Surface acidity in promoted molybdena and tungsta hydrodesulphurisation catalysts

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Abstract. Acidity of Ni- and Co-promoted molybdena and tungsta hydrodesulphurisation (HDS) catalysts have been determined by volumetric adsorption of ammonia. A direct correlation between the adsorption of ammonia, and hence the acidity, and the HDS activity could be observed for reduced catalysts. A relation between ammonia adsorption and anion vacancy concentration is thus indicated, as the latter is related to HDS activity. Contrary to unpromoted molybdena there is a decrease in acidity on sulphidation of Ni-promoted molybdena catalyst. This decrease is attributed to the influence of Ni in suppressing the formation of anion vacancies by catalysing the crystallisation of MoS_2. Promoted tungsta catalysts were found to have lower acidities as compared to promoted molybdena catalysts, which is consistent with their lower desulphurisation activity.

Keywords. Surface acidity; molybdena; tungsta; hydrodesulphurisation catalyst; ammonia adsorption.

1. Introduction

Molybdena and tungsta catalysts are widely used hydrodesulphurisation (HDS) catalysts (Mitchell 1977) and they have been the object of a number of studies (in particular Co–Mo catalysts). The term 'molybdena' or 'tungsta' denotes the composite catalyst consisting of molybdenum oxide or tungsten oxide supported on alumina. In order to study the factors that determine the catalytic properties of these systems, some investigations (Iannibello *et al* 1979; Laine *et al* 1979; Sivasankar *et al* 1979) were centred on the characterisation of surface acid properties. The present work is an attempt to study the surface characteristics of Ni- and Co-promoted molybdena and tungsta by ammonia adsorption in the reduced and sulphided forms. Low surface area alumina has been used as the support material for the preparation of the catalysts. It has been shown earlier (Desikan and Amberg 1964) that other more basic molecules like pyridine and ammonia as well as alkali can completely poison both the hydrogenation and desulphurisation activities of sulphided Co–Mo catalysts indicating that practically all the catalytic sites involved in the HDS reactions are acidic in nature. Due to the intense black colour of the sulphided samples, they are not as easily amenable for study as calcined samples using spectroscopic techniques. Adsorption studies are, therefore, best suited to characterise qualitatively the number and the nature of the acid sites on sulphided forms of molybdena and tungsta catalysts.

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2. Experimental

2.1 *Catalysts*

A list of catalysts studied is given in table 1. Nickel molybdena catalysts were prepared by co-impregnating alumina with solutions of ammonium paramolybdate and nickel nitrate (AR grade, BDH). The concentrations of the solutions were adjusted to give samples containing 13% MoO_3 by weight and Ni/(Ni + Mo) atomic ratios in the range 0 to 0·54. After co-impregnation the samples were dried in an oven at 110°C for 3 h and finally calcined at 500°C for 6 h.

Two additional nickel molybdena samples were prepared by successive impregnation rather than the co-impregnation described above. Both catalysts have an Ni/(Ni + Mo) ratio of 0·47. In one case, (Sample 9) the alumina was impregnated first with a solution of ammonium paramolybdate and dried in a oven at 100°C for 3 h. After 6 h calcination at 500°C, the powder was impregnated with nickel nitrate solution and dried in a oven for 3 hrs at 110°C. The dried sample was then calcined at 500°C for 6 h.

The other sample (No. 8) was prepared in a similar way but the order of impregnation was reversed. That is, alumina was impregnated first with nickel nitrate solution and then with a solution of ammonium paramolybdate.

Cobalt-promoted molybdena and nickel-and cobalt-promoted tungsta catalysts have also been prepared by co-impregnation. Tungstic acid ($WO_3 \cdot H_2O$, extra pure AR, supplied by SISCO Research Laboratories, Bombay) has been used for the incorporation of tungsten oxide. In nickel tungsta catalyst (sample 12) and cobalt molybdena catalyst (sample 10), the atomic ratios of Ni/(Ni + W) and Co/(Co + Mo) are 0·37 and 0·34, respectively, which are comparable to the Ni/(Ni + Mo) ratio of sample 4. The value of the Co/(Co + W) ratio in the cobalt tungsta catalyst was 0·27 which was comparable to the Ni/(Ni + Mo) ratio of sample 3. Catalyst notation used is such that 8 Ni–13 Mo–Al_2O_3 denotes 8% of NiO and 13% of MoO_3 by weight. For the sake of simplicity all catalyst concentrations are referred to in their oxidic forms. BET surface areas of catalysis were evaluated in a conventional volumetric set-up (Srinivasan 1957) by N_2-adsorption at liquid-N_2 temperature.

