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Metal Sulfide–Support Interactions

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Alumina-supported Ni catalysts have been prepared and their activity for the hydrodesulfurization (HDS) of thiophene measured in a flow microreactor at atmospheric pressure. The HDS activity has been compared with that obtained for a standard silica-supported Ni catalyst. The results show that on a unit mass basis the Ni/SiO_2 catalyst is almost an order of magnitude more active than the Ni/Al_2O_3 catalysts and that this difference is independent of whether or not the Ni/Al_2O_3 catalysts are calcined before use. The amount of O_2 adsorbed at 195 K or of CO adsorbed at ambient temperature onto presulfided catalysts was measured in a static volumetric system, and the data were used to estimate the dispersion of the active sulfide phase. The specific activity of the catalysts was determined using the adsorption data. It was found that the Ni/SiO_2 catalyst was significantly more active than any of the Ni/Al_2O_3 catalysts. Comparison with activity data for unsupported Ni_3S_2 and Ni/C catalysts shows that the Ni/SiO_2 has activity comparable to that of Ni_3S_2. It is proposed that the low activity of sulfided Ni/Al_2O_3 catalysts arises because of a metal sulfide–support interaction which may alter the morphology or composition of the Ni sulfide phase.

INTRODUCTION

Ni-promoted Mo sulfide catalysts are used extensively as hydrotreating catalysts. It is generally agreed that the active catalyst is a MoS_2 crystallite promoted by Ni ions, which may be decorating the edges of the MoS_2 (*1*). Recently, however, de Beer and co-workers (*2*, *3*) have questioned this conventional interpretation and pointed out that even by itself Ni sulfide can exhibit high activity on certain types of support. Thus, Ni/mordenite (*4*) and Ni/C (*2*, *3*) have higher activities than Ni/alumina (*5*). Pratt *et al.* (*6*) have shown that unsupported Ni sulfide has a high activity, similar, in fact, to that of MoS_2 itself. Bachelier *et al.* (*5*, *7*) have shown that with Ni/alumina catalysts the activity of the sulfided catalyst can be increased if the calcination temperature is lowered, or the sulfiding temperature is raised.

It is implicit in these publications of Bachelier, de Beer, and others that the low activity of alumina-supported Ni is caused by a strong interaction between Ni and the support. During preparation or pretreatment Ni ions may react to form Ni aluminate which is difficult, if not impossible, to sulfide. It is, of course, possible that the low activity of Ni/alumina catalysts is due to a loss of Ni by reaction with the support. However, this is not a wholly satisfactory explanation since, in their work, Bachelier *et al.* allowed for this by determining the amount of free Ni. They observed that as the Ni content was increased, from 0.91 to 6.67%, the percentage Ni which could be sulfided increased from about 75 to 100%. However, the hydrodesulfurization (HDS) activity (calculated as the conversion of thiophene per hour per gram of Ni) hardly varies over this range of Ni contents.

An alternative explanation for the influence of the support on the activity of Ni sulfide is that the support changes the morphology of the Ni sulfide. The Ni–S phase diagram is very complex (*8*), but there are two sulfides (Ni_3S_2 and NiS) which are relatively stable (*9*). These have fundamentally different structures (*10–12*). Ni_3S_2 has a

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rhombohedral structure in which there is a slightly distorted body-centered cubic arrangement of S with the metal atom at some of the pseudotetrahedral sites. NiS has two polymorphs. Below 620 K, NiS has the rhombohedral symmetry, but at higher temperatures it has the NiAs-type structure. In the rhombohedral form the Ni is surrounded by five S atoms in a tetragonal pyramidal structure, whereas in the NiAs structure each Ni is octahedrally coordinated to S.

The free energies of formation of Ni_3S_2 and NiS are quite comparable (*9*). Which of these sulfides is stable under reaction conditions will depend on the temperature and on the H_2/H_2S ratio in the gas phase. We can calculate from the free energy data that at 620 K an H_2S/H_2 ratio of about 10^{-2} is required to produce NiS as compared with a ratio of about 10^{-4} to form Ni_3S_2. There is, therefore, quite a delicate balance between the stabilities of these compounds. Thus, it would seem quite possible that the more stable Ni_3S_2 would normally be present, but that in certain circumstances support interactions could lead to the formation of NiS. Tanaka and Okuhara (*13*) have demonstrated that Ni ions fully coordinated by S ions are inactive even for simple hydrogenation reactions. They conclude that the catalytic behavior of sulfided Ni is controlled by the coordinative unsaturation of the Ni ion, the activity increasing as the degree of unsaturation increases. It seems reasonable, therefore, to expect that Ni_3S_2, in which the Ni is coordinated by only four S ions, would be inherently more active than NiS, in which the Ni is surrounded by six S ions in the high temperature modification and by five S ions in the low temperature modification. Moreover, the removal of a single S ion from the surface of Ni_3S_2 will produce a very exposed Ni cation due to the very open nature of the tetrahedral structure.

