

The Influence of Sulfide Structures on the Hydrodesulfurization Activity of Carbon-Supported Catalysts

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All transition metals in the first, second, third rows and some in the fourth row, supported on carbon at low concentration, have been tested in their sulfided form to evaluate their activity toward the hydrodesulfurization (HDS) reaction at four different temperatures. The first row shows two maxima on V/Cr and Co whatever the temperature with two orders of magnitude between the lowest and the highest activities (one order between Ni and Co). The second and third rows present a single maximum on Rh and Ir, respectively, with three orders of magnitude between the lowest and the highest activities. Electronic considerations have been proposed (S. Harris and R. R. Chianelli, *J. Catal.* **86**, 400, 1984) to account for these different activities. A new complementary approach is developed by introducing the structural properties of the sulfides. © 1986 Academic Press, Inc.

In a preceding work (1), we found, by using the metal solid NMR technique, a new cobalt sulfide phase very active for the hydrodesulfurization (HDS) reaction. This phase can be prepared in pure form by impregnating small amounts of cobalt on an active carbon support and its structure is derived from Co_9S_8 , where the octahedral Co atoms have disappeared and the tetrahedral ones subsist in a distorted form. A very active Co/C catalyst had already been found by Prins *et al.* (2, 3), and these authors have extended their studies to many other metals (4). Their results, showing a maximum of activity for Ru, Rh, Ir, and Os sulfides, were in very good agreement with a preceding study made by Chianelli *et al.* (5, 6) on bulk sulfides. However, the very high conversion in their reaction (meaning uncertainties in rate determination) and the

high loading in metal (meaning formation of bulky sulfide; see (1)) led us to conclude that we could not use their absolute activity values to evaluate the activity of our catalysts. We needed these values to show the validity of the hypothesis (1) on the additivity of the individual Co and Mo activities. In addition, we wanted to check the exact position of the maximum found on Ru, Os by Chianelli and Pecoraro (5) or on Rh, Ir by Prins *et al.* (4) because, as we shall see in this work, its position has a fundamental importance.

In the following, after presentation of the preparation of the catalysts and the experimental details, we examine the results of the HDS activity of the sulfided transition metal catalysts. In this latter section, we also refer to the bulk structure of the most stable transition metal sulfides for comparison purposes. We are aware of the fact that, in their highly dispersed form, on the

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TABLE I
 First-Row Transition Metals

Cat.	wt%	No. of atoms/g of cat. ($\times 10^{18}$)	Salt solvent	$r (\times 10^{-10})$ Highest conversion NTR (h^{-1})					$E \pm 1$ kcal/mole at 20 Torr
				227°C	250°C	280°C	350°C	60 Torr	
Sc	0.175	23	Nitrate	5	17.4	67.3	635.8	26.8	
			Water	0.02%	0.066%	0.22%	0.843%		
Ti	0.465	58.5	Acac	8.6	30.0	151.5	1,771	29.9	
			Ethanol	0.019%	0.067%	0.323%	1.097%		
				0.032	0.11	0.56	6.57		
V	0.40	47.3	Acac	262.1	664.5	1591	7,520 ^a	16.3	
			Ethanol	0.733%	1.073%	1.44%	—		
Cr	0.405	46.9	Nitrate	1.20	3.01	7.29	34.5	21.0	
			Water	295.8	789.2	2087.5	18,510 ^a		
				0.725%	0.952%	1.764%	—		
Mn	0.39	42.8	Nitrate	1.37	3.65	9.65	85.5	19.5	
			Water	8.5	20.6 ^a	56.7	472.4		1.107
				0.027%	—	0.152%	1.532%		1.08% ^b
Fe	0.66	71.2	Nitrate ^c	0.043	0.104	0.29	2.39	56	18.8
			Water	58.4	154.9	399	2,386	—	
				0.130%	0.387%	0.975%	1.848	—	
Co	0.42	42.9	Nitrate	0.178	0.47	1.22	7.27	15.0	
			Water	559.7	1050	2487	10,650		20,780
Co	2.84	290.3	Nitrate	2.84	5.33	12.61	53.99	105.3	15.0
			Water	4055	2,229%	2.90	—	—	
				82.5	227.5	710.1	3,745	—	
Ni	0.43	44.1	Nitrate	0.119%	0.219%	0.420%	0.783%	23.4 (<280°C)	
			Water	0.41	1.10	3.49	18.4	16.5 (>280°C) ^d	
Ni	1.61	165.1	Nitrate	300	912.3	2439	12,050	24.8 (<280°C)	
			Water	0.114%	0.319	0.403	1.105%	15.8 (>280°C)	
Cu	0.445	42.2	Nitrate	0.40	1.20	3.20	15.8	22.3	
			Water	3.8	11.9 ^a	41.6	364		866.8
				0.012%	—	0.12%	0.675		0.88% ^b
Zn	0.40	36.9	Acetate	0.020	0.061	0.21	1.87	4.45	20.6
			Water	10.3	18.5	47.8	452.3	927.4	
				0.022%	0.038%	0.087%	0.306%	0.377%	
				0.061	0.109	0.28	2.66	5.46	

Note. Acac, acetylacetonate.

^a Extrapolated.

^b 20 Torr and 400°C.

^c Iron(III) nitrate.

^d Calculated for six temperatures.

supported catalysts, these sulfides might not retain the bulk structure (particularly in the case of three-dimensional structures). However, it seems very likely that, on the catalysts, the basic structural units of the bulk structure, and particularly the sulfur coordination of the metals, are retained. This coordination number depends mainly upon the orbital interaction between the metal and the sulfur atoms, the lattice contribution being of second order. There exists experimental evidence of this in the more-studied CoMo catalysts, both on Mo sites and on Co sites. Of course, in the dis-

persed catalysts, the units are probably distorted (bonding angles) and exhibit defects such as vacancies; also they can be interconnected quite differently as compared to the bulk structure because of possible interaction with the support and with the other metal(s) in mixed catalysts.