2.2 *Ammonia adsorption*

Ammonia adsorption was carried out in an all-glass volumetric adsorption apparatus (Srinivasan 1957). The catalyst tube containing a catalyst charge of 1 g was attached to the adsorption set-up. The catalyst was initially reduced in pure H_2 (flow rate 20 ml/min) for 4 h at a temperature of about 400°C. Before starting the adsorption experiment the sample was degassed at 400°C for 5 h under a vacuum of $1·3 \times 10^{-9}$ bar. The sample was then cooled to the isotherm temperature. The adsorption of ammonia was measured at temperatures of 200–330°C. The reduced catalyst samples were sulphided with a mixture of C_4H_4S/H_2 (8% by volume) at 400°C for 4 h and these sulphided samples were also subjected to ammonia adsorption measurements.

2.3 *Hydrodesulphurisation activity*

Hydrodesulphurisation of thiophene on different catalysts was measured with a

Table 1. Composition and surface area of catalysts.

Catalyst		Composition (atomic ratio)								Surface area $(m^2\,g^{-1})$
Sample	Notation	$\dfrac{Ni}{Mo}$	$\dfrac{Co}{Mo}$	$\dfrac{Ni}{W}$	$\dfrac{Co}{W}$	$\dfrac{Ni}{Ni+Mo(?)}$	$\dfrac{Co}{Co+Mo}$	$\dfrac{Ni}{Ni+W}$	$\dfrac{Co}{Co+W}$	
1	13Mo–Al$_2$O$_3$	0·00	0·00	—	—	0·00	0·00	—	—	7·2
2	0·3Ni–13Mo–Al$_2$O$_3$	0·04	—	—	—	0·04	—	—	—	4·3
3	3Ni–13Mo–Al$_2$O$_3$	0·44	—	—	—	0·31	—	—	—	9·1
4	3·9Ni–13Mo–Al$_2$O$_3$	0·58	—	—	—	0·37	—	—	—	7·5
5	6Ni–13Mo–Al$_2$O$_3$	0·89	—	—	—	0·47	—	—	—	10·2
6	6·7Ni–13Mo–Al$_2$O$_3$	0·99	—	—	—	0·50	—	—	—	8·5
7	8Ni–13Mo–Al$_2$O$_3$	1·19	—	—	—	0·54	—	—	—	9·3
8*	6Ni–13Mo–Al$_2$O$_3$	0·89	—	—	—	0·47	—	—	—	5·5
9**	6Ni–13Mo–Al$_2$O$_3$	0·89	—	—	—	0·47	—	—	—	12·3
10	3·5Co–13Mo–Al$_2$O$_3$	—	0·52	—	—	—	0·34	—	—	4·6
11	24W–Al$_2$O$_3$	—	—	0·00	0·00	—	—	0·00	0·00	4·4
12	4·5Ni–24N–Al$_2$O$_3$	—	—	0·58	—	—	—	0·37	—	7·0
13	2·8Co–24W–Al$_2$O$_3$	—	—	—	0·36	—	—	—	0·27	6·4

* Ni was impregnated first; ** Mo was impregnated first.

microcatalytic pulse reactor. Analysis of the product stream was carried out with a gas chromatograph. Before carrying out the reaction the catalyst in the reactor was reduced in pure H_2 at a flow rate of 20 ml/min for 4 h at 400°C. In thiophene desulphurization reaction, the reactant H_2 also served as the carrier gas. A large number of thiophene pulses of 5 μl were introduced at 10-min intervals in order to obtain steady state activity after which no significant changes in activity occurred on further injection. Fractional conversion (x) of thiophene was calculated using the data obtained from the analysis of the product stream. All conversions were normalised to 0·38 g of catalyst, this being the average weight of all catalysts. The reaction temperature was 400°C.

Following observations made earlier (Bassett and Habgood 1960; Habgood 1967) under the conditions of thiophene desulphurisation by the gas chromatographic method, first-order kinetics can be assumed. The apparent first-order rate constant, k was calculated from the expression

$$k = \frac{F^\circ}{273 \, R \, W} \ln \frac{1}{1-x},$$ (1)

where F° is the flow rate of carrier gas corrected to standard temperature (0°C) and W is the weight of catalyst.

3. Results and discussion

Figures 1 and 2 show the variation in ammonia adsorption at 200°C for various catalysts in the reduced and in the sulphided states. Adsorption capacities are greatly influenced by the metal ions present in the catalyst. Comparison, consistent with activity, is made in the lower pressure region. Figures 3 and 4 report the strength distribution of sites adsorbing ammonia. This was obtained by calculating the isosteric heat of adsorption, q_{st}, at various coverages in the range 0·3–2·0 × 10^{-4} of A, the number of moles of ammonia (at NTP) adsorbed per gram catalyst, using the integrated form of the Clausius–Clapeyron equation. In general, isosteric heat decreases with surface coverage, indicating the non-homogeneous nature of the ammonia adsorption centres. Two regions of surface coverage may be generally distinguished in the calculated dependence of the isosteric heats upon the adsorbed amount of ammonia.

