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Sorption on Hydrodesulfurization Catalysts

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The adsorption of hydrocarbons, thiophenes, esters, acids, and anilines on MoS_2 and on sulfurized Co–Mo–Al_2O_3 and Al_2O_3 catalysts has been investigated by a chromatographic method at 200°C. The polarity of catalysts, estimated from differences in the adsorption of alkanes and aromatic hydrocarbons, decreases in the order Al_2O_3 > Co–Mo–Al_2O_3 > MoS_2. This order correlates with the ratio of the activity for H_2S elimination from saturated sulfur compounds (proceeding without participation of hydrogen) to the hydrogenation–dehydrogenation activity of the catalysts which decreases in the same sequence. The nonspecificity of the MoS_2 surface compares with the surface of graphitized carbon black, and both acids and anilines are eluted easily from this surface. Adsorption capacities of alkanes at the origin of the isotherm, related to unit BET surface, differ for individual catalysts. These are 9:3:1 for MoS_2:Co–Mo–Al_2O_3:Al_2O_3, respectively, this ratio being little dependent upon the *n*-alkane used for comparison (C_7–C_{10}). The pore distribution has been determined from the desorption branch of N_2 isotherm. The surface of Co–Mo–Al_2O_3 catalyst consists of pores which are approximately five times smaller than those of MoS_2 and Al_2O_3 catalysts.

INTRODUCTION

Hydrodesulfurization can be explained in terms of polyfunctional catalysis (*1–3*). The hydrogenation–dehydrogenation activity of a hydrodesulfurization catalyst operates in the hydrogenation of aromatic sulfur compounds to saturated sulfur compounds and in the hydrogenation of unsaturated hydrocarbons while the activity of the catalyst for H_2S elimination controls the decomposition of saturated sulfur compounds without participation of hydrogen. The ratio of the hydrogenation to elimination rates depends upon pressure, temperature, the type of aromatic sulfur compound and the catalyst and determines the amount of saturated sulfur compound present in the gas phase during the reaction (*3*). In hydrodesulfurization of thiophene on MoS_2 or MoS_2/C this amount is greater than on Co–Mo–Al_2O_3, and on Al_2O_3 the hydrogenation is so slow that the hydrodesulfurization nearly does not take place. If tetrahydrothiophene is introduced on the catalyst without hydrogen, the ratio of its dehydrogenation producing thiophene to the elimination giving H_2S is higher on MoS_2 or MoS_2/C than on Co–Mo–Al_2O_3, the elimination being nearly an exclusive reaction on Al_2O_3 (*4–6*), in accordance with the above facts.

The aim of the present work was to compare the polarity of these catalysts or the ability of their surface to exhibit specific interactions (*7*) by means of gas–solid chromatography. We assumed that this polarity relates to the above differences observed for the catalysts in reactions of sulfur compounds. The specificity of surfaces is demonstrated in gas–solid

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chromatography by differences in the adsorption of compounds capable of specific interaction compared to *n*-alkanes which interact only nonspecifically (*7*). From this viewpoint silica gel and graphitized carbon black have been frequently investigated (*7, 8*). In contrast, MoS_2 and Al_2O_3 have been studied by gas–solid chromatography less frequently and especially from the point of view of their utilization in analytical chromatography [MoS_2 (*9, 10*), Al_2O_3 modified by salts (*11*)]. Sulfurized Co–Mo–Al_2O_3 has been examined by gas–solid chromatography with the aim of obtaining the adsorption coefficients of C_6 and C_7 hydrocarbons and of thiophene (*12*). A simplified method was employed in this study which did not take into account the unsymmetrical shape of peaks. Our intention was to compare the adsorption of a broader series of compounds on the catalysts activated than is usual in hydrodesulfurization.

METHODS

MoS_2 catalyst was prepared by decomposition of crystalline $(NH_4)_2MoS_4$ which was obtained (*13*) from $(NH_4)_2MoO_4$ and H_2S. The content of sulfur and the surface of the sulfide depend upon the method of decomposition (*14–16*). With regard to conditions used for hydrodesulfurization we proceeded as follows: N_2, 20 to 450°C, 0.5 hr; N_2, 450°C, 0.5 hr; H_2, 150 to 450°C, 0.3 hr; N_2, 450 to 20°C, 0.3 hr. The sulfide powder was pressed (25 MPa) and then crushed to 0.16- to 0.25-mm particles.

