# CHARACTERIZATION OF THE SURFACE OF HYDRODESULPHURIZATION CATALYSTS BY ADSORPTION OF HYDROCARBONS

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Reversible adsorption of heptane and benzene on model and industrial hydrodesulphurization molybdena catalysts has been studied by elution chromatographic method at 150°C. An increase in the adsorption of heptane on sulphidation of adsorbents was small for $Al_2O_3$ and great for $MoO_3$. Supported catalysts behaved as a mixture of $Al_2O_3$ and $MoO_3$. The portion of surface which can be transformed by sulphidation into $MoS_2$ ranged from 0 to 65% for individual commercial catalysts, as determined from the change in heptane adsorption after sulphidation of a given sample. The polarity of catalysts, including their acidity, was estimated from the difference between adsorption of benzene and heptane. The polarity of model and industrial catalysts in oxidic form was similar to that of alumina in most cases. The decrease in the polarity after sulphidation of the adsorbents was small for $Al_2O_3$ and great for $MoO_3$. The decrease in polarity resulting from sulphidation of supported catalysts was relatively small, since the reaction of $MoO_3$ monolayer with hydrogen sulphide leads to partial reformation of the alumina surface. The acidity of supported sulphided hydrodesulphurization catalysts has been shown by this method to be comparable with the acidity of the support itself.

The electronic and chemical properties of surface can be evaluated from the adsorption of molecules, the structure and reactivity of which are known. Such an approach has been applied also to hydrodesulphurization catalysts. The active molybdenum centres were determined by irreversible chemisorption of oxygen[1], the surface sulphhydryl groups were identified by chemisorption of silver ions[2], the surface acidity was studied by the adsorption of ammonia and pyridine (for review see ref.[3]), the state of supported transition metals was studied by selective adsorption of nitrogen monooxide[4], the electron acceptor properties of the surface were evaluated from ESR signal of adsorbed aromatic hydrocarbons[5], *etc.*

If an adsorbate interacts with surface too strongly and original bonds are cleaved, the nature of the interaction taking place during adsorption is difficult to interpret. Thus, for example, it is questionable whether the only partial reversible adsorption of basic molecules such as butylamine, pyridine or ammonia on the surface containing transition metal ions can be ascribed solely to acid–base interaction. In the present work we have studied the reversible adsorption of saturated and aromatic hydrocarbons. In this case, the interaction is weak and does not lead either to modification of the surface or to the cleavage of bonds in the hydrocarbon probe. Alkanes possess only $\sigma$ bonds, do not have permanent dipole, are little polarizable and have high ionisation potential. Aromatic hydrocarbons possess $\pi$-electron system and are thus easily polarizable, have the lower ionisation potential and behave as weak $\pi$ bases. By comparison in alkane–aromate

couple one can therefore evaluate the electronic properties of surface, *i.e.* its polarity or acidity. Mosely and Archibald[6] determined the acidity of cracking catalysts from the difference in adsorption of xylene and octane. Barthoumeuf and Ha[7] used the difference in benzene and cyclohexane adsorption to determine the quality of the surface field of zeolites containing different amounts of Na and Al. Kuchkaeva and coworkers[8] and Bolotina and collaborators[9] characterized in similar way the surface of nickel and cobalt hydroxides and of nickel oxide, Belyakova and Kiselev[10] used this method for characterization of the surface of $MoS_2$. We have used these probe molecules in the study of surface polarity of a commercial $Co–Mo/Al_2O_3$ catalyst and $MoS_2$ (refs[11,12]), bismuth oxide, molybdenum oxide and their mixture[13] and modified aluminas[14].

The aim of this work was to study by this technique in more detail the model catalysts CoO, $MoO_3$, $Co/Al_2O_3$, $Mo/Al_2O_3$, and $Co–Mo/Al_2O_3$ prepared in laboratory and to compare results with those obtained for a series of commercial hydrodesulphurization catalysts, both in oxidic and sulphidic form.

