactions must be the same, but also the specific ones, if all the hydroxyls involved in adsorption are of the same kind. It can be now observed that specific contributions for the π-electron-proton interaction of cyclohexene and cyclohexadiene (ΔQ_a values in Table 4) on MgO and Al_2O_3 are in very good agreement. In addition, the Q_a value for benzene is intermediate between those for the other two adsorbates both on MgO and Al_2O_3. This probably means that of the two different proton types (i. e. bonded to the water oxygen and to the lattice oxygen, respectively, according to ANDERSON[12]), only the former, similarly to the SiO_2 and Al_2O_3 case, displays electrostatic interactions with the double bond of cyclic olefins and with the π-system of benzene. As a straightforward consequence of the close comparability of both specific and non-specific interactions on the two oxides, a numerical coincidence is also found for the very Q_a values on MgO and Al_2O_3 (Table 4).

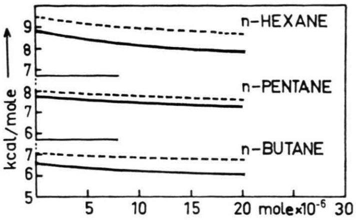

Fig 3. Dependance of the heat of adsorption on surface coverage for n-butane, n-pentane and n-hexane on: ——— MgO; — — — Al_2O_3.

Adsorbate	Al_2O_3 Q_a	Al_2O_3 ΔQ_a	MgO Q_a	MgO ΔQ_a
cyclohexane	8.60		8.80	
cyclohexene	10.00	1.40	10.20	1.40
1.4-cyclohexadiene	11.50	1.50	11.60	1.40
benzene	10.60		11.10	

Table 4. Comparison of the heats of adsorption (kcal/mole) of some cyclic hydrocarbons on MgO and Al_2O_3.

Contrary to the above conclusions for the cyclic molecules, the Q_a trends for the linear olefins show characteristic differences on MgO and Al_2O_3. From Fig. 4 it can be seen that the higher specific interaction contributions with Al_2O_3 are shown by the shorter molecules. With MgO the opposite is true: specific interactions become significant with the longer molecules and increase with increasing chain length, the corresponding contribution reaching a value of 1.50 kcal/mole (close to that found for the cyclic molecules in these systems) only for the pair 1-nonene – n-nonane. Possible explanations of these facts are still of speculative nature only, and need further support on a different experimental basis.

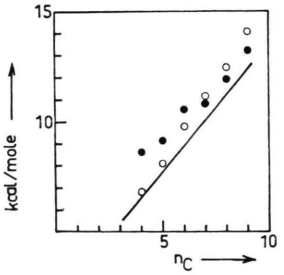

Fig. 4. Heats of adsorption of 1-alkenes on MgO and Al_2O_3 compared with n-alkanes on Al_2O_3. ○ 1-alkenes on MgO; ● 1-alkenes on Al_2O_3; ——— n-alkanes on Al_2O_3.

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[10] The approximate constancy of ϱ is related to surface O^{2-} ions of whatever kind (i. e., with or without the accompanying proton).

[11] For two solid adsorbents 1 and 2, Eq. (6) can be written $A_1/(B_1+C)=A_2/(B_2+C)$, from which it follows $B_1/A_1+C/A_1=B_2/A_2+C/A_2$. If highly unlikely fortuitous compensations between A_1, A_2, B_1, B_2 are excluded, the latter equations can be only verified if $A_1=A_2$ and $B_1=B_2$, i. e. when $\varrho\, r_e^{-4}$ has the same constant value with both solids, and so α_s/χ_s. The constancy of the latter parameter is an immediate consequence of the assumption that the only centers displaying dispersion interactions are the O^{2-} ions (see Ref. [6], pp. 983–984).

[12] See Ref. [1], p. 2756.