Co–Mo–Al_2O_3 catalyst (G-35, Girdler-Südchemie, München, 12% by weight CoO + MoO_3; at. Mo:Co = 3:1) was crushed to 0.16- to 0.25-mm particles, reduced, and sulfurized in the following way: $N_2 + H_2(10{:}1)$, 450°C, 0.5 hr; H_2, 450°C, 2 hr; $H_2S + H_2(1{:}10)$, 300–450°C, 0.5 hr; $H_2S + H_2(1{:}10)$, 450°C, 3 hr; N_2, 450–20°C, 0.5 hr.

TABLE 1

Adsorption Capacities $c_0{}^a$ at 200°C in Helium

Adsorbate	Catalyst		
	MoS_2	Co–Mo–Al_2O_3	Al_2O_3
Heptane	3.3	36.8	7.4
Octane	8.3	72.5	14.2
Nonane	15.2	131	28.1
Decane	30.0	198	49.6
Toluene	3.9	72.6	40.5
m-Xylene	8.7	156	69.3
1,3,5-Trimethylbenzene	18.2	256	97.3
2,5-Dimethylthiophene	6.7	130	70.6
Benzothiophene	35.8	431	231
Ethyl butyrate	5.6	—	—
Propyl butyrate	11.8	—	—
Butyl butyrate	17.1	—	—
Propionic acid	3.3	—	—
Butyric acid	4.5	—	—
Isovaleric acid	5.8	—	—
Aniline	17.3	—	—
o-Toluidine	28.0	—	—

[a] Adsorption capacities at the origin of the isotherm c_0 are approximated by the quotient (s/p), where s is the adsorbed amount at 0.1 kPa and p is the pressure of 0.1 kPa, and are given in 10^{-6} mol g^{-1} kPa^{-1}.

Al_2O_3 catalyst (R-10-11, Badische Anilin & Soda–Fabrik AG, Ludwigshafen) was crushed, reduced, and sulfurized in the same way. Organic compounds were commercial chemicals, and their purity was verified by gas chromatography. Helium and hydrogen were deoxygenated on manganese and palladium catalysts, respectively, and dried over molecular sieves. Hydrogen sulfide (purity >99.5%; Merck-Schuchardt, Darmstadt) was used without further purification.

Column (length, 0.5 m; i.d., 4 mm) was made of stainless steel, and the pulses of compounds (5 to 15 μl) were injected by means of a microsyringe (heated in the case of benzothiophene). A stainless-steel thermal conductivity detector was thermostated at 230°C. After passing through the detector, the pulses of compounds were trapped in a microcondenser (−78°C;

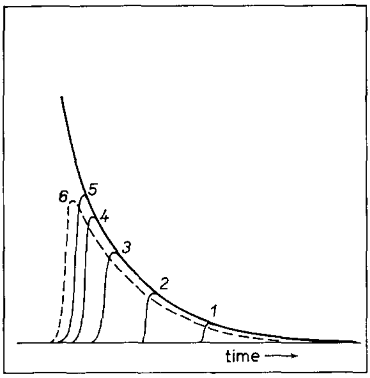

Fig. 1. Chromatographic peaks of benzothiophene on MoS_2 (schematically): 200°C; He flow rate, 40 ml (STP) min^{-1}; 10-μl pulses. *1 to 5*, fresh catalyst; *6*, catalyst deactivated by other compounds.

efficiency, 80 to 90%) and analyzed by gas chromatography. For combinations of the compounds and catalysts listed in Table 1 the condensate did not contain decomposition products. The response of the thermal conductivity detector for individual compounds, which was needed to calculate isotherms, was calibrated by using the column filled with glass balls. In the case of lower-boiling substances the injection port was cooled by dry ice so that peak heights, and thus the concentration range, could be comparable in calibration and adsorption experiments. Helium was used as a carrier gas (40 ml (STP) min^{-1}, flow rate).