## EXPERIMENTAL

Data on catalysts are presented in Table I. Laboratory catalysts L2—L5 were prepared from the alumina CHEROX 33-00 and the sample L7 from the alumina SPHERALITE SCS-79. The support was crushed into 0·16—0·25 mm particles and its suspension in solution of the appropriate salt (ammonium paramolybdate and cobalt nitrate) was evaporated on a rotary evaporator. In preparing the sample L5, molybdenum was deposited as the first component. The catalysts were calcinated at 530°C for 5 h in a stream of air. $MoO_3$ was prepared by thermal decomposition of ammonium paramolybdate in a tube reactor in a stream of air. The temperature was increased fast to 530°C and the decomposition was completed after 1 h. The powder obtained was pressed to tablets and from their granules the 0·16—0·25 mm fraction was obtained by sieving. CoO was prepared by thermal decomposition of cobalt nitrate which was first dehydrated and partially decomposed at 250°C on a plate and the solid compound so obtained was then calcinated in a tube reactor at 530°C for 1 h in a stream of air. The material obtained was crushed and sieved to give the 0·16—0·25 mm fraction. Commercial catalysts were crushed to the same granulation. The part of each catalyst was pre-sulphided by $H_2 + H_2S$ mixture, using procedure described earlier[11] and the sample was stored in air.

Adsorption isotherms at 150°C and hydrocarbon pressures from 0—3 kPa were measured by the conventional chromatographic technique (for description see *cf.*[15]) which was used by us also in our previous work[14]. The carrier gas was helium. No significant irreversible adsorption or reaction of the hydrocarbons has been detected. The conditions for calculating isotherms from unsymmetrical elution peaks were fulfilled in the same way as for aluminas in our previous work[14].

## RESULTS AND DISCUSSION

Examples of adsorption isotherms for heptane (H) and benzene (B) on different catalysts are shown in Figs 1 and 2. They demonstrate that observed effects which will be later discussed in terms of chemical potentials are great. Thus, for example, the catalyst L4 (CoMo/Al) in oxidic form showed nearly two times greater adsorption than the support itself and its sulphidation increased again twice the adsorption; on the other hand, pre-sulphidation had no effect on the adsorption of the support

L1 (Al). Sulphidation of $MoO_3$ increased several times the adsorption and at the same time it changed the sequence of the adsorption of benzene and heptane.

Adsorption isotherms were compared by the procedure used already in our previous works[12,14]. Interaction of the hydrocarbon $i$ with the catalyst $I$ at adsorbed amount $S$ was characterized by the chemical potential of adsorbed hydrocarbon $\mu^a(i, I, S)$. The adsorption was reversible and $\mu^a$ was calculated according to the equation

$$\mu^a(i, I, S) = \mu^0(i) + RT \ln P(i, I, S) - RT \ln P^0 , \qquad (1)$$

where $\mu^0(i)$ is the standard chemical potential (hydrocarbon $i$, gaseous phase, pressure 100 kPa, temperature of adsorption), $P^0$ is the standard pressure (100 kPa) and $P(i, I, S)$ is the partial pressure read for $S$ from the isotherm. Differences in adsorp-

