

NOTES

Hydrogenating Properties of Unsupported Transition Metal Sulphides

Group VI and Group VIII transition metal sulphides (TMS) have been widely used in hydrotreating catalysis. In addition to hydrogenation reactions, these processes involve removal of sulphur (hydrodesulphurization: HDS) and nitrogen (hydrodenitrogenation: HDN). Until now, HDN has not received as much attention as HDS, probably because sulphur compounds have historically been of prime importance. As petroleum feedstocks dwindle, the need for hydroprocessing oils containing larger amounts of heteromolecules will increase and industry will require more active materials. For this purpose, researchers may either improve the current catalysts or develop a new generation of catalysts based on transition metal sulphides presenting higher activities, stabilities, and selectivities toward desired compounds.

A few years ago, Pecoraro and Chianelli (1) examined the catalytic properties of various unsupported transition metal sulphides for dibenzothiophene (DBT) HDS. Variations in the TMS catalytic activities of about three orders of magnitude were observed according to the position of the elements in the periodic table. Furthermore, comparable results were observed by Vissers *et al.* (2) and by Ledoux *et al.* (3) for carbon-supported TMS in thiophene HDS. Very recently, the periodic trends in the HDN activity of carbon-supported TMS catalysts and of Group VIII metals supported on alumina or silica have been published, respectively, by Eijssbouts *et al.* (4), Sudhakar *et al.* (5) and van der Eijk *et al.* (6). The comparison of these HDN experiments with the previous HDS results

shows differences as well as resemblances. Nevertheless, a complete description of the TMS catalytic properties should involve the hydrogenating function.

The objective of the present work is to classify the hydrogenation performances of well-defined unsupported transition metal sulphides. These catalysts have been chosen since their characterization by physicochemical techniques, mainly X-ray diffraction (XRD), is easier than that for supported materials. Actually, it has been shown in several cases that the catalytic properties are closely related to the crystalline structure and the stoichiometry of the different phases which can be encountered for a given element. The catalysts were tested in the hydrogenation of biphenyl (HN of BP) as well as in the hydrodesulphurization of dibenzothiophene (HDS of DBT) in order to compare the present results to previous studies. To evaluate the hydrogenating function, the HN of BP has been chosen preferably to the consecutive HN of BP resulting from the HDS of DBT.

Catalytic Activity Measurements

Both reactions were carried out in the vapor phase using dynamic flow microreactors equipped with an automatic on-line analysis system. The HDS of DBT, studied in the 523- to 573-K temperature range, was performed under atmospheric pressure with 67 Pa of reactant. The HN of BP was studied between 510 and 560 K under a total pressure of 22.5×10^5 Pa with a hydrocarbon pressure of 8×10^2 Pa and a H_2S partial pressure of 4.5×10^2 Pa. Under these conditions DBT was mainly transformed into BP. The HN of BP led essen-

tially to cyclohexane and dicyclohexyl. All the reaction products were analysed by gas chromatography with a FID detector. The specific activity A_s is determined by the relation $A_s = (Qx\tau)/m$, where Q = hydrocarbon flow, m = catalyst weight, and τ = conversion. For all the samples studied, the conversion was kept lower than 15% by adjusting the catalyst weight.

Catalyst Preparation and Characterization of Sulphides

The synthesis of Mn, Fe, Co, Ni, Cu, Zn, Rh, Pd, and Cd sulphides was carried out by using the method developed by Pecoraro and Chianelli (1). The preparation of chromium(III) sulphide was performed by direct sulphidation by H_2S of chromium chloride according to the procedure described by Udy (7). This method was successfully extended to the preparation of Zr and Hf disulphides. Since titanium tetrachloride is a highly hydrolyzable liquid, the TiS_2 catalyst was prepared by sulphiding a commercial anatase (Degussa P25) by carbon sulphide at 773 K. Ru sulphide was precipitated from an aqueous solution of ruthenium chloride by H_2S . The decomposition of ammonium thiosalts was used for the preparation of Mo, W, V, and Re sulphides (8–10). The Nb trisulphide was the only sample prepared by the ceramic method. The high reactivity of metallic niobium toward sulphur allows its preparation at 773 K (11).

All the sulphides were characterized by X-ray diffraction and elemental analysis. The XRD patterns were recorded using a Siemens D diffractometer ($CuK\alpha$ radiation) equipped with an automatic identification of phases according to the JCPDS index. The freshly-prepared sulphides were treated at 673 K in an H_2 – H_2S flow. The aim of this sample pretreatment was to stabilize each catalyst at a temperature higher than the reaction temperature.