Catalyst (1 to 10 g) was introduced to the column, and the remaining space was filled with glass balls. The column was purged with helium, 400°C, 1 hr, hydrogen, 400°C, 1 hr, and again with helium, 400°C, 1 hr, and then experiments were commenced. During this procedure hydrogen sulfide evolved from the catalysts: for MoS_2, 0.22; for Co–Mo–Al_2O_3, 0.12; and for Al_2O_3 0.01 mmol g_{cat}^{-1}. The hydrogen sulfide was absorbed in an ammoniacal solution of $CdCl_2$ and determined by iodometric titration. After 1 hr in H_2 at 400°C the rate of H_2S evolution was slower than 0.01 mmol H_2S hr^{-1} g_{cat}^{-1}, and in subsequent treatment with He the hydrogen sulfide could not be detected by $CdCl_2$ solution. The stage of the column packing was periodically tested by the injection of benzothiophene pulses. In the case of a decrease in the adsorption capacity of the catalyst this was regenerated by hydrogen at 400°C. At the conclusion of experiments it was verified by benzothiophene that the adsorption capacity was the same as at the beginning, the catalyst was cooled in helium atmosphere and transferred from the column in air, and then its surface area (BET method, N_2) and pore distribution (N_2, desorption branch of the isotherm, using the model of cylindrical pores) were determined. Chromatograms were treated by the method of graphical integration of the tailed back side of the peak (*8*) to give adsorption isotherms in graphical form for the pressure range up to approx. 2 kPa. The results obtained with different amounts of catalyst agreed well with one another.

RESULTS

The adsorption capacity of the column packing was periodically checked by injecting benzothiophene pulses. A decrease (5 to 10%) was observed only after several pulses of some higher boiling substances (decane, butyl butyrate, *o*-toluidine). In such a case the results were recalculated by a linear coefficient to the initial stage, and the catalyst was regenerated by hydrogen at 400°C. At the beginning of the experiments and, to a lesser extent, also after each regeneration, part of the benzothiophene was adsorbed irreversibly. As seen in Fig. 1, the irreversibly adsorbed amount diminishes for subsequent peaks. Judging from the tails of peaks, this process is not accompanied by a change in the adsorption capacity of the catalyst. Only part of the adsorbed benzothiophene (15%) could be desorbed by increasing the temperature to 400°C. After approximately five pulses nearly 90% of the benzothiophene feed was eluted (calculated from the peak area and the calibration of the thermal conductivity detector), and then further compounds were injected. These, starting from the first pulse, eluted to 90 to 100%.

An example of the isotherms obtained is shown in Fig. 2. For further interpretation we used the adsorption capacities, $c_p = (ds/dp)_p$ (mol g^{-1} kPa^{-1}), at the origin of the isotherm, $c_0 = (ds/dp)_{p \to 0}$ where s is the adsorbed amount (mol g^{-1}) and p is the partial pressure (kPa). These were approximated, $c_0 \approx (s/p)$, where s is the adsorbed amount at 0.1 kPa and p is the pressure of 0.1 kPa. This is a reasonable approximation for purposes of relative comparison, since isotherms of all the compounds are parallel and the relations between c_p are only slightly pressure dependent (Fig. 2). The determined adsorption capacities at the origin of the isotherm are listed in Table 1. Esters, anilines, and acids decomposed or adsorbed very strongly on Co–Mo–Al_2O_3 and Al_2O_3, and therefore their adsorption isotherms and adsorption capacities could not be obtained. We examined also the adsorption of 2,3-dihydrobenzothiophene and styrene, i.e., probable intermediate products in hydrodesulfurization of benzothiophene, on MoS_2 and Co–Mo–Al_2O_3. 2,3-Dihydrobenzothiophene dehydrogenates so that the trapped pulses contained 30 to 70% benzothiophene. In spite of this, experiments show that the adsorption of dihydrobenzothiophene does not differ from that of benzothiophene more than by 10%. The trapped pulses in the adsorption of styrene contained more than 90% ethylbenzene even on repeated feeding, and the part of the pulse mass adsorbed irreversibly. Naphthalene was fed as a solution in ethylbenzene. On all the catalysts it adsorbed comparably to benzothiophene.