Our purpose, as shall be discussed in the last section, is to show that besides the influence of the electronic structure on the catalytic HDS activity which is evidenced by its serial dependence in the periodic table, there is also a correlation between a high activity of the catalyst and the possi-

TABLE 2
 Second-Row Transition Metals

Cat.	wt%	No. of atoms/g of cat. $\times 10^{18}$	Salt solvent	r ($\times 10^{-10}$) Highest conversion NTR (h^{-1})					$E \pm 1$ kcal/mole at 20 Torr
				227°C	250°C	280°C	350°C 20 Torr	350°C 60 Torr	
				Zr	1.13	74.6	Nitrate Water	26.3 0.023% 0.076	
Nb	0.435	28.2	Chloride Ethanol	110.3 0.111% 0.85	210.1 0.193% 1.62	460 ^a — 3.54	2,149 — 16.5	7,500 — 57.7	14.9
Mo	0.21	13.6	Hepta-m Water	193.6 ^a — 3.18	527.3 0.304% 8.67	1,819 — 29.9	— — —	— — —	23.3
Mo	0.79	49.6	Hepta-m Water	724.7 0.287% 3.17	1,864 0.470% 8.15	4,830.4 0.524% 21.1	23,300 — 101.9	38,915 — 170.1	20.1
Mo	0.95	59.6	Hepta-m Water	815.9 0.255% 2.97	1,764 0.504% 6.42	5,014 — 18.2	26,640 0.416% 96.9	40,470 0.953% 147.1	19.3
Mo	3.90	244.7	Hepta-m Water	3,052 2.089% 2.57	— — —	— — —	— — —	— — —	—
Ru	0.365	21.7	Acac Ethanol	727.5 0.116% 7.27	1,904 0.138% 19.0	5,752 — 57.5	28,960 — 289.4	48,660 — 486.2	21.5
Rh	0.775	45.4	Acac Ethanol	119 0.694% 57.0	37,000 0.755% 177.0	170,400 ^a — 813	2,485,000 ^a — 11,870	— — —	26.4
				At 60 Torr \rightarrow 14,200	0.262% 67.9	80,700 385.8	2,485,000 ^a — 11,870	— — —	32.9
Pd	0.87	49.3	Acac Ethanol	681.8 0.401% 3.00	1,841 0.652% 8.10	4,575 0.93% 20.14	39,180 ^a — 172	— — —	20.1
Ag	0.72	40.2	Nitrate Water	6.8 0.019% 0.037	20.9 0.058% 0.112	47.1 0.128% 0.254	424 0.795% —	— — —	20.1

Note. Hepta-m, heptamolybdate; Acac, acetylacetonate.

^a Extrapolated.

bility of the metal to exhibit two different stoichiometries (or coordinations) in the bulk. Our speculation is that, in the dispersed catalysts, such metals exhibit a "Sabatier behavior," the two stoichiometries or coordinations being in a dynamic equilibrium under the HDS reaction.

EXPERIMENTAL

Materials. An inactive ultrapure HDS carbon (activated charcoal Fluka) was used as support. The surface area was found to be ~ 1000 m²/g and the particles were sieved between 0.2 and 0.5 mm.

The salt and the solvent used for the impregnation of each metal, are reported on Tables 1, 2, and 3. The use of chloride was avoided because of the unpredictable be-

havior of the support in the presence of chlorine. As an exception, the chlorides were used for Ta and Nb because most of the other salts are insoluble in neutral solvents; as for Au, salts other than AuCl are too unstable.

When nitrate or ammonium salts were not easily available, we used the acetylacetonate complexes, synthesized as already reported (7). The wet impregnation procedure was not used because of its inhomogeneous results. The carbon was first covered with the pure solvent, water, ethanol, or methanol (3 ml, all values are reported per gram of carbon), a solution of the salt was added (2 ml), and then the mixture was stirred gently at 100°C until evaporation of the solvent was complete (~ 4 h). The cata-

TABLE 3
Third-Row Transition Metals

Cat.	wt%	No. of atoms/g of cat. $\times 10^{18}$	Salt solvent	r ($\times 10^{-10}$) Highest conversion NTR (h^{-1})				$E \pm 1$ kcal/mole at 20 Torr
				227°C	250°C	280°C	350°C	
Ce	1.165	50.1	Nitrate Water	27.4	61.6	167.3	2,764	18.9
				0.024%	0.054%	0.156%	1,804.8	0.395%
Th	1.13	29.3	Nitrate Water	0.12	0.27	0.72	11.96	24.6
				5.5	16.2	66.5	621.6	7.81
U	1.37	34.7	Acac Ethanol	0.009%	0.027%	0.080%	0.330	22.6
				0.041	0.12	0.49	4.60	10.7
Hf	1.07	36.1	Acac Ethanol	10.9	27.8	96.0	974.5	22.0
				0.019%	0.048%	0.127%	0.40%	0.397%
Ta	0.45	15.0	Chloride Ethanol	0.068	0.174	0.60	6.09	23.1
				9.2	36.6	111.4	1,104	2,380
W	1.64	53.7	Paratungstate Water	0.014%	0.060%	0.140%	0.479%	0.558%
				0.055	0.22	0.67	6.63	14.30
Re	1.685	54.5	Rhenate Water	11.1	40.9	154.7	3,134	24.4 (<280°C)
				0.012%	0.043%	0.149%	0.412%	0.422
Os	0.32	10.1	Acac Ethanol	0.160	0.59	2.24	21.3	21.7
				268.8	569	1,778	12,200	45.3
Ir	1.11	34.8	Acac Ethanol	0.045%	0.087%	0.156%	0.417%	29.8
				1.08	2.30	7.18	49.4	83.1
Pt	1.775	54.8	Acac Ethanol	8.624	34.3	181.9	45,700	23.6
				0.104%	0.211%	0.367%	1.195%	3.367%
Au	0.68	20.8	Chloride Water	4.60	13.7	34.3	181.9	36.8
				369.6	964.7	2,835	27,700	598
				0.026%	0.065%	0.125%	0.296%	17.9 (<280°C)
				7.93	20.7	60.9	594	29.5 (>280°C)
				3874	14,540	72,980	1,584,600 ^a	13.75
				0.121%	0.460%	1.019%	—	
				24.14	90.6	454.9	9,873	
				At 60 Torr \rightarrow 63,300	At 60 Torr \rightarrow 63,300	0.490%	190,300	
				111.6	553.2	3,914	1,186	
				0.027%	0.139%	0.320%	151,120 ^a	
				0.44	2.19	15.5	598	
				5.9	14.8	37.1	680.6	
				0.006%	0.020%	0.053%	7.09	
				0.062	0.15	0.39	—	