The aim of the work described here was to investigate metal sulfide–support interactions in Ni HDS catalysts, the objective being to determine whether the intrinsic activity of a Ni sulfide particle was affected by the choice of support. In order to differentiate between changes in intrinsic activity and changes in activity due, for example, to loss of Ni as Ni aluminate, it is necessary to determine the dispersion of the Ni. Recent work (*5, 14*) has shown that oxygen adsorption can provide an estimate of the number of active sites in Ni sulfide catalysts. For a series of related catalysts there is a good correlation between the quantity of oxygen adsorbed and the HDS activity. We have used selective chemisorption of oxygen and of CO to probe support effects in Ni catalysts.

EXPERIMENTAL

Catalysts containing 2.93 (Ni3Al), 4.76 (Ni5Al), 8.97 (Ni9Al), 19.1 (Ni19Al), and 27.7 (Ni28Al) wt% Ni on alumina (Ketjen 000-3P, surface area 244 $m^2\ g^{-1}$) were prepared by wet impregnation with solutions of Ni nitrate (Fisons AnalaR grade). Excess water was removed by rotary evaporation at 360 K, after which the samples were dried for 16 h at 390 K. Most samples were calcined in air for 4 h at 773 K. However, the effect of calcination on catalytic activity was checked by investigating uncalcined samples of Ni19Al and by calcining Ni28Al for 16 h at 773 K. A Ni/silica catalyst (Ni9Si) containing 8.99% Ni was also investigated. This was a sample of the NPL/SCI/IUPAC standard Ni catalyst, some characteristics of which have been described elsewhere (*15*). The silica had a surface area of 197 $m^2\ g^{-1}$. For our experiments the catalyst was dried and then calcined in air for 4 h at 773 K.

The catalysts (0.3 g) were placed in an all-glass reactor and presulfided in 10% H_2S/H_2 by heating at 12.5 K/min to 650 K and holding at this temperature for 1 h. After sulfiding, the samples to be used for catalytic experiments were cooled *in situ* to the reaction temperature, 620 K, and the activity for the HDS of thiophene was measured under flow conditions by injecting thiophene (10% v/v in *n*-hexane, total flow rate of 0.4 cm^3 h^{-1}) into a heated, stainless-steel tube, through which H_2 was passed at a flow rate of 1200 cm^3 h^{-1}. Products from the reaction were separated using a Carlo Erba gas chromatograph, containing a 6-m column of 20% silicone fluid on Chromosorb P, and the areas of the peaks given by the flame ionization detector were determined with an Infotronics electronic integrator.

The amount of oxygen adsorbed by the sulfided catalysts was determined by connecting the reactor to a conventional all-glass volumetric apparatus. The samples were cooled down in H_2S/H_2 and then evacuated for 10 min at room temperature before cooling to 195 K where pumping was continued for a further 10 min. The total amount of oxygen adsorbed after 20 min was determined using an initial pressure of 35 Torr. Reversibly adsorbed oxygen was removed by evacuation and a second adsorption at 35 Torr performed. The amount of oxygen adsorbed irreversibly was obtained from the difference between the two measurements. Preliminary work had established that this gave reproducible adsorption data.

An independent estimate of the dispersion of the Ni sulfide catalyst was obtained by measuring the total amount of CO adsorbed at ambient temperature on the presulfided samples. The equipment used for the CO measurements was the same as that described above for oxygen adsorption.

RESULTS AND DISCUSSION

Table 1 gives the HDS activities for the Ni catalysts, and the corresponding amounts of oxygen and CO adsorbed. For the calcined samples there is a small decrease in HDS activity with increasing Ni content. Omitting the calcination step produces a slightly higher HDS activity. These results are consistent with the pattern of activity reported by Bachelier *et al.* (*5, 7*). The Ni/silica catalyst is significantly more active than the corresponding 9% Ni/alumina catalyst, and is also much more active than the uncalcined Ni/alumina catalyst.

TABLE 1

Hydrodesulfurization Activities and Chemisorption Capacities of Ni Catalysts

Catalyst	R_T[a]	R_T[b]	O/Ni[c]	CO/Ni
Ni3Al	0.04	1.37	0.080	0.030
Ni5Al	0.05	1.05	0.106	0.027
Ni9Al	0.07	0.78	0.116	0.022
Ni19Al	0.14	0.73	0.143	0.012
Ni19Al(u)[d]	0.17	0.89	0.038	—
Ni28Al(c)[e]	0.13	0.47	0.038	—
Ni9Si	0.61	6.79	0.073	0.031

[a] Activity for the HDS of thiophene at 620 K; units are mmol/h/g catalyst.

[b] Activity for the HDS of thiophene at 620 K; units are mmol/h/g Ni.

[c] O/Ni atomic ratio.

[d] Uncalcined sample.

[e] Sample calcined for 16 h at 773 K.