3.1 Reduced catalysts

On incorporation of Mo onto alumina there is a decrease in both the number (figure 1a) and the strength (figure 3a) of the acid sites. Sivasankar and coworkers (Sivasankar et al 1979) have reported a marked reduction in acidity of alumina on incorporation of molybdenum oxide onto alumina. But an entirely different result with respect to the change in acidity on deposition of molybdenum on alumina was observed by other workers (Kiviat and Petrakis 1973; Laine et al 1979; Iannibello et al 1979). An increase in acidity on incorporation of molybdenum has been reported in their work.

On deposition of nickel on molybdena samples, the acidity is found to increase. In order to understand the effect of the nickel content on the acidity of different Ni–Mo
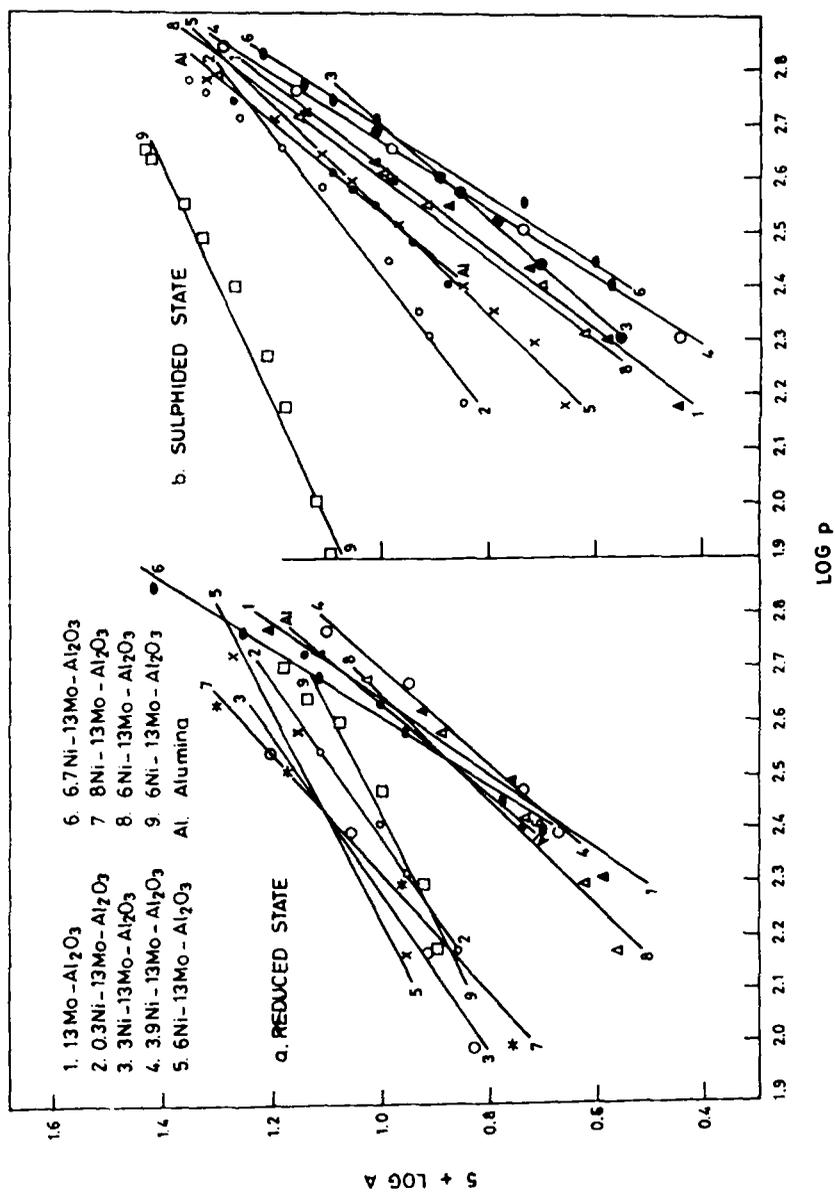
Figure 1. Comparison of ammonia adsorption capacity of various catalysts; dependence on the pressure p(Torr) at 200°C. A, the amount adsorbed is expressed in mol g^{-1}.
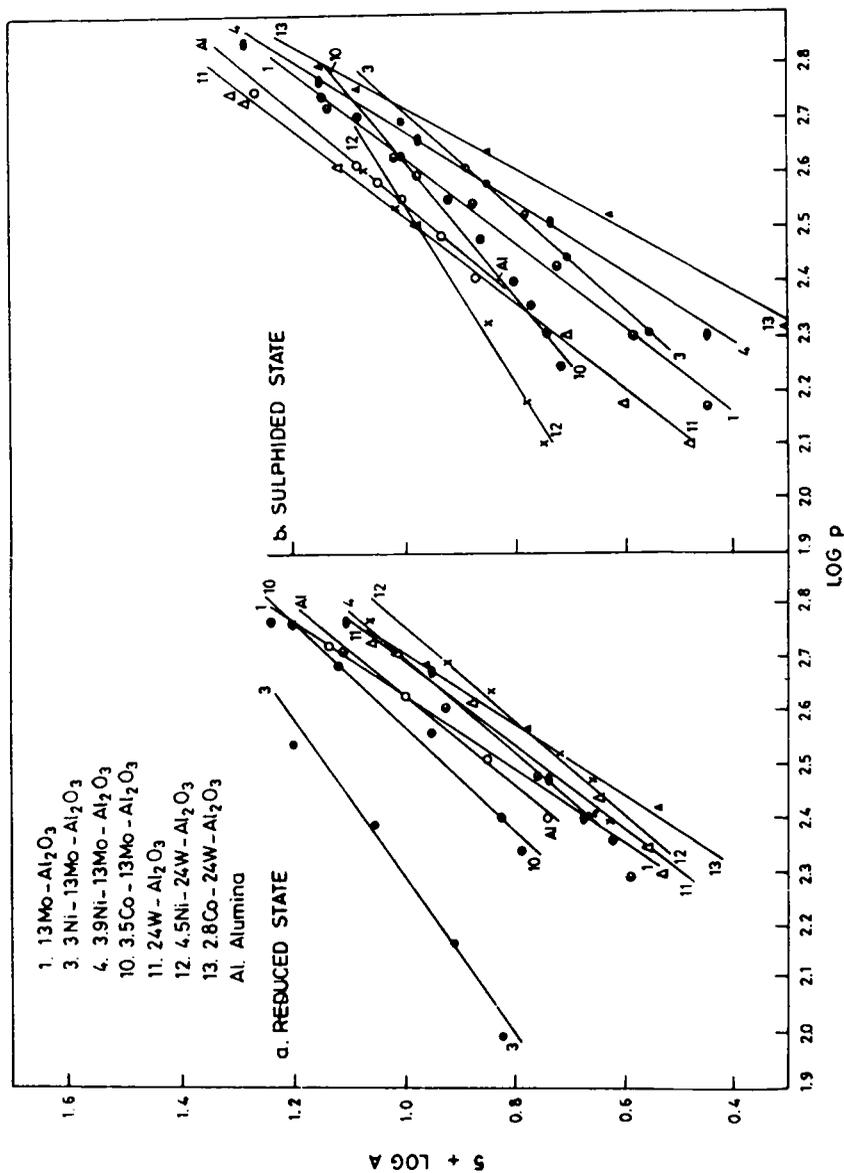