^a Extrapolated.
Note. Acac, acetylacetonate.

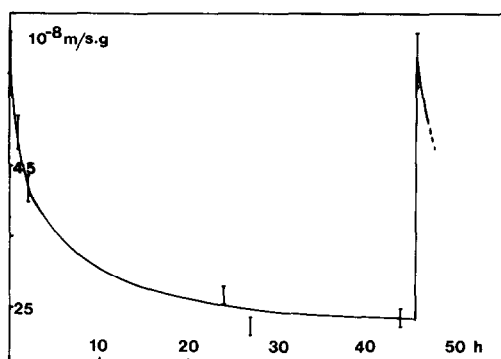


FIG. 1. Activity of Mo/C catalyst versus time (280°C).

lyst was left 12 h at 120°C in air, weighed after cooling, and introduced into the reactor. About 50 mg of material was always introduced; for the very active catalyst small amounts were mixed with unimpregnated support.

The metal content was determined by atomic adsorption on two or four samples for each metal and the maximum of the relative inhomogeneity was always found to be $\leq 2.25\%$.

If one assumes an average area of 20 \AA^2 per metal atom in the sulfide, the total surface area of the sulfide was always kept two orders of magnitude below the area of the support in order to obtain a total dispersion, with each atom of metal potentially accessible. By measuring the nominal turnover rate (NTR), shown in Table 1, for two concentrations of Co and Ni and three for Mo, we found the same values, within the range of experimental error, meaning that at least the same ratio of atom (and probably all) is accessible; that does not mean a monolayered or monodispersed phase. This dispersion probably depends also upon the nature of the carbon and it is difficult to compare our results with the values found in (2) or other works.

Reaction. The flow apparatus, working under atmospheric pressure (thiophene partial pressure from 6 to 60 Torr and temperature between 227 and 450°C), used for all these measurements has been described

elsewhere (1). In order to determine the activity of the sulfide material for HDS, we decided to study the initial activity. For most of the metals, this initial activity, in all the temperature ranges we studied, is equal to the steady state activity, because the catalysts are not reduced after sulfidation even in the absence of H_2S in large amounts in the gas phase. However, this is not true for the lamellar sulfides (i.e., Mo, Re, and probably V, Nb, Ta, Th, U), where we observed a slow deactivation with time (15% after 1 h) due to the reduction of the sulfide; the initial activity is immediately restored after a short (30 min) pulse of 2% $\text{H}_2\text{S}/\text{H}_2$ even at the reaction temperature of 227°C. For these reasons, the catalyst was kept under $\text{H}_2\text{S}/\text{H}_2$ flow between reactions (see Fig. 1).

Before the first test at 227°C, the catalysts were presulfided at 450°C for 2 h under 2% $\text{H}_2\text{S}/\text{H}_2$ flow (temperature increased from room to 450°C at 13°C/min). We assume that all the dispersed metals are sulfided after such a treatment; our NMR on cobalt like the XPS measurements in (4) are conclusive in this sense. However, we think that Au was not totally sulfided.

Kinetics. The rate r (in mole/s · g. of catalyst), as the experiments were performed in a differential fixed bed reactor, was determined by varying the ratio ω/F versus the conversion α , always kept below 1.5% (ω , weight of catalyst; F , flow of thiophene). All the catalysts were tested under the constant pressure of 20 Torr of thiophene, a certain number were tested under 60 Torr. The kinetical function of the thiophene HDS reaction was studied by many authors and reviewed by Vrinat (8). In agreement with many of these authors, in a study of some very active catalysts, we found a complex kinetical function of the form $r = k_0 \cdot x/(1 + x)^n$ (x being the product of the thiophene pressure by the equilibrium constant of adsorption and $k_0 = K \cdot e^{-E/RT}$) in the range of 0–60 Torr of thiophene under normal H_2 pressure (the partial pressure of H_2S being neglected because of

the very low conversion). Depending upon the nature of the metal, the curve plotting r versus the partial pressure of the thiophene in the range 0–60 Torr, can either increase in the whole range or reach a maximum and then decrease (for instance, Rh, Ir, Pt . . .). We did not find any catalyst where the maximum was below 20 Torr and we found for most of them, when a maximum existed, that this maximum was not far from 20 Torr. Thus the comparison we report in Figs. 2, 3, 4, and 5, has been established at this pressure. However, one must keep in mind that this value is not the optimum for many catalysts.