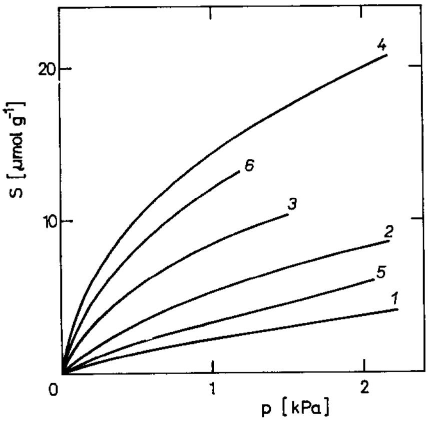

FIG. 2. Adsorption isotherms on MoS_2 at 200°C. *1*, toluene; *2*, *m*-xylene; *3*, 1,3,5-trimethylbenzene; *4*, benzothiophene; *5*, isovaleric acid; *6*, *o*-toluidine.

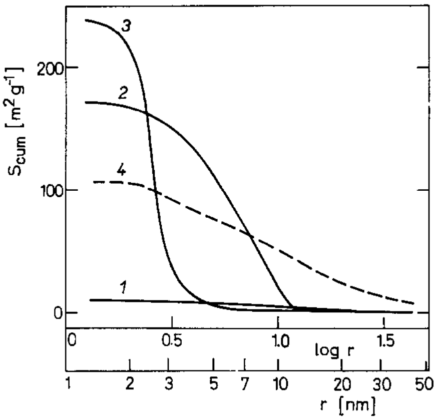

FIG. 3. Cumulative distribution of catalyst surfaces. *1*, MoS_2; *2*, Al_2O_3; *3*, Co–Mo–Al_2O_3; *4*, MoS_2, plotted as $10 \cdot S_{cum}$.

The surface areas for MoS_2, Co–Mo–Al_2O_3, and Al_2O_3 were 10.5, 246, and 176 m^2 g^{-1}, respectively. Cumulative distribution of the surface area of the catalysts, S in square meters per gram, plotted against pore radii, r in nanometers, is shown in Fig. 3.

DISCUSSION

The adsorption capacities at the origin of isotherm, c_0, are proportional to Henry constants (*8*), separation factors, (*17*), or elution volumes of the zero sample. The difference $\Delta \log (c_0)$ for two compounds is therefore proportional to the difference in their free enthalpies of adsorption $\Delta\Delta G_a$,

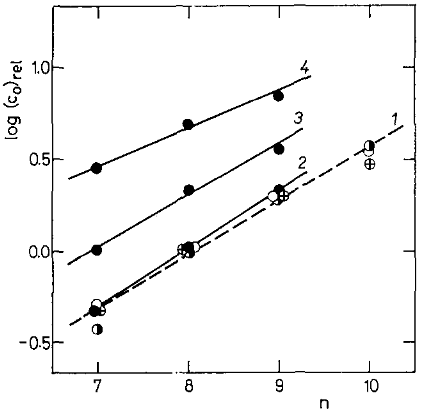

FIG. 4. Dependence of relative adsorption capacity on the number of carbon atoms *n* for hydrocarbons at 200°C. For each catalyst adsorption capacities are related to octane. *1*, alkanes; ◑, MoS_2; ⊕, Co-Mo-Al_2O_3; ○, Al_2O_3; *2-4*, benzenes (●); *2*, MoS_2; *3*, Co-Mo-Al_2O_3; *4*, Al_2O_3.

i.e., $\Delta\Delta G_a = -2.3RT\Delta \log (c_0)$ (e.g., *11*, *17*). Interactions taking place during adsorption can be classified as specific and nonspecific (*7*, *8*), and ΔG_a is then the sum of $\Delta G_a{}^{\text{nonspec}}$ and $\Delta G_a{}^{\text{spec}}$ (e.g., *11*). The ability of surfaces to interact specifically, in other words their polarity, can be compared similarly to the polarities of stationary phases in gas-liquid chromatography, i.e., by comparing the adsorption of the compounds capable of specific interactions with the adsorption of the alkanes which adsorb only nonspecifically.