TABLE I
Catalysts studied

| Catalyst I | Type | BET surface area $m^2\ g^{-1}$ |
|---|---|---|
| L1(Al) | alumina CHEROX 33-00[a] | 140 |
| L2(Mo/Al) | 5% $MoO_3/Al_2O_3$ | — |
| L3(Mo/Al) | 10% $MoO_3/Al_2O_3$ | — |
| L4(Co/Al) | 4% $CoO/Al_2O_3$ | — |
| L5(CoMo/Al) | 4% CoO + 10% $MoO_3/Al_2O_3$ | — |
| L6(Al) | alumina SPHERALITE SCS-79[b] | 80 |
| L7(Mo/Al) | 5% $MoO_3/Al_2O_3$ | — |
| $MoO_3$ | decomposition of ammonium paramolybdate | 2 |
| CoO | decomposition of cobalt nitrate | — |
| CH-3601 | Co—Mo/$Al_2O_3$, CHEROX 36-01[a] | 131 |
| G-35 | Co—Mo/$Al_2O_3$, GIRDLER G-35[c] | 244 |
| ICI-61-1 | Ni—Mo/$Al_2O_3$, ICI 61-1[d] | 211 |
| ICI-41-6 | Co—Mo/$Al_2O_3$, ICI 41-6[d] | 288 |
| CH-3630 | Ni—Co—Mo/$Al_2O_3$, CHEROX 36-30[a] | 317 |
| CH-PPS | Co—Mo/$Al_2O_3$, CHEROX, pilot plant sample[a] | 195 |
| HT-400E | Co—Mo/$Al_2O_3$, HARSHAW HT-400E[e] | 220 |

[a] Chemical Works, Litvínov, Czechoslovakia; [b] Rhone Poulenc Industries, France, supplied by Rhodia (V.K.) Ltd., London; [c] Girdler-Südchemie, Federal Republic of Germany; [d] Imperial Chemical Industries, Great Britain; [e] Harshaw, U.S.A.

tion were expressed as differences in chemical potentials $\Delta\mu^a$; on comparing the adsorption of two hydrocarbons $i$ and $j$ on the same catalyst according to the relation

$$\Delta\mu^a(i/j, I, S) = \mu^a(i, I, S) - \mu^a(j, I, S) = \\ = \Delta\mu^0(i/j) + \boldsymbol{RT}\ln P(i/j, I, S) \qquad (2)$$

(where $\Delta\mu^0(i/j)$ is independent of catalyst), on comparing the adsorption of hydrocarbon $i$ on two catalysts $I$ and $J$ according to the expression

$$\Delta\mu^a(i, I/J, S) = \mu^a(i, I, S) - \mu^a(i, J, S) = \boldsymbol{RT}\ln P(i, I/J, S) \qquad (3)$$

and on comparing the adsorption of hydrocarbon $i$ on sulphidic $I(s)$ and oxidic $I(o)$ form of the catalyst $I$ according to the relation

$$\Delta\mu^a(i, I(s)/I(o), S) = \mu^a(i, I(s), S) - \mu^a(i, I(o), S) = \\ = \boldsymbol{RT}\ln P(i, I(s)/I(o), S)\,. \qquad (4)$$

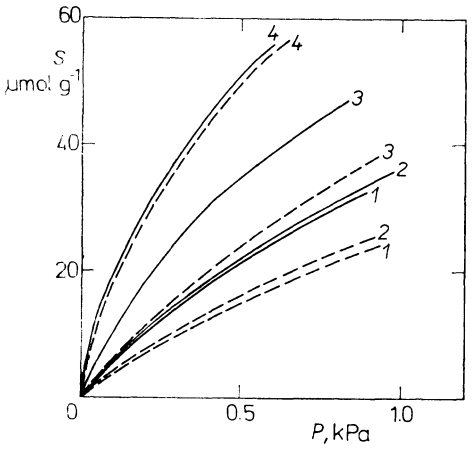


FIG. 1

Adsorption isotherms of hydrocarbons on support and supported catalyst in oxidic (o) and sulphidic (s) forms at 150°C (full line benzene, dashed line heptane, *1* L1(Al) (o), *2* L1(Al) (s), *3* L4(CoMo/Al) (o), *4* L4 (CoMo/Al) (s)