Figure 2. Comparison of ammonia adsorption capacity of various catalysts; dependence on the pressure p(Torr) at 200°C. A, the amount adsorbed is expressed in mol g^{-1}.
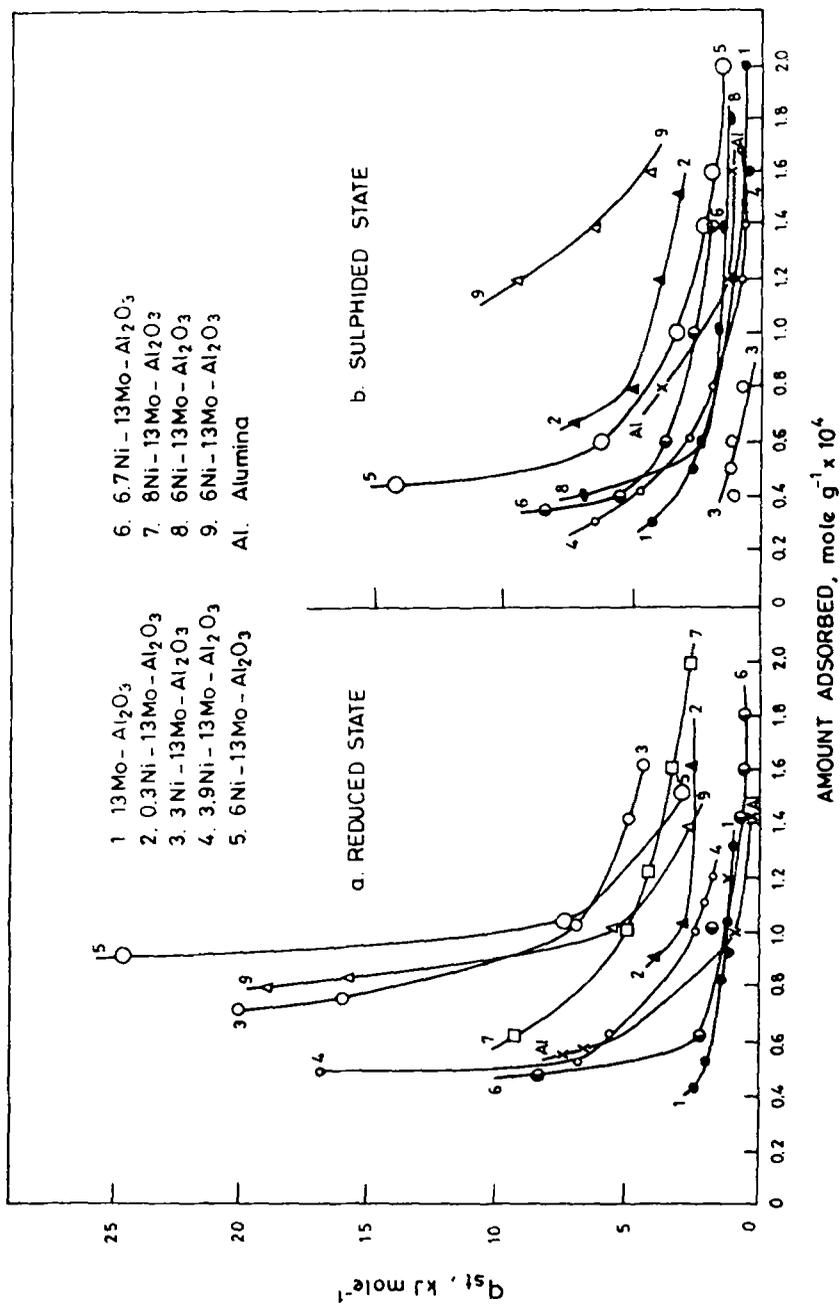
Figure 3. Calculated values of dependence of the isosteric heat of adsorption q_{st} upon the adsorbed amount of ammonia.
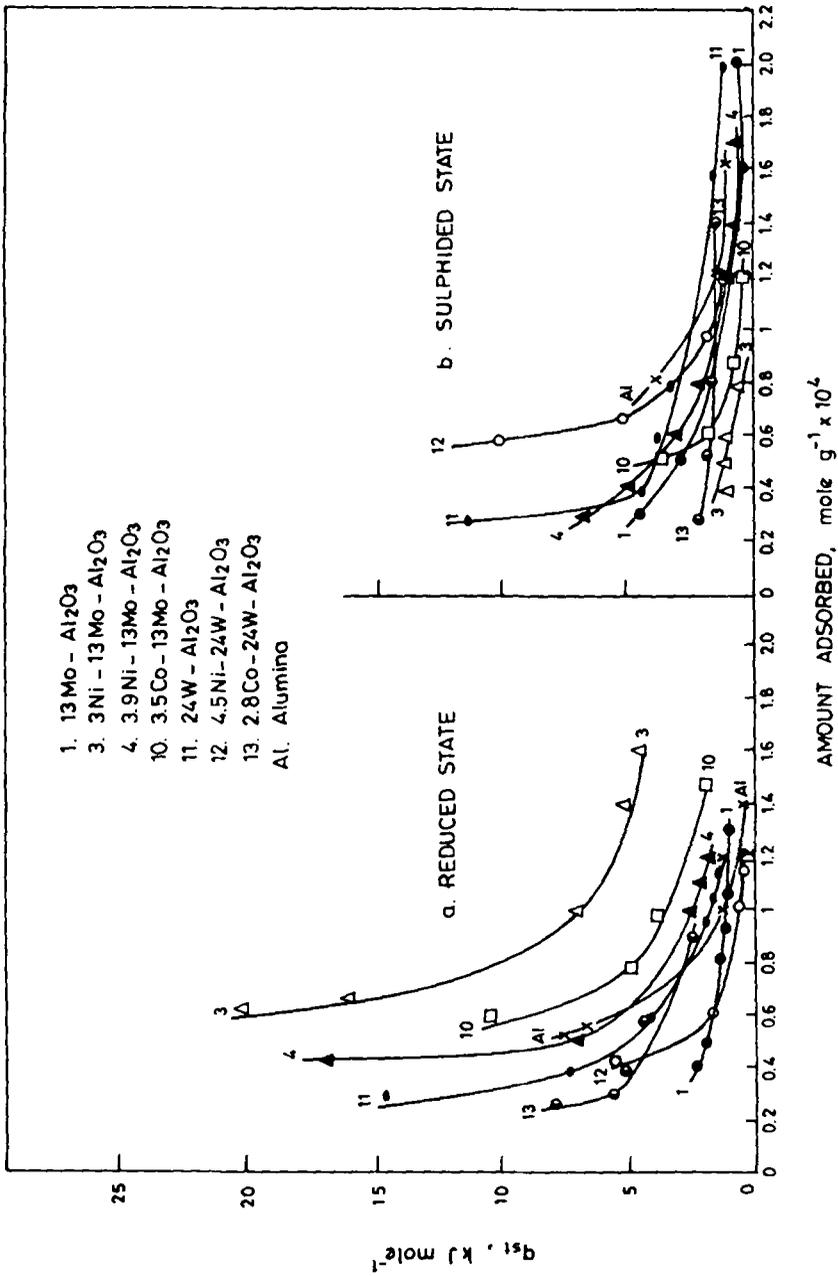
Figure 4.   Calculated values of dependence of the isosteric heat of adsorption, q_{st}, upon the adsorbed amount of ammonia.