All the catalysts have been tested at at least four temperatures (227, 250, 280, and 350°C) and sometimes, in order to increase the accuracy of the activation energy determination, additional temperatures have been used. Some points are missing either because of technical trouble or because of the impossibility of obtaining small enough conversions (Rh 280°C—20 Torr, 350°C—20 Torr, and 350°C—60 Torr, Ir 350°C—20 Torr, Pt 350°C—20 Torr, Cr 350°C—20 Torr); these missing points were extrapolated using the calculated activation energy in order to complete the different figures. This energy was calculated from the equation $r = K \cdot e^{-E/Rt} \cdot x/(1+x)^n$, where r is the rate of reaction (in moles/s · g of catalyst), x is already defined, and $K = A_0 \cdot K_{H_2} \cdot P_{H_2}$. The expression $\ln[K \cdot x/(1+x)^n]$ remains virtually constant on the same catalyst at constant thiophene pressure because of the low conversion (first order, $n = 1$) and E is the slope of the line plotting $\ln r$ versus $1/T$. For most of the catalysts, the four points (227, 250, 280, and 350°C) were perfectly aligned. For two metals, i.e., Ni and Re, two very distinct activation energies were found, the one below 280°C was higher than the one above 280°C. Diffusion phenomena cannot explain this change because the accuracy of the measured activities was carefully checked by plotting α versus ω/F . There is probably a change in the nature or the phase of the sulfide in the range of 280°C.

RESULTS

In the three Tables 1, 2, and 3 the nominal turnover rates (NTRs) in molecule of thiophene transformed per atom of metal per hour are reported, (in h^{-1}). The rates (in moles per second per gram of catalyst), calculated as being the slope of the line plotting the conversion α versus ω/F and the highest α used, are also reported in these tables. Figs. 2–5 show, on a logarithmic scale, the activity (NTR) of the three rows of transition metals at the four temperatures studied. The general shape is close to that found by Chianelli and Pecoraro (5)

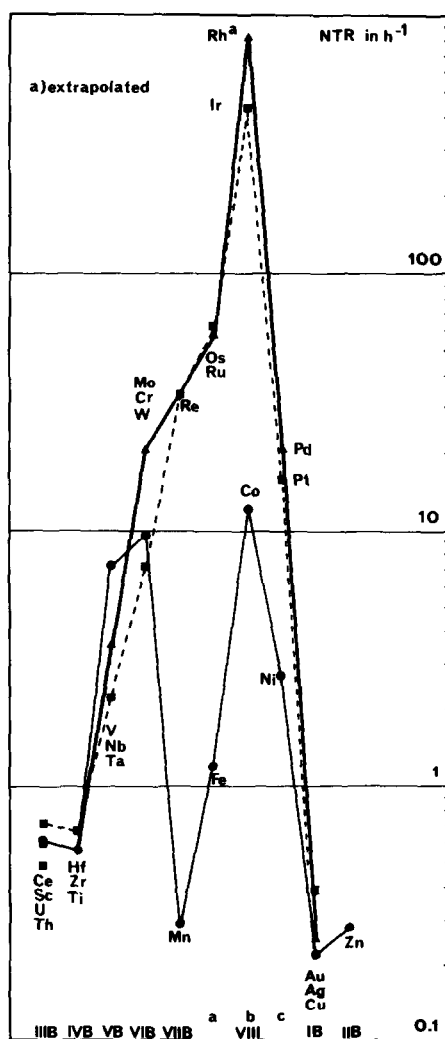


FIG. 2. Compared activity for the three rows at 280°C.

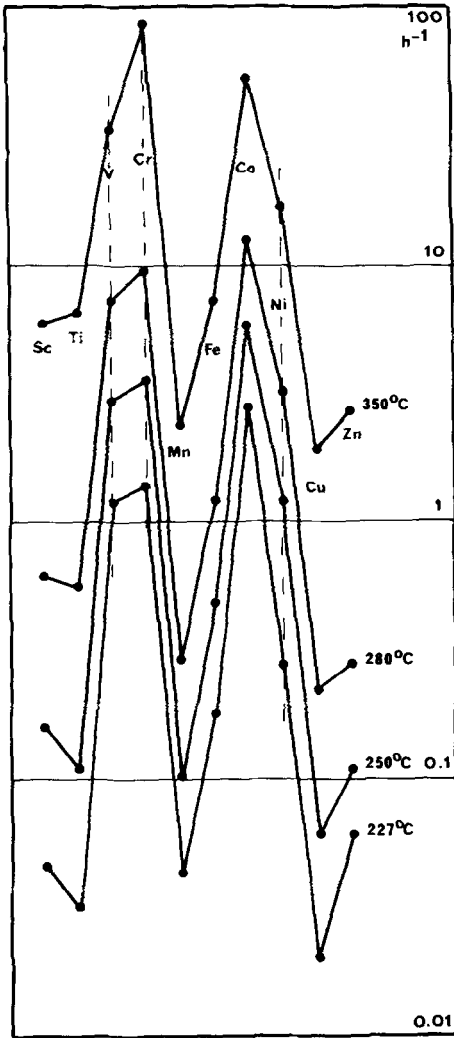


FIG. 3. Compared activity for the first row at four temperatures.

and Prins *et al.* (4) with however very significant discrepancies that we shall now examine in detail.

Groups III and IV. Y was not studied but Th and U from the fourth row were added. Sc is slightly more active than Ti but Ce has an activity in the same range as Fe and Ni. A complete study of the rare earth sulfides is in progress and will be published later. Ti, Zr, and Hf together with U and Th are the poorest catalysts of the left side of the table. The values found at 280°C are the more accurate for these groups and show in fact that they are all very close (Fig. 2). The