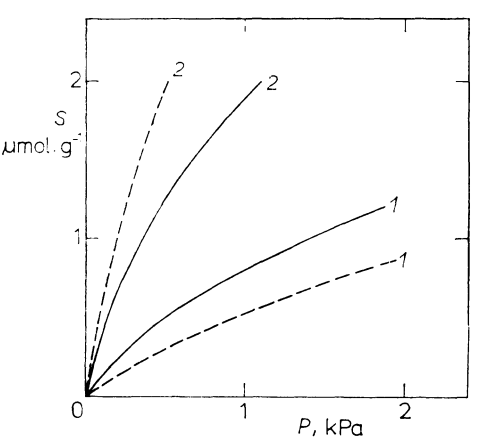


FIG. 2

Adsorption isotherms of hydrocarbons on unsupported molybdenum catalysts at 150°C (full line benzene, dashed line heptane, *1* $MoO_3$ (o), *2* $MoO_3$(s)

Similarly as in previous works[12,14], we have observed that $\Delta\mu^a$ quantities were independent of $S$ in the range from 0 to 25 μmol $g^{-1}$. Therefore, they can be taken as the suitable measure of the surface-adsorbate interaction in this region of $S$ and can be obtained without mathematical modelling the isotherms by the method reported earlier[14]. It is of importance that $\Delta\mu^a$ characterizes the surface–adsorbate interaction not only at $S \to 0$ but in the whole range of $S$ (0–25 μmol $g^{-1}$). However, in the broader range of $S$, $\Delta\mu^a$ depends on $S$; for $S \to S(\max)$, $\Delta\mu^a(i/j, I, S) = \Delta\mu^0(i/j) + \boldsymbol{RT} \ln (P^s(i)/P^s(j))$, where $P^s$ is the tension of saturated vapors, $\Delta\mu^a(i, I/J, S)$ and $\Delta\mu^a(i, I(s)/I(o), S)$ equal to 1.

The results for laboratory catalysts in oxidic form are presented in Table II. On comparing heptane adsorption, the support L1 (Al) was chosen as the standard. The catalysts prepared by impregnating the same support have similar surface areas and thus in this case we compared the potentials of adsorbed heptane at a constant adsorbed amount $S(g)$ related to the mass of the catalyst. The supports L1 (Al) and L6 (Al) and catalyst $MoO_3$ that differed markedly in surface area were compared according to the chemical potentials of heptane at the constant adsorbed amount $S(m)$ related to the surface area of the catalyst. The calculation of $\Delta\mu^a$(B/H, $I$, $S$) for purposes of estimation of surface polarity is independent of the definition of $S$.

Deposition of molybdenum on alumina increased the affinity of the surface to heptane. The decrease in $\Delta\mu^a(H, I/L1, S(g))$ was at the same time similar to that observed for 5% $MoO_3$ and 10% $MoO_3$ on alumina and was comparable also to

TABLE II

Relative chemical potentials $\Delta\mu^a$ of hydrocarbons adsorbed on laboratory catalysts in oxidic form, kJ $mol^{-1}$

| Catalyst $I$ | $\Delta\mu^a$ (H, $I$/L1, $S$) | | $\Delta\mu^a$ (B/H, $I$, $S$) |
|---|---|---|---|
| | $S = S(g)$ | $S = S(m)$ | |
| L1 (Al) | 0·00 | 0·00 | −1·71 |
| L2 (Mo/Al) | −2·03 | — | −2·03 |
| L3 (Mo/Al) | −1·87 | — | −1·46 |
| L4 (Co/Al) | 1·38 | — | −2·03 |
| L5 (CoMo/Al) | −2·03 | — | −2·03 |
| L6 (Al) | 6·51 | 3·99 | −1·95 |
| L7 (Mo/Al) | 3·90 | — | −3·17 |
| $MoO_3$ | 8·95 | −3·25 | −2·03 |
| CoO | 8·54 | — | −0·41 |