Table 2. Reaction rate constants for various catalysts (400°C).

Catalyst		Rate constant $(mol\,atm^{-1}\,g^{-1}\,s^{-1})$	
Sample	Notation	Initial state (1st pulse)	Steady state (14th pulse)
1	$13Mo-Al_2O_3$	2.18×10^{-6}	5.18×10^{-6}
2	$0.3Ni-13Mo-Al_2O_3$	8.80×10^{-6}	5.33×10^{-6}
3	$3Ni-13Mo-Al_2O_3$	1.05×10^{-5}	4.93×10^{-6}
4	$3.9Ni-13Mo-Al_2O_3$	1.43×10^{-5}	5.18×10^{-6}
5	$6Ni-13Mo-Al_2O_3$	2.29×10^{-5}	8.46×10^{-6}
6	$6.7Ni-13Mo-Al_2O_3$	2.10×10^{-5}	6.46×10^{-6}
7	$8Ni-13Mo-Al_2O_3$	1.60×10^{-5}	6.23×10^{-6}
8*	$6Ni-13Mo-Al_2O_3$	2.57×10^{-5}	6.99×10^{-6}
9**	$6Ni-13Mo-Al_2O_3$	1.56×10^{-5}	8.71×10^{-6}
10	$3.5Co-13Mo-Al_2O_3$	5.80×10^{-6}	4.48×10^{-6}
11	$24W-Al_2O_3$	1.00×10^{-7}	2.10×10^{-7}
12	$4.5Ni-24N-Al_2O_3$	4.50×10^{-7}	8.5×10^{-7}
13	$2.8Co-24W-Al_2O_3$	1.00×10^{-7}	2.7×10^{-7}

* Ni was impregnated first; ** Mo was impregnated first.

catalysts, the ammonia adsorption data illustrated in figures 1a and 3a can be examined.

Figure 1a shows the variation in ammonia adsorption capacity for different catalysts containing various concentrations of nickel. It follows that the amount adsorbed, A, expressed in moles, increases as additional amounts of nickel are incorporated upto a certain limit of nickel concentration corresponding to sample 5 ($r = 0.47$) and then decreases. Thus for sample 6 ($r = 0.5$) or 7 ($r = 0.54$), adsorption was lower than that for sample 5. For sample 4 ($r = 0.37$) ammonia adsorption was abnormally low. However, a catalyst with Ni concentration, $r = 0.41$ (4.6 Ni–13 Mo–Al_2O_3) did show higher adsorption capacity. The catalyst composition exhibiting the highest NH_3 adsorption, $r = 0.47$ is also the optimum composition for maximum HDS activity (activity data are presented in table 2).