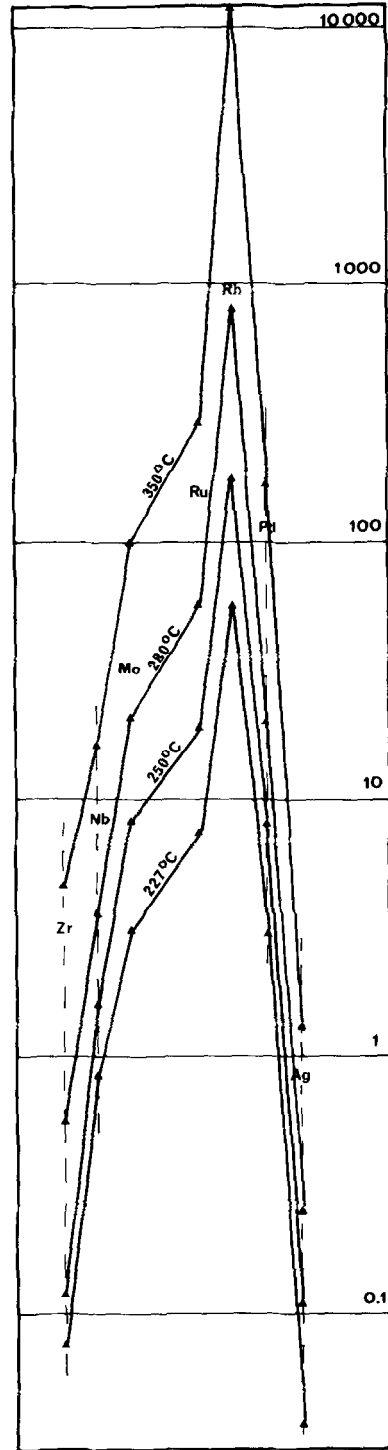


FIG. 4. Compared activity for the second row at four temperatures.

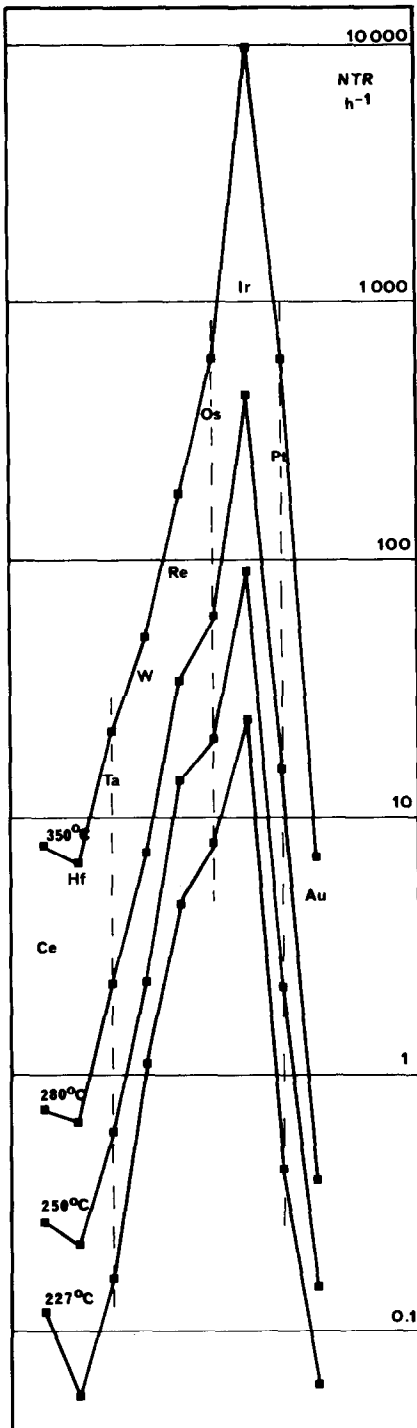


FIG. 5. Compared activity for the third row at four temperatures.

activity scale $\text{Th} < \text{Ti} = \text{Zr} < \text{Sc} = \text{U} < \text{Hf} < \text{Ce}$ already shows that there is no correlation with activation energy, respectively 25, 30, 21, 27, 23, 22, and 19 kcal/mole even if Ti has the highest and Ce the lowest. The crystalline structure of the bulk sulfide is also not correlated to the activity, Sc_2S_3 and Ce_2S_3 (or CeS , Ce_3S_4 and CeS_2) are all cubic with a coordination of 6 for the metal and TiS_2 , ZrS_2 , HfS_2 , ThS_2 , and US_2 all layered (isostructural with $\text{Cd}(\text{OH})_2$ or PbCl_2) with also a coordination of 6 for the metal atom.

Group V. A very strong increase in activity (one order of magnitude at "low" temperature, slightly smaller at higher temperature) is observed when examining this group containing V, Nb, and Ta. To check that these metals were totally sulfided, two temperatures of sulfidation (450 and 600°C) on V were used and no difference in activity was observed. In addition, the NMR study did not show any traces of oxide or oxidic phase, only a highly dispersed sulfided phase. This group and group VI (Cr and W) are the only in which the first-row metal is more active than the second- or third-row metals. The fact that Nb and Ta have been prepared from the chloride salt could possibly account for this result. Pecoraro and Chianelli (5) have found on bulk sulfides a very poor activity for these three metals, with Nb and Ta better than V (second row > third row > first row), when compared to the next group. When well dispersed, V was found very close to Cr, Nb not so close to Mo, and Ta quite far from W. The bulk sulfides VS_2 , NbS_2 , and TaS_2 have the same layered structure (iso to $\text{Cd}(\text{OH})_2$); but for Nb with Nb_2S_3 and NbS , as for V with VS , a large range of metal-sulfur concentrations is available. Even amorphous Nb and V sulfided phases have been reported with probably a very fluctuating coordination (24). The very low activation energies found for V (16.3) and Nb (14.9) compared to the "normal" value found for Ta (23.1) is consistent with the formation of these amorphous phases (see below).

Group VI. The activity of the three metals, Cr, Mo, and W are very close in activity to the members of group V. The activity of Mo, whatever the temperature, is always higher than the activity of Cr and W, respectively. (As discussed in the preceding paragraph, Cr is an exception to the rule, with a first-row metal being more active than a third-row one.) Mo and W sulfides (MoS_2 and WS_2) are lamellar with coordination of 6 for the two metals but the Cr-S system is very complex. The more stable phase under our reaction conditions seems to be CrS with a structure intermediate between those of NiAs and PtS (9), both of which are layered sulfides but not lamellar (in a lamellar sulfide, the layers are bonded through van der Waals forces). The coordination of Cr is still 6, but in a very elongated octahedral which is very similar to the coordination 4 of Pt atoms in PtS. The activation energies fall in the normal range: 21, 18.7, and 19.4 kcal/mole.