Acids, esters, and anilines decomposed on Co-Mo-Al_2O_3 and Al_2O_3 or were eluted with great difficulty. For that reason we estimated the ability of these surfaces to interact specifically only from differences between the adsorption of alkylbenzenes and that of alkanes. Alkylbenzenes are capable of specific interaction through the π-electron density of their aromatic nucleus with surface acid sites. Alkanes are assumed to interact on all the surfaces only nonspecifically. Differences between individual catalysts are demonstrated graphically in Fig. 4 in which are plotted the relative log (c_0) related to octane for each catalyst to the number of carbon atoms, *n*, in the hydrocarbon. The difference in $\Delta G_a{}^{\text{spec}}$ for the benzene nucleus on two catalysts *i* and *j*, $\Delta\Delta G_a{}^{\text{spec}}$ $(\text{Ar}^{i,j})$, is proportional to the horizontal distance between the lines for alkylbenzenes on these catalysts. The ability of catalyst surfaces to interact specifically thus increases in the order MoS_2 < Co-Mo-Al_2O_3 < Al_2O_3. The difference $\Delta\Delta G_a{}^{\text{spec}}$ $(\text{Ar}^{\text{Co-Mo-Al}_2\text{O}_3,\text{MoS}_2})$ is approx. 2.9 kJ mol^{-1} (0.7 kcal mol^{-1}), and $\Delta\Delta G_a{}^{\text{spec}}$ $(\text{Ar}^{\text{Al}_2\text{O}_3,\text{MoS}_2})$ is approx. 6.3 kJ mol^{-1} (1.5 kcal mol^{-1}). The values of $\Delta\Delta G_a{}^{\text{spec}}$ so obtained are independent of the parameter used to characterize the adsorbate. In Fig. 4 it is the number of carbons, *n*, but it could also be, e.g., the coefficient of static polarizability α, boiling point temperature T_b, etc. The absolute values of $\Delta G_a{}^{\text{spec}}$ (Ar^i) can be obtained by comparing these data with those for adsorption on graphitized carbon black, the latter being an adsorbent capable of only nonspecific interactions (*7*, *8*). Suitable data for carbon black at 200°C have been published in the form of Kováts retention indices I_x. With the use of the adsorption capacities at the origin of isotherm the above index for substance *x* is defined as

$$I_x = 100\left(\frac{\log (c_0)_x - \log (c_0)_n}{\log (c_0)_{n+1} - \log (c_0)_n} + n\right),$$

where *n* stands for the number of carbon atoms of the nearest *n*-alkane which adsorbs less than substance *x*, $(c_0)_x$ is the adsorption capacity in the origin of the isotherm of substance *x*, and $(c_0)_n$ and $(c_0)_{n+1}$ are the capacities for the *n*-alkanes having *n* and $n + 1$ carbon atoms, respectively. It is obvious from the definition that the higher the index for a given alkylbenzene on a given catalyst compared to graphitized carbon, the higher is $\Delta G_a{}^{\text{spec}}$ (Ar^i). For adsorption on carbon black at 200°C, I_x for toluene is 704, for *m*-xylene it is 828, and for 1,3,5-trimethylbenzene it is 949 (*18*). As follows from the data listed in Table 1 for MoS_2 at 200°C, I_x for toluene is here 718, for *m*-xylene it is 808, and for 1,3,5-trimethylbenzene it is 927. The ability of the MoS_2 surface to cause specific interactions (or its polarity) is thus comparable with the carbon surface, i.e., it is very low. This is confirmed also from the data for the adsorption of esters, acids, and anilines presented in Table 1. Similar to carbon black (*8*) these strongly polar substances elute readily from MoS_2, e.g., propionic acid as heptane, aniline as nonane, etc. This similarity between MoS_2 and graphitized carbon accords with the expectation based on the similarity in the crystal structure of MoS_2 and graphite (*9, 10*). This means that the method of preparation of MoS_2 used in the case of its catalytic application leads to a nonpolar surface which is essentially not able to interact specifically. Data presented in Table 1 also allow us to calculate the I_x of alkylbenzenes for other catalysts; thus, for example, I_x for toluene is 718 on MoS_2, 800 on Co–Mo–Al_2O_3, and 964 on Al_2O_3. This illustrates in another way the differences in the polarity of these catalysts which were already depicted in Fig. 4.