molybdenum deposited on the support L6. According to $\Delta\mu^a(H, I/L1, S(m))$, the affinity of $MoO_3$ surface to heptane was substantially higher compared to both aluminas; the greater adsorption of heptane on $MoO_3/Al_2O_3$ samples compared to $Al_2O_3$ is thus caused by finely dispersed molybdenum oxides on the surface. Deposition of cobalt decreased the affinity of alumina surface to heptane and did not affect essentially the behaviour of $Mo/Al_2O_3$ catalyst. The greater stability of the alkane on $Co–Mo/Al_2O_3$ compared to $Al_2O_3$ has been observed by us earlier[11] and was reported also by Barbul and coworkers[16]; data reported by these authors and obtained under comparable conditions were used to calculate the value of $\Delta\mu^a$ (alkane, $(Co–Mo/Al_2O_3)/(Al_2O_3)$, $S(m)$) which was found to be ca. $-2{\cdot}8$ kJ mol$^{-1}$.

The quantity $\Delta\mu^a(B/H, I, S)$ characterizes the ability of surface to interact specifically with benzene, in other words the surface polarity or acidity. For both supports, it has a value of around $-2{\cdot}0$ kJ mol$^{-1}$, which was found also by other authors[16] and is typical of the usual unmodified alumina[14]. For comparative purposes, we have calculated from literature data[17] the value $+3{\cdot}0$ kJ mol$^{-1}$ for nonpolar graphite and the value of ca. $-8{\cdot}0$ kJ mol$^{-1}$ for highly polar zeolites[7]. Specific centres on alumina surface which can interact with benzene are the acidic hydrogens of OH groups and the coordinatively unsaturated $Al^{3+}$ ions; the method does not distinguish different types of the acidity. Sample of $MoO_3$ had similar polarity as alumina; hence, it is not surprising that the catalysts L2, L3, L5, and L7 prepared by depositing $MoO_3$ on alumina, showed identical polarity. As shown in Table II, the sample of CoO exhibited somewhat lower polarity than $MoO_3$. This is in accordance with the results of other authors[8,9,18] who found by using a similar method that $Co(OH)_2$, $Ni(OH)_2$, NiO and Ni are all little polar; based on their literature data, the calculated values of $\Delta\mu^a(B/H, I, S)$ for the above compounds changed in the range from $-0{\cdot}8$ to $-1{\cdot}6$ kJ mol$^{-1}$. Neither the addition of CoO to the catalyst L3 (Mo/Al) had any significant effect on $\Delta\mu^a(B/H, I, S)$, and the similar value of polarity was calculated by us for $Co–Mo/Al_2O_3$ catalyst also from data reported by Barbul and collaborators[16].

The results for commercial catalysts in oxidic form are presented in Table III. Data on adsorption of heptane do not provide much information as they cannot be compared to the adsorption on the support itself. The chemical potentials of adsorbed heptane were different, even when they were compared at constant $S(m)$. The differences observed cannot be ascribed solely to the different quality of the surface of the catalysts, since by comparison at constant $S(m)$, the effect of physical factor is not sufficiently eliminated, namely that of dispersity of the adsorbent which is not determined sufficiently by BET surface area. In the same way we have earlier interpreted the great fluctuation in $\Delta\mu^a(H, I, S(m))$ for different aluminas[14].

Except for the sample ICI-61-1, the polarity of commercial catalysts did not differ much from that of usual unmodified aluminas[14], $MoO_3$ and our laboratory $Co–Mo/Al_2O_3$ catalyst. The polarity of the sample of ICI-61-1 catalyst was, however,

higher and was comparable to the polarity found earlier[14] for the aluminas modified by $H_2SO_4$ or HCl. The behaviour of this sample cannot be related to the Ni content, as the catalyst CH-3630 contains Ni, too, and does not exhibit enhanced polarity; the difference in polarity between $Ni(OH)_2$ and $Co(OH)_2$ was not observed also by Bolotina and coworkers[9]. Detailed composition and preparation of the sample ICI-61-1 is not available and thus this result cannot be interpreted; the higher polarity could be *e.g.* due to the content of $SiO_2$ which increases the acidity of alumina.