Group VII. Tc was not studied. The very low activity of Mn contrasts with the high activity of Re, almost twice as active than Mo. The coordination of the metal atoms is 6 for the two Mn sulfides (MnS cubic NaCl type and MnS_2 , C_2 pyrite) and for the Re sulfide (ReS_2 , iso- MoS_2 hexagonal). Two important points must be emphasized in regard to ReS_2 . First, ReS_2 is a lamellar sulfide with a structural change around 280°C (11) which could account for the important change in the activation energy (24.4 to 16.2 kcal/mole) which appears at this temperature region. Second, the formation of an amorphous Re_2S_7 phase is known to occur when the concentration of sulfur is high enough (13, 24).

Group VIIIa. The contrast is very sharp between the Fe activity and the Ru and Os activities, almost two orders of magnitude, although a strictly equivalent C_2 pyrite structure for the three sulfides with a coordination of 6 for the metal atom is the usual structure. However, Chianelli (24) has recently reported the existence of an amorphous Os sulfide. Even if Ru and Os are very active, they are still one order of mag-

nitude below Rh and Ir; an even bigger difference is observed between Co and Fe. This observation contradicts the results of Pecoraro and Chianelli (5) on bulk sulfides, where the most active catalysts are Ru and Os. The activation energies for these three metals, Fe, Ru, and Os, also fall in the "normal" range: 18.8, 21.5, and 21.7 kcal/mole.

Group VIIIb. One finds with Co, Rh, and Ir the best catalysts in their respective rows. The structures of the sulfides of these three metals will be discussed later. The activation energy found for Co, 15 kcal/mole, is the lowest (with Nb); for Rh and Ir very high energies have been found, 26.4 and 29.8, respectively (32.9 kcal/mole for Rh at 60 Torr of thiophene). When the activation energy for HDS reaches 30 kcal/mole, one can suspect the formation of metal on the surface by decomposition of the sulfide.

Group VIIIc. Pd and Pt have an activity in the range of the Mo activity when Ni is a very poor catalyst at the same level as Fe. The stable phase for Pd and Pt sulfides is the isostructural PdS and PtS (iso-PbO), a tetragonal structure where the metal has a coordination of 4 (10, 11). The active phase in the Ni-S system is very controversial, but either Burmistrov *et al.* (12), who found a stoichiometry of 1 : 1 on SiO_2 or the phase diagram in (13) leads us to propose the rhombohedral structure of the NiS(L) phase below 280°C and the hexagonal structure of the NiS(H) phase above 280°C . In both structures, Ni atoms have a coordination of 6. This structural change could explain the change in activation energy at 280°C (see below). The high temperature activation energy on Ni, like the Pd activation energy, falls within the "normal" range; however, with Pt, we found the highest (36.8 kcal/mole).

Group IB, IIB. Cu, Ag, Au, and Zn have very low activity, equivalent to that of Mn. In all their stable sulfide phases, these metals have coordination 4. The energy of activation found on them, 22.3, 20.1, 20.6, and 18 (below 280°C) kcal/mole, are just in the average range and provide a very good

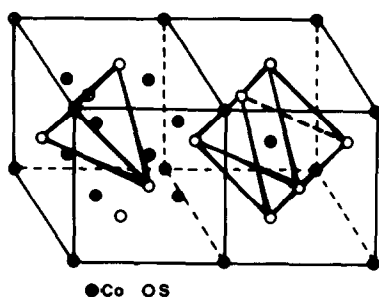


FIG. 6. Tetrahedral and octahedral sites in Co_9S_8 .

example of the lack of correlation between activation energy and activity.

DISCUSSION

The Harris and Chianelli theory (6) explains well the difference in activity between the different sulfides. They found a correlation between the HDS activity and the product of the number of d electrons in the HOMO by a factor B which takes into account the nature and the strength of the metal d -sulfur p covalent bond.

The poor activity of groups III and IV and the increasing activity from group V to group VIIa (metal with coordination 6) can be understood through this electronic description because these authors have used a coordination 6 cluster as a model for their calculation. The high activity of groups VIIIb and c and the poor activity of groups IB and IIB cannot be explained by this theory in its present form, because the metal atom has coordination 4 for all these sulfides except Ni. However, it is possible to propose a complementary approach in which the structural properties of the sulfides are taken into account and the concept of Sabatier is developed. "The stability of the catalyst site must be balanced by the possibility to form a pseudostable intermediate (adsorption of the reactants on the site) which decomposes into the reaction products and the original naked site."

The Co sulfide catalyst. In a preceding paper (1), because of the use of the metal-solid NMR, we were able to show that the active phase of the cobalt sulfide on the car-

bon support is a distorted tetrahedral structure reminiscent of the cubes containing the tetrahedral Co atoms in Co_9S_8 (see Fig. 6). To explain the high activity of this structure, we assumed that the Harris and Chianelli theory (6) was applicable to a tetrahedral environment and thus found, 3 electrons in the HOMO, of t_{2g} symmetry, a configuration equivalent to that found for Mo. Naturally, we concluded that this analogy explained the equivalent activity found for Co and Mo.