The strength distribution of ammonia sites in nickel molybdena catalysts is a function of nickel content (figure 3a). The dependence of adsorption heat upon the amount adsorbed decreases monotonously with surface coverage. Sample 5 with an optimum composition $r = 0.47$ produces the highest proportion of stronger sites (q_{st} between 7.5 and 25 kJ/mole). The negligible slope in this range of adsorption heat probably suggests that most of these sites have a strength near or equal to that of the strongest sites ($q_{st} = 2.5$ kJ/mole). Two types of acid sites are generated as a result of the incorporation of nickel onto an Mo–Al_2O_3 catalyst, namely the weaker sites (the region of higher adsorbed amounts) and the stronger sites (the region of lower adsorbed amounts). The values of heats of adsorption in the region of lower adsorbed amounts are of important consideration in relating the acid properties of the catalysts with HDS activity. In the region below 1×10^{-4} mol per gram the values of heat of adsorption for sample 5 are more than those for sample 3. But the reverse situation is observed in the region of higher adsorbed amounts (above 1×10^{-4} mol g^{-1}), the measured adsorption heats for sample 5 are lower than those for sample 3. This suggests that for sample 5 there is an increase in the number of relatively stronger sites
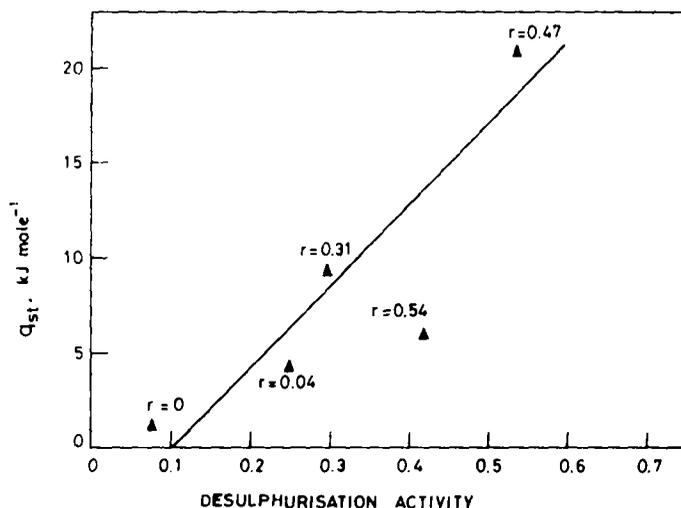
Figure 5. Correlation between q_{st} values of ammonia at a coverage of 0.9×10^{-4} mole g^{-1} and desulphurisation activities of nickel molybdena catalysts with different Ni concentrations. $r = $ Ni/(Ni + Mo) activity is given as fractional conversion at initial state of pulse reaction at 400°C.

and a decrease in the number of weaker sites as compared to sample 3. A direct relation exists between the values of heat of adsorption in the region of lower adsorption and desulphurisation activities of catalysts (figure 5). The stronger acidic sites at low surface coverage are tentatively identified with anion vacancies as the latter is related to HDS activity (Lipsch and Schuit 1969). With increase in the nickel content in nickel molybdena catalysts more anionic vacancies can be created. But there exists an optimum concentration of nickel at which the concentration of these sites is the highest. Figure 3a shows that the varying mode of preparation induces different acid-site distribution. The sample prepared by adding Ni to Mo-Al$_2$O$_3$ (sample 9) shows remarkably greater strength of acid-sites than the one wherein nickel has been deposited first (sample 8) (the values of heat adsorption were very small for sample 8 and hence could not be presented in figure 3a). But the number and the strength of acid sites are obviously less for sample 9 as compared to the one where both Mo and Ni were incorporated simultaneously (sample 5) as observed from figures 1a and 3a, respectively. Thus, catalysts with good acid properties may be prepared by co-impregnation, while inferior catalysts are obtained by sequential impregnation.

3.2 Sulphided catalysts

Figures 1 and 3, respectively, show various changes originating in the number and strength of sites adsorbing ammonia on sulphidation of reduced nickel molybdena catalysts. In general it becomes evident that sulphidation transforms the catalyst surface in such a way that increase in acidity occurs in the unpromoted catalyst, whereas there can be decrease in acidity in the case of a promoted catalyst. An explanation for the decrease in acidity can probably be advanced in terms of coke formation, or crystal growth (Laine and Pratt 1978) which are factors causing a decline in activity.

As an attempt to explain the results obtained with sulphided catalysts, samples of alumina and $Mo-Al_2O_3$ may be considered first. On sulphidation in the presence of hydrogen, there is an increase in the amount of NH_3 adsorbed for both Al_2O_3 and $Mo-Al_2O_3$ (figure 1). There is also a notable increase in the strength of acidic sites of these samples across the whole spectrum of surface coverage (figure 3). The increase in the strength of the acid sites of alumina on sulphidation shows that the electron-deficient nature of the Al^{3+} ions on the surface is further enhanced by loss of the additional hydroxyl groups leading to an increase in the overall positive charge of the aluminium ions and hence an increase in acidity. The number of exposed aluminium ions, capable of bonding to nucleophilic agents like NH_3, is probably also increased during the process of sulphidation. The phenomenon of disappearance of the O–H band and loss of surface –OH groups on the adsorption of thiophene on calcined $Co-Mo-Al_2O_3$ has been reported in an earlier IR spectroscopic study (Ratnasamy and Knozinger 1978). The creation of additional oxygen anion vacancies on sulphidation has also been reported by Massoth (1975) for the $Mo-Al_2O_3$ system. The increase in acidity of $Mo-Al_2O_3$ on sulphidation is probably due to the formation of new acidic sites mostly involving the anionic vacancies in the MoS_2 species created on reduction-cum-sulphidation of calcined $Mo-Al_2O_3$ as indicated below (Sivasankar *et al* 1979).

$$S^{2-} + H_2 = \square_s + 2e + H_2S$$
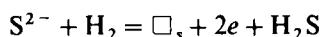
where $\square_s$ is an anion vacancy.