The effect of sulphidation of samples on adsorption was followed with the use of model series of laboratory catalysts L1 (Al), $MoO_3$, CoO, L3 (Mo/Al), L4 (Co/Al), and L5 (CoMo/Al) and of the series including all the commercial catalysts.

The results obtained with laboratory samples are given in Table IV. The adsorption of heptane on the support L1 (Al) as such and on CoO sample changed only little by sulphidation. On the other hand, the adsorption on $MoO_3$ has changed by one order of magnitude. Transition between these extremes for $Al_2O_3$ (negligible change) and $MoO_3$ (marked change) is the increased adsorption of heptane after sulphidation of samples L3 (Mo/Al) and L5 (CoMo/Al); these samples behaved thus as a mixture of $Al_2O_3$ and $MoO_3$. This agrees with data on the structure of the catalysts of this type obtained by other methods (for review see *e.g.*[19,20]). The $MoO_3$ monolayer on alumina is deteriorated by sulphidation under formation of dispersed $MoS_2$ and with reformation of alumina surface. The adsorption of heptane on $MoS_2$ is greater than on $MoO_3$, and on $Al_2O_3$ it is smaller than on $MoO_3$ (compare the results for oxidic samples); therefore, the increase in the adsorption due to sulphidation for

TABLE III

Relative chemical potentials $\Delta\mu^a$ of hydrocarbons adsorbed on commercial catalysts in oxidic form, kJ mol$^{-1}$

| Catalyst *I* | $\Delta\mu^a$ (H, *I*/CH-3601, *S*) | | $\Delta\mu^a$ (B/H, *I*, *S*) |
|---|---|---|---|
| | $S = S$ (g) | $S = S$ (m) | |
| CH-3601[a] | 0·00 | 0·00 | −0·81 |
| G-35 | −1·06 | 1·63 | −1·14 |
| ICI-61-1 | 1·63 | 3·66 | −4·64 |
| ICI-41-6 | 3·00 | 6·51 | −2·44 |
| CH-3630 | −1·71 | 2·44 | −0·81 |
| CH-PPS | 2·51 | 4·23 | −1·95 |
| HT-400E | 1·63 | 2·03 | −1·30 |

[a] $\Delta\mu^a$ (H, CH-3601/L1 (Al), $S$(g)) = −2·44 kJ mol$^{-1}$; $\Delta\mu^a$ (H, CH-3601/L1 (Al), $S$(m)) = = −2·84 kJ mol$^{-1}$.

supported $MoO_3$ is smaller than for the unsupported oxide. The increase in the adsorption was greater for the promoted catalyst than for the unpromoted one, which indicates that the higher dispersed $MoS_2$ is formed in the presence of promotor.

The effect of sulphidation on the adsorption of hydrocarbons on the commercial catalysts is summarized in Table V. The increase in heptane adsorption after sulphidation, indicating according to previous discussion the disperzity of supported molybdenum was different for individual samples. The dispersion of supported molybdenum can be evaluated by oxygen chemisorption on reduced samples. Kraus and

TABLE IV

Relative chemical potentials of adsorbed hydrocarbons on sulphided laboratory catalysts, kJ $mol^{-1}$

| Catalyst *I* | $\Delta\mu^a$ (i, *I*(s)/*I*(o), *S*(g)) | | $\Delta\mu^a$ (B/H, *I*, *S*) |
|---|---|---|---|
| | *i* = H | *i* = B | |
| L1 (Al) | −0·41 | −0·24 | −1·70 |
| L3 (Mo/Al) | −2·52 | −0·73 | −0·08 |
| L4 (Co/Al) | −1·63 | −0·81 | −1·38 |
| L5 (CoMo/Al) | −4·47 | −2·44 | −0·33 |
| $MoO_3$ | −8·70 | −5·12 | 1·87 |
| CoO | −0·81 | 0·81 | 0·16 |