However, in the conclusion of the same paper (1), we proposed another explanation for the very high activity of the Co sulfide supported on C: the tetrahedral Co atoms are almost perfect Sabatier catalysts; their stable form is tetrahedral but they can adopt an octahedral configuration in order to stabilize either their bulk (in bulk Co_9S_8 , 8 Co atoms are tetrahedral and 1 is "slow" octahedral, Fig. 6), or their dispersed tetrahedral cubes on MoS_2 substrate by forming what we call in (1) the "rapid" octahedral Co ("slow" and "rapid" because of their long or short relaxation time in the NMR measurements). The adsorption of a sulfided molecule (i.e., thiophene) on such a tetrahedral phase can be compared to a temporary formation of an almost octahedral configuration (to be more accurate, two simultaneous adsorptions will give a proper octahedral configuration) which will decompose back to the tetrahedral form because the extrastabilization is not necessary on the catalysts, being already ensured either by the "Co rapid" on CoMo or by the small pores of the support on carbon.

In Fig. 6 is represented the crystal structure of Co_9S_8 . It is an all-face-centered cube ($O_h^2 - Fm\bar{3}m$) which could be simply described as a checkered sequence of sulfur cubes containing either one Co atom in octahedral symmetry or eight Co atoms in tetrahedral symmetry (1). This π phase has been studied by Knop *et al.* (15, 16) and Bøhm *et al.* (17). The number of sulfides occurring in this kind of structure is relatively small; Co_8FeS_8 , Co_8NiS_8 , Co_8RhS_8 ,

Co_8RuS_8 , $\text{Fe}_4\text{Ni}_4\text{PdS}_8$, $\text{Fe}_4\text{Ni}_4\text{RhS}_8$, $\text{Fe}_4\text{Ni}_4\text{RuS}_8$, and $(\text{Fe,Ni})_9\text{S}_8$: In Co containing compounds, Co atoms occupy the tetrahedral sites, Fe, Pd, Rh, and Ru the octahedral site, Ni is randomly distributed. In the composed compounds where the eight Co atoms are replaced by four Fe and four Ni atoms, Fe and Ni occupy the tetrahedral sites. There is a lack of structural knowledge about the site occupancy in the pseudo-binary alloy $(\text{Fe,Ni})_9\text{S}_8$. In the periodic table cobalt occupies an intermediate situation in terms of coordination in the sulfided form. Its sulfide prefers coordination 4 but needs some coordination 6 atoms to be stable (we have already developed the possible catalytic consequence of this behavior). Nickel and iron which, when taken separately, prefer coordination 6, can reproduce when mixed (see above), a structural behavior similar to that observed for Co. If our structural theory on HDS activity is true, one can predict a high activity for catalysts alloying Ni and Fe, provided that the distorted tetrahedral structure can be stabilized in the absence of the octahedral cubes of the bulk either by the carbon support or by MoS_2 . The first attempt to prepare such a catalyst has been successful. A catalyst containing 0.28 wt% of Ni and 0.53 wt% of Fe, i.e., 0.81 wt% metal on C, shows the same activity as the 0.66% Ni/C catalyst. Many other experiments, varying the concentrations and adding Rh, Ru, and Pd, are in progress. The large change in the activation energy on Ni can also be understood if one assumes that above 280°C a tetrahedral Ni sulfide derived from the π phase becomes stable enough; the high temperature activation energy, 15.8 kcal/mole, is very close to that found on the Co tetrahedral phase, 15.0 kcal/mole. Because of this temperature condition of existence, it will probably be difficult to see this Ni phase with the NMR analysis made at low temperature, unless it can be quenched.

Rh and Ir sulfides. The Ir-S system has not been studied or published seriously; only Knop (14) has observed an unidenti-

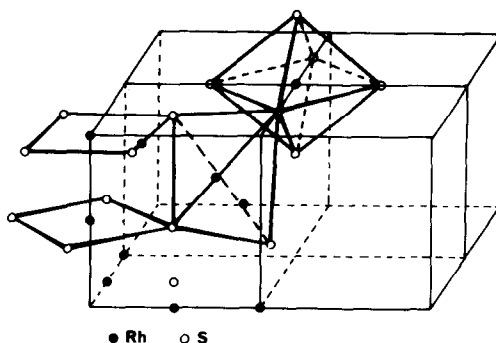


FIG. 7. Tetrahedral and octahedral sites in $\text{Rh}_{17}\text{S}_{15}$.

fied phase which could be related to the π phase (e.g., Co_9S_8 in Fig. 6) or the ρ phase (e.g., $\text{Rh}_{17}\text{S}_{15}$ in Fig. 7) (14, 15). For this reason, and lacking more details, we shall assume throughout that Ir behaves like Co or Rh.

The crystal structure of $\text{Rh}_{17}\text{S}_{15}$ is represented in Fig. 7. It belongs to the space group $O_h^1 - Pm\bar{3}m$, isostructural with $\text{Pd}_{17}\text{Se}_{15}$ (18), this structure is called the ρ phase (14). The only other known sulfides with the same structure are $\text{Rh}_{16}\text{AgS}_{15}$ and $\text{Rh}_{16}\text{PdS}_{15}$. Attempts to prepare the equivalent Ir sulfide (14) were not successful but that does not exclude the possibility of finding an equivalent system.

Such a sulfide presents the same property as Co_9S_8 : a large number of metal atoms in coordination 4, sixteen, are stabilized by a single metal atom in coordination 6. According to our hypothesis if one can stabilize the coordination 4 atoms either by carbon support or by another sulfide on a mineral support in the same way in which it has been possible to stabilize the distorted tetrahedral phase of Co sulfide, one will obtain another very active catalyst because of the large number of Sabatier sites available. We believe that this explains the very high activity of Rh on carbon support. Attempts to prepare active Rh-Mo/ Al_2O_3 and Rh-Re/ Al_2O_3 catalysts are in progress.