The relative abilities of the catalyst for specific interactions or their polarity so determined correlate well with the ratio of their activity for H_2S elimination to hydrogenation–dehydrogenation activity observed in the reactions of sulfur compounds. In the absence of hydrogen, tetrahydrothiophene decomposes on Al_2O_3 only to H_2S, on Co–Mo–Al_2O_3 the rates of its decomposition to H_2S and its dehydrogenation to thiophene are comparable, and on MoS_2 its dehydrogenation is the prevailing reaction (*4–6*). In hydrodesulfurization of thiophene or benzothiophene on MoS_2 the gas phase contains more tetrahydrothiophene or 2,3-dihydrobenzothiophene than in the reaction on Co–Mo–Al_2O_3 (*3, 6*). Hence, the elimination of H_2S from saturated sulfur compounds seems to proceed above all on the sites capable of specific interactions. The value of ΔG_a^{spec} (Ar^i) may depend upon both the amount and type of the surface sites capable of specific interaction (obviously mainly –SH and –OH groups). The data do not allow us to conclude which of two factors mentioned is responsible for the observed differences.

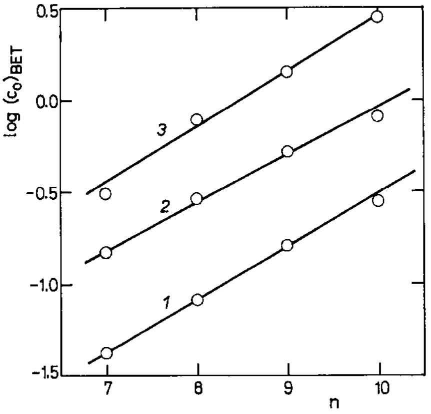

FIG. 5. Dependence of adsorption capacity $(c_0)_{\text{BET}}$ (in 10^{-6} mol m^{-2} kPa^{-1}) on the number of carbon atoms for *n*-alkanes at 200°C. *1*, Al_2O_3; *2*, Co–Mo–Al_2O_3; *3*, MoS_2.

The catalysts differ not only in their ability to interact specifically but also in the absolute values of the adsorption capacities related to 1 m^2 of BET surface, $(c_0)_{\text{BET}}$, for alkanes. This is shown in Fig. 5. The capacity decreases in the sequence MoS_2 > Co–Mo–Al_2O_3 > Al_2O_3, and the differences between the catalysts do not depend much upon the alkane for which we compare the capacities, as judged from Fig. 5. The ratio of these capacities is approx. MoS_2 : Co–Mo–Al_2O_3 : Al_2O_3 = 9 : 3 : 1. The observation of the greater adsorption of alkanes on Co–Mo–Al_2O_3 compared to Al_2O_3 is supported by our earlier results obtained under other conditions (350°C, Cherox catalysts, CHZ ČSSP, Litvínov, Czechoslovakia) where $(c_0)_{\text{BET}}$ values for cycloalkanes on Co–Mo–Al_2O_3 were greater by a factor of 5 compared to Al_2O_3 (*19*). These differences in $(c_0)_{\text{BET}}$ for alkanes between the catalyst stem obviously from several causes which require further experimental study. That is why we limit ourselves here only to a statement of some facts concerning this phenomenon.

If the differences between the catalysts were due to different polarizabilities and the concentrations of force sites on the surface which determine the range of nonspecific adsorption forces (*20*), the contributions $\Delta G_a^{\text{nonspec}}$ (CH_2^i) should differ substantially for individual catalysts. This we did not observe for alkanes having a C_7–C_{10} chains (Fig. 5). The assumption that these differences are due to the chemisorption of alkanes does not accord with the observed additivity of adsorption with molecular mass [see also (*19*)], which is typical for physical interaction during which the character of the adsorbate as a chemical individual is not substantially distorted.