TABLE V

Relative chemical potentials of adsorbed hydrocarbons on sulphided commercial catalysts, kJ $mol^{-1}$

| Catalyst *I* | $\Delta\mu^a$ (*i*, *I*(s)/*I*(o), *S*(g)) | | $\Delta\mu^a$ (B/H, *I*, *S*) |
|---|---|---|---|
| | *i* = H | *i* = B | |
| CH-3601 | 0·57 | 0·73 | −0·41 |
| G-35 | 0·16 | −0·16 | −1·38 |
| ICI-61-1 | −4·64 | −0·65 | −0·41 |
| ICI-41-6 | −5·45 | −3·33 | −0·33 |
| CH-3630 | −1·87 | −0·57 | 0·33 |
| CH-PPS | −3·82 | −2·60 | −0·73 |
| HT-400E | −5·69 | −4·64 | −0·33 |
| L5 (CoMo/Al) | −4·47 | −2·43 | −0·33 |

coworkers[1] reported data for catalysts CH-3601, G-35, L5 (CoMo/Al), and HT 400E of our series. It can be stated that our findings correlate excellently with their results. Samples CH-3601 and G-35 adsorbed a small amount of oxygen, 0·16 and 0·23 NTP ml $O_2$ $g^{-1}$ respectively, and the adsorption of heptane on samples changed only little after their sulphidation; both methods thus indicate the low dispersion of supported molybdenum. In the case of catalyst CH-3601 this is caused obviously by the fact that this catalyst is prepared by co-precipitation[21] and the part of molybdenum is thus closed within the catalyst mass. The technology of the production of G-35 catalyst has not been reported. On the other hand, catalysts L5 (CoMo/Al) and HT 400E adsorbed substantially more oxygen, 0·40 and 0·57 NTP ml $O_2$ $g^{-1}$ resp., and also the change in the potential of adsorbed heptane due to sulphidation was proportionally greater, $-4{\cdot}47$ and $-5{\cdot}69$ kJ $mol^{-1}$, resp.

Fig. 3 shows that the change in benzene adsorption on sulphidation of samples $Al_2O_3$, $Mo/Al_2O_3$, $Co\text{–}Mo/Al_2O_3$, and $MoO_3$ correlated with the change in heptane adsorption. On going from $MoO_3$ to $MoS_2$, the nonspecific part of the interaction with surface increases similarly for benzene and heptane but at the same time its specific part disappears. This is the reason why the change in $\Delta\mu^a$ due to sulphidation is smaller for benzene than is for heptane and the slope of correlation line in Fig. 3 is less than 1.

According to Fig. 3, the same correlation holds also for the commercial samples, except for ICI-61-1. The reason for deviation of the ICI-61-1 catalyst is obviously the extraordinarily high polarity in oxidic state. The specific component of the benzene--surface interaction is here great compared to the other samples, and the increase in nonspecific interaction on going from $MoO_3$ to $MoS_2$ thus affects only little the overall affinity of the surface; that is why $\Delta\mu^a$(B, $I$(s)/$I$(o), $S$) for the sample ICI-61-1 was so small.

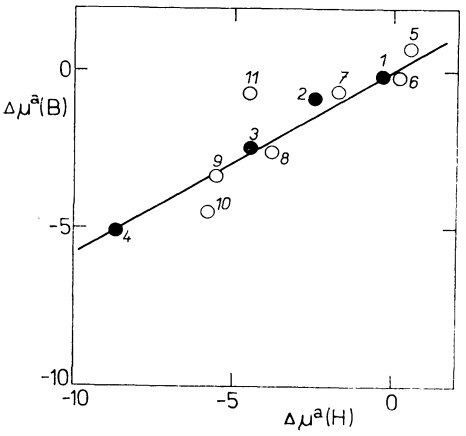


FIG. 3

Correlation of relative chemical potentials $\Delta\mu^a(i, I(s)/I(o), S(g))$ of benzene and heptane on catalysts in sulphided and oxidic forms. ● Model catalysts *1* $Al_2O_3$(L1), *2* $Mo/Al_2O_3$(L3), *3* $Co\text{-}Mo/Al_2O_3$(L5), *4* $MoO_3$; ○ commercial catalysts *5* CH-3601, *6* G-35, *7* CH-3630, *8* CH-PPS, *9* ICI 41-6, *10* HT 400E, *11* ICI 61-1