For the alumina-supported catalysts the CO/Ni ratio parallels the change in HDS activity per gram of Ni. The O/Ni ratio, however, follows more closely the trend in HDS activity per gram of catalyst. The fact that the trends in the adsorption of CO and O_2 are different indicates that these two adsorbates are attached to different sites on the surface. At this stage of our understanding of the adsorption characteristics of sulfide catalysts it is not possible to choose which of the two, if indeed either, genuinely measures the dispersion of the Ni sulfide. Since there is no obvious way to resolve this dilemma we show in Table 2 the specific activities of the Ni catalysts, defined as the rate of HDS of thiophene divided either by the number of oxygen atoms or by the number of CO molecules adsorbed. If either of these probe molecules measures the dispersion of the active phase then these data should correspond to the specific activities of the various catalysts. It is clear from Table 2 that based on the oxygen (or CO) adsorption data the Ni/silica catalyst is about nine (or five) times more active than the Ni/alumina catalysts.

TABLE 2

Specific Activities of Ni Catalysts for the HDS of Thiophene

Catalyst	R_T[a] (O/Ni)	R_T[a] (CO/Ni)
Ni3Al	1.00	2.67
Ni5Al	0.57	2.22
Ni9Al	0.43	2.27
Ni19Al	0.28	3.33
Ni19Al(u)	1.32	—
Ni28Al(c)	0.79	—
Average[b]	0.614	2.62
Ni9Si	5.48	12.9
Si/Al[c]	8.93	4.92

[a] Units are mol/h/mol adsorbed oxygen atoms or CO molecules.

[b] Calculated from the data for calcined Ni/alumina catalysts.

[c] Ratio of the value of specific activity for catalyst Ni9Si to the average value for the calcined Ni/alumina catalysts.

Using the first-order rate equation

$$kc = r = -F/W(\ln(1 - x))$$

where

k is the rate constant
r is the rate of reaction
c is the initial concentration of thiophene
F is the flow rate of thiophene
W is the mass of catalyst, and
x is the fractional conversion of thiophene,

we can derive comparative rate constants from published data on Ni catalysts. Table 3 summarizes some related HDS activity data calculated using this expression and assuming an activation energy of 62 kJ mol^{-1} (*6*). The results show clearly that our Ni/alumina catalysts are of comparable activity to the Ni/alumina catalysts investigated by Bachelier *et al.* (*7*). Furthermore, our Ni/silica catalyst is of similar activity to an unsupported Ni_3S_2 catalyst, and within a factor of 2 of the activity of a carbon-supported Ni catalyst. We can be confident, therefore, that the difference in activity between our Ni/alumina and Ni/silica catalysts is not an artifact of the method of preparation, pretreatment, or testing. Furthermore, since calcination had little effect on the HDS activity, and because even at high Ni loadings the activity was invariably low, we can be sure that the low activity of the alumina-supported catalysts is not due to loss of Ni as Ni aluminate nor to difficulties in sulfiding.

A more plausible explanation is that the alumina alters the morphology of the Ni sulfide and converts it into a less active form of the sulfide. Comparison of the data for our Ni/silica catalyst with those for unsupported Ni_3S_2 and for carbon-supported Ni catalysts leads us to propose that the active form of Ni sulfide is the Ni_3S_2 phase. As pointed out in the Introduction, this is the more stable form of Ni sulfide under typical HDS conditions, and is the structure to be expected in the absence of support effects. The close similarity among the activities of unsupported Ni_3S_2, carbon-supported Ni sulfide, or silica-supported Ni sulfide strongly suggests that Ni_3S_2 is present also on these essentially noninteracting supports. We would propose, therefore, that the low activity of alumina-supported Ni sulfide arises because in this case the Ni is present not as Ni_3S_2 but as some other sulfide phase, with NiS being the obvious alternative choice. It would

TABLE 3

Relative Rate Constants for HDS of Thiophene over Ni Catalysts at 620 K

Catalyst	Rate constant	Reference
Ni6.67Al[a]	0.95	(*5*)
Ni9Al	1.00	This work
Ni9Si	8.69	This work
Ni2C[b]	16.8	(*2, 3*)
Ni_3S_2[c]	7.40	(*6*)

[a] Numbers refer to wt% Ni.

[b] Carbon-supported Ni catalyst.

[c] Unsupported catalyst.

seem reasonable that the close-packed hexagonal structure of the NiAs form of NiS might be created by epitaxial growth on the close-packed (100) surface of alumina.

The essence of our proposal is that for metal sulfides which can exist in more than one crystallographic form under desulfurization reaction conditions the stable form of the sulfide may be dependent on a metal sulfide–support interaction. If the structure which is stabilized contains only metal ions having a low degree of coordinative unsaturation we would expect the catalyst to have a low activity. This seems to be possible in the case of the Ni sulfides investigated in this work, and would also be anticipated for Co sulfides, for example. Mo and W sulfides would not be affected in the same way. It is known (*2*, *3*) that Mo/C catalysts are more active than Mo/Al_2O_3 catalysts for the desulfurization of thiophene, which appears to contradict our proposed dependence of activity on morphology. However, in the absence of reliable measurements of the dispersion of MoS_2 in the different catalysts it is impossible to say whether these support effects change the dispersion or the inherent activity of the MoS_2. In the case of Ni we propose that support effects modify the morphology of the sulfide and hence directly alter the intrinsic activity of the supported sulfide. Much further work will be required to ascertain whether metal sulfide–support interactions are genuine and of a general nature.

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