Left-hand side catalysts with coordination 6. On Mo, W, Re, or even V, Cr, and Nb, we believe, like most authors, that the

sulfur vacancies in crystalline-like MoS_2 particles are very active sites, but we think that the ability to form a superficial amorphous phase in the presence of extra sulfur (i.e., MoS_3 , Re_2S_7 , amorphous Cr and V sulfides) gives the crystalline lamellar MoS_2 , ReS_2 , etc., the opportunity to catch more sulfur. It is also a good example of a Sabatier system. This theory will explain why the Mo sulfide loses activity after partial reduction under H_2 . If the under-stoichiometric-vacancies theory were exact, we would observe an increase in activity. This deactivation could be due to a strong adsorption of the thiophene on the reduced sites. In addition, under working conditions, the pressure of the S compounds (hydrocarbon sulfide or H_2S) must be selected in order to keep the system MoS_2 - MoS_3 in equilibrium. Many other arguments support the hypothesis of the role of MoS_3 . Studies of the stoichiometry on active Mo by different authors (19-21) have often shown a sulfur/metal ratio ≥ 2 , but other authors (26, 27) have found a lower ratio. EXAFS of working Mo catalysts (22, 23) or W catalysts (12) have shown an increase in the Mo-S coordination number (or W-S), approaching 6, which, on small particles of 10 Å (22) containing, for instance, 7 Mo atoms, involves 20 S atoms, almost the stoichiometry of MoS_3 .

Therefore, the coordination 6 sulfides without known amorphous phases, like Sc, Ti, Zr, Ce, Ta, Th, U, and Hf, will be the worst catalysts for HDS. Even if Ni is on the right-hand side, its NiS stable sulfide belongs to this group because of the coordination 6 of the metal, at least below 280°C. V, Cr, Nb, Mo, W, and Re, all with known sulfur-rich amorphous phases (not solid solutions which do not involve bond formation), will be fairly good catalysts.

In spite of their very high activity, Ru and Os sulfides are not known to present amorphous phases. However, Chianelli (24) has recently reported the existence of an amorphous Os sulfide; if Ru can present the same property, these two metals will

enter in the class of Mo-type catalysts and their high activity will result from the Sabatier system where OsS_2 crystalline is in equilibrium with the amorphous phase.

Right-hand side catalysts with coordination 4. The coordination 4 sulfides for which no sulfur-rich amorphous phases are known, must be poor catalysts for HDS. This is observed for Cu, Zn, and Ag. For Au, its poor ability to form any bond with any element is enough to explain its lack of activity. The change in the energy of activation found above 280°C can be explained by the formation of metallic gold, the sulfide being unstable at high temperature.

The relatively high activity found for Pd and Pt can be explained by the fact that PdS and PtS phases have the ability to form higher sulfides, PdS_2 (C_6 pyrite, coordination 4 by a pair of sulfur atoms, a pseudo-8 coordination number) and PtS_2 (CdI_2 layered, coordination 6) by simply twisting their crystalline atomic positions, and thus the ability to form another kind of Sabatier system. Grønvold and Røst (10) have, for instance, never succeeded in preparing the pure phase of PdS_2 when starting from PdS, these two phases being mixed and reversible depending upon the temperature and sulfur concentration.

However, for these two metals we cannot exclude the possibility of the reverse Sabatier system, i.e., reduction of PdS and PtS to lower sulfides or even metal. The very high activation energy 36.8 kcal/mole, found on Pt catalyst would be understood if the HDS reaction occurred on a metallic surface rather than on a sulfide surface, where the average value falls generally in the neighborhood of 20 kcal/mole. This different behavior can also be explained if the mechanism of the HDS reaction is different; results obtained on a single crystal of sulfided Pt (25) show a different adsorption of the thiophene molecule as compared to other metals. We hope that metal-solid NMR of Pt sulfide catalysts will allow us to choose between these different possibilities.

In order to explain the proposed relationships between amorphous phase and low activation energy, or between metallic phase and high activation energy, one must take into consideration some mechanistic hypotheses. The desulfurization mechanism goes through, at least temporarily, as we explain here, the formation of an extra sulfur-metal bond. Among many other elementary steps, the formation of this bond could be the determinant of the value of the activation energy. Then, without going into further detail and intuitively, one can see that the formation of a metal-sulfur bond is "easy" with an amorphous phase, less "easy" with a crystalline bulk sulfide, and even less "easy" with a metal.

It is obvious that the ability for all the active sulfides to form systems where two sulfidic coordinations of the metal are in equilibrium is a necessary but not sufficient condition for high HDS activity. The electronic approach proposed by Harris and Chianelli (6) clearly explains the differences in activity found between 3d, 4d, and 5d transition metals in our study.

The combination of these two approaches is a fairly good example of the complementarity between the well-known concepts of geometric effect and electronic effect.

CONCLUSION

We have shown in this thorough study that the most active dispersed catalysts for the HDS reaction are based on metals which in their most stable bulk sulfided forms (under conditions similar to those of the HDS reaction) exhibit the possibility of being coordinated differently with sulfur. This can occur either by the existence of two phases with different stoichiometry (as the crystalline MoS_2 and the amorphous MoS_3) or the existence in the same bulk structure of two sites coordinated differently (as in Co_9S_8). The speculation about the existence of a Sabatier system related to the peculiarity of such sulfides has on the

basis of structural considerations only, led us to the discovery of new, very active catalysts such as the NiFe sulfide and the Rh (Ir) sulfide.

A thorough study of these systems has to be made because one can hope to obtain more active catalysts with Rh or Ir than with Co; at low temperature, 227°C, tetrahedral Rh is 20 times more active than tetrahedral Co and at high temperature, 350°C, it is 200 times more active!

Mixtures of Ru and Pd (and of Os and Pt) also have to be explored to check the existence of a possible effect similar to that observed when Fe and Ni are mixed. These systems must also be studied on supports other than carbon.

Finally, the role of dispersant shown by Co and Ni toward Mo in the sulfided form (which will be discussed in another publication) should be researched with other metals such as Rh, Ir, and Ni-Fe . . . on Mo, Re, W, V, Nb, and so on, which could form a pair similar to the "rapid" octahedral Co-Mo pair which we believe is responsible for the stability of the very dispersed Mo sulfided phase.

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