By linear interpolation between $Al_2O_3$ and $MoO_3$, we have calculated the approximate proportion of the surface of the catalysts which could be converted into $MoS_2$ by sulphidation, using the change in heptane adsorption after sulphidation: $Al_2O_3$ 0%, CH-3601 0%, G-35 0%, CH-3630 21%, L2 (Mo/Al) 29%, CH-PPS 44%, L3 (CoMo/Al) 51%, ICI-61-1 53%, ICI-41-6 63%, HT 400E 68%, and $MoO_3$ 100%. The sulphide $MoS_2$ is not the only active form of molybdenum on the surface, as the catalysts CH-3601 and G-35 essentially do not contain $MoS_2$ on the surface, as judged from our results, and they are still, even though relatively little, active[1].

Similarly to the change of surface properties due to sulphidation, the marked difference between support L1 (Al) and $MoO_3$ has been found also in their polarity. The polarity of $Al_2O_3$ did not change by sulphidation (from $-1{\cdot}71$ to $-1{\cdot}70$ kJ . . $mol^{-1}$) and for $MoO_3$ it decreased by 3·90 kJ $mol^{-1}$ (from $-2{\cdot}03$ to $+1{\cdot}87$ kJ . . $mol^{-1}$). As a result of presulphidation, the polarity of samples L3 (Mo/Al) and L5 (CoMo/Al) decreased more than that of L1 (Al) and less than that of $MoO_3$. This comports again with the model[19,20] according to which sulphidation deteriorates the $MoO_3$ monolayer on surface, leads to formation of $MoS_2$ particles and to a partial re-formation of alumina surface.

The polarity of the commercial catalysts in sulphidic form have also been lower than in oxidic form, which can be related evidently to the transormation of $MoO_3$ into $MoS_2$ on their surface. Of course, the value of $\Delta\mu^a$ (B/H, *I*, *S*) for mixed catalysts is the overall characteristics which has not to reflect some differences between samples. The catalyst with high dispersity of $MoS_2$ on a polar support can be comparable with the catalyst with low dispersity of $MoS_2$ on a nonpolar support.

The polarity for $MoO_3$(s) (*i.e.* $MoS_2$) from Table IV agrees well with data obtained by us for $MoS_2$ prepared by thermal decomposition of $(NH_4)_2$ $MoS_4$ (ref.[11]) and with data for $MoS_2$ reported by other authors[22]. The surface of $MoS_2$ is nonpolar, without the ability to interact specifically, and is similar to the surface of graphite. On storing in air, this surface is oxidized, and the surface polar groups so formed could have interacted with benzene. Notwithstanding, neither we nor other authors[22] have observed specific interactions in chromatographic expreiments. It seems likely that on heating the sample in an inert gas, the surface oxygen is transferred into the bulk of the sample and by this way, the nonpolar, nonspecific character of the surface is reformed. Temperature limitation of the rate of oxygen diffusion into the catalyst mass was studied by oxygen chemisorption in connection with the determination of active molybdenum (for review see[1]). The same behaviour can be expected also for $MoS_2$ in supported catalysts. For that reason, when interpreting our results, the surface oxidation during storage of presulphided samples in air has been disregarded.

The results obtained show that the $MoS_2$ surface in supported catalysts can be evaluated from the adsorption of hydrocarbons and that in this respect the commercial catalysts exhibit markedly different behaviour. The acidity of surface was estimated from the specific interactions of benzene as a weak π-base. It was found that

the acidity of hydrodesulphurization catalysts in the working, sulphided state does not exceed the acidity of the support.

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