Another explanation could be based on the different pore structure of the catalysts studied. Other authors have observed that $(c_0)_{\text{BET}}$ for alkanes differ for surfaces with the same chemical character but different porosity. Thus, $(c_0)_{\text{BET}}$ for *n*-pentane on silica gel with pore radii of approx. 10 nm is roughly half that found for silica gel with 2.5-nm pores (7). Similarly, $(c_0)_{\text{BET}}$ values for *n*-pentane differ by more than 100% on two graphitized carbon blacks (*21*). These experimental results are not connected with the phenomenon of capillary condensation because they were obtained (as in our case) at very low pressures of hydrocarbon. They are ascribed to heterogeneity of sites for nonspecific adsorption (*21*). The nonspecifically adsorbed hydrocarbon can interact with more force sites of the solid on more active sites. The concentration of such sites is expected to be higher on a more porous surface than on a less porous or flat one. However, in such a situation the increment $\Delta G_a^{\text{nonspec}}$ (CH_2^i) should be higher on more active sites, but this increment was not measured in the papers cited above. The results in Fig. 3 show that our catalysts differ in pore structure, and this could be, in the terms mentioned above, the reason for the observed differences in $(c_0)_{\text{BET}}$ for alkanes between different catalysts. The absolute position of the distribution curves of the surface in the direction of the pore radii axis in Fig. 3 may depend on the model adopted for the shape of pores. However, relative comparison of the catalysts does not depend on this fact. The majority of the Co–Mo–Al_2O_3 surface is formed by pores which are approximately half an order of magnitude smaller than in the case of Al_2O_3 and MoS_2 whose surfaces are formed by pores of comparable size. This might explain why $(c_0)_{\text{BET}}$ for alkanes on Co–Mo–Al_2O_3 is greater than on Al_2O_3, but it does not account for the higher $(c_0)_{\text{BET}}$ for alkanes on MoS_2. Moreover, we have not observed substantial differences in the contributions $\Delta G_a^{\text{nonspec}}$ (CH_2^i) on various catalysts (Fig. 5) so that the pore structure does not explain satisfactorily differences in $(c_0)_{\text{BET}}$ for alkanes between different catalysts. Speculatively, differences between catalysts could also be caused by the existence of bottle-like pores with a narrow neck which would let in nitrogen but not alkanes.

The adsorption capacity for 2,5-dimethylthiophene on all the catalysts compares well with that for *m*-xylene, and also the extents of the adsorption of benzothiophene and naphthalene are comparable to each other. This agrees with our earlier observation of the analogous behavior of thiophenes and benzenes for a broader series of their alkyl derivatives at 350°C on Co–Mo–Al_2O_3 and Al_2O_3 (*19*) and is also in accordance with the fact that the electronic structure and the physical and chemical properties derived from it are similar in both series (e.g., *22*, *23*).

The chromatographic method employed detects reversible adsorption whose equilibrium is established quickly. The character of the adsorbate as a chemical individual is preserved to a great extent, which in our case is confirmed especially by the observed structure effects [see also Ref. (*19*)]. We believe that this adsorption is the necessary first step of a series of consecutive steps of hydrodesulfurization. It can be compared to dissolution in liquid-phase reactions. In this reversible adsorption the structure of the reactant and the polarity of the catalyst surface play a role, just as do the structure of the reactant and the polarity of the solvent during dissolution. The overall rate of hydrodesulfurization is affected by all the subsequent steps of the reaction, and hence these effects should also manifest themselves in its course. Differences in $(c_0)_{\mathrm{BET}}$ for alkanes between catalysts indicate that the specific activities of hydrodesulfurization catalysts, i.e., activities related to 1 m^2 of BET surface, are not necessarily suitable parameters for comparing the catalysts but that the situation is more complex. This should be taken into account especially in interpreting the correlations of specific activities with intensive physicochemical parameters of catalysts which are expected to be of more than empirical importance.

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