In constrast to the case of $Mo-Al_2O_3$, Ni-promoted molybdena catalysts (prepared by co-impregnation), showed reduction in both the number and strength of sites adsorbing ammonia on sulphidation. The decrease in acidity on sulphidation for Ni-containing molybdena catalysts may be attributed to the influence of nickel in suppressing the formation of anionic vacancies preventing the loss of sulphur [for catalysts with very low Ni contents, as in sample 2 ($r = 0.04$), an increase in strength of acid sites on sulphidation may occur]. Phenomenon similar to this has been reported with the Co–Mo system (Sivasankar *et al* 1979; Wentreck and Wise 1978) where cobalt was found to suppress the loss of S^{2-} ions. Ben Yaacov (1975) also concluded from thiophene TPD measurements that dispersion of the molybdenum sulphide monolayer decreased with increasing cobalt content in $Co-Mo-Al_2O_3$ catalysts indicating that MoS_2 crystallites in $Co-Mo-Al_2O_3$ are larger than in $Mo-Al_2O_3$. The influence of Ni in catalysing the crystallisation of MoS_2 is evident from results of the X-ray phase analysis carried out in our laboratory.

X-ray powder patterns revealed the presence of MoS_2 (ASTM 1967) in nickel-promoted molybdena catalysts with nickel concentration, $r \geqslant 0.3$ (sample 3 and others with higher Ni contents). The line patterns for the sulphided forms of these samples showed a line at $d = 6.14$ Å corresponding to the most intense signal of the MoS_2 spectrum [the X-ray analysis of a commercial MoS_2(BDH) resulted in a set of sharp peaks with a very intense signal at $d = 6.18$ Å] low intensity signal due to MoS_2 at $d = 2.71$ Å was also observed. No other signals of MoS_2 could be detected in the X-ray pattern. For the sulphided form of $Mo-Al_2O_3$ or nickel molybdena (sample 2) with a very low Ni content, $r = 0.04$, no diffraction lines of MoS_2 could be observed. It is quite probable in these cases that the MoS_2 phase is dimensionally too small to be 'seen' by X-ray diffraction. From these results it may be inferred that the concentration of incorporated Ni influences the formation of the MoS_2 phase in sulphided catalysts. MoS_2 is easily detected for samples with higher Ni contents as

compared to those with lower concentrations of Ni. Addition of Ni to Mo–Al_2O_3 facilitates the growth of MoS_2 resulting in a less amorphous sulphide phase. For catalysts with lower Ni contents, there was evidence of Bragg reflections of $Al_2(MoO_4)_3$, whereas for catalyst samples with higher Ni contents and detectable amounts of the MoS_2 phase no diffraction bands corresponding to $Al_2(MoO_4)_3$ were observed. It is known (Badilla-Oblbaum and Chadwick 1980) that formation of the $Al_2(MoO_4)_3$ phase inhibits the process of sulphidation.

For nickel molybdena catalysts prepared by sequential impregnation (samples 8 and 9), an increase in acidity seems to occur on sulphidation. There is an increase in both the number and strength of acid sites for sample 9 (figures 1 and 3). For sample 8, even though there is a decrease in the total amount of NH_3 adsorbed, there is a remarkable increase in the strength of acid sites on sulphidation (q_{st} values for reduced catalyst, sample 8 were very small and hence are not presented in figure 3a).

On deposition of tungsten on alumina, a decrease in the number of strong acid sites occurs (figure 4a). Decrease in adsorption capacity is observed for the full range of pressure involved (figure 2a). On deposition of both Ni and Co on W–Al_2O_3 (samples 12 and 13), a decrease in the strength of acid sites is observed, especially in the region of lower adsorbed amounts. On deposition of cobalt on Mo–Al_2O_3 an increase in acidity occurs (figure 4a). Nickel- and cobalt-promoted tungsta catalysts exhibit relatively lower acidities as compared to promoted molybdena catalysts of comparable composition. Thus, promoted molybdena catalysts, samples 4 ($r = 0.37$) and 10 (Co/Co + Mo = 0.34), show higher strengths of acid sites in comparison to promoted tungsta catalyst, sample 12 (Ni/(Ni + W) = 0.37), across the whole spectrum of surface coverage. Similarly the strength of sites for the molybdena catalyst, sample 3 ($r = 0.31$), is obviously greater than that for the tungsta catalyst, sample 13 (Co/(Co + W) = 0.27). The lower acidities of tungsta catalysts are consistent with their lower desulphurisation activities (table 2).

Unlike Mo–Al_2O_3, W–Al_2O_3 on sulphidation shows a decrease in the strength of acidic sites in the region of lower adsorbed amounts (figure 4) although an increase in the number of acid sites is observed (figure 2). As compared to promoted molybdena catalysts, promoted tungsta catalysts with lower activities show decrease in acidity on sulphidation (figure 4).

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