The structures, stoichiometries, and surface areas of the different solids are given in Table 1. XRD and sulphur-to-metal ratios

indicate that the techniques used for the low-temperature TMS synthesis allow the preparation of the expected most stable binary sulphides. These solids are generally stable under the test conditions, but structural changes occur for some of them: Ni, Co, and Pd monosulphides are transformed into Ni_3S_2 , Co_9S_8 , and Pd_4S , whereas the fibrous NbS_3 structure leads to a mixture of NbS_3 and $Nb_{1.12}S_2$ (11). In order to compare the catalytic properties of the different sulphides, it would be desirable to obtain samples of comparable surface areas. Nevertheless, taking into account the wide variety of preparation processes used, it is impossible to avoid quite high variation in the textural properties. In several cases, namely, Ni, Co, Mo, V, Ru, and Rh, the influence of the surface areas on the catalytic activities in BP HN has been examined (Table 2) and the reaction rates appear to be proportional to the surface areas. This result can be expected for isotropic sulphides, but is surprising for layered compounds for which the active sites are located in the edge planes and the ratio of edge plane to basal plane can be influenced by the preparation method (1). Nevertheless, if the preparation method is constant, the edge plane area can be proportional to the overall area and a good correlation between total surface area and catalytic activities can be obtained (12). Therefore, the intrinsic rates (per m^2) can be used for the comparison of the catalytic activities.

The catalytic properties are schematized in Fig. 1. Although the experimental conditions used in this work are different from those used by Pecoraro and Chianelli (1) for the DBT HDS, namely, a dynamic micro-reactor working under atmospheric pressure, low temperatures (523–573 K) and pure DBT on the one hand, and a batch reactor, higher temperatures (623–673 K) and pressures (31×10^5 Pa), and DBT dissolved in decalin on the other hand, the general tendencies are similar. These tendencies can be summarized as follows: high activities for Ru, Rh, Re, and Pd sulphides,

TABLE I

Crystalline Phases, Stoichiometries (S/Me), and Surface Areas (SA) of Transition Metal Sulphides before and after Catalytic Tests

Transition metal	Before catalytic test			After catalytic test		
	Observed structure	S/Me	SA _{BET} (m ² g ⁻¹)	Observed structure	S/Me	SA _{BET} (m ² g ⁻¹)
Ti	TiS ₂	1.9	56	TiS ₂	1.7	58
V	V ₂ S ₃	1.47	60	V ₂ S ₃	1.44	60
Cr	Cr ₂ S ₃	1.51	50	Cr ₂ S ₃	1.5	33
Mn	α-MnS	1	14	α-MnS	0.96	10
Fe	FeS	0.95	6	Fe _{1-x} S	0.91	6
Co	Amorphous	0.95	26	Co ₉ S ₈	0.93	26
Ni	β-NiS	1.05	20	Ni ₃ S ₂	0.7	20
Cu	Cu ₃ S	0.54	5	Cu ₃ S	0.53	5
Zn	β-ZnS	0.99	31	β-ZnS	0.90	30
Zr	ZrS ₂	1.9	70	ZrS ₂	1.8	56
Nb	NbS ₃	3	3	Nb _{1.12} S ₂ +NbS ₃	2.7	3
Mo	MoS ₂	2.20	51	MoS ₂	2.09	38
Ru	RuS ₂	2.2	75	RuS ₂	1.87	73
Rh	Rh ₂ S ₃	1.5	55	Rh ₂ S ₃	1.45	55
Pd	PdS	1.1	23	Pd ₃ S	0.25	22
Cd	CdS	0.98	10	CdS	0.96	7
Hf	HfS ₂	1.8	6	HfS ₂	1.8	6
W	WS ₂	2.18	63	WS ₂	2.08	44
Re	Amorphous	2.05	30	ReS ₂	2.01	10

good activities for Mo and W sulphides, and very low activities for the sulphides of the first row elements (except V sulphide). However, important differences are observed for V and Nb sulphides whose ac-

TABLE 2

Catalytic Activities in BP HN for Samples of TMS Presenting Different Surface Areas

Sample	SA _{BET} after test (m ² g ⁻¹)	Specific activity (10 ⁻⁸ mol s ⁻¹ g ⁻¹)	Intrinsic activity (10 ⁻⁸ mol s ⁻¹ m ⁻²)
Ni ₃ S ₂	20	0.76	0.038
Ni ₃ S ₂	12	0.48	0.04
Co ₉ S ₈	26	1.2	0.046
Co ₉ S ₈	13	0.6	0.046
MoS ₂	38	5.7	0.15
MoS ₂	24.5	3.7	0.15
RuS ₂	73	74	1.0
RuS ₂	43	46	1.1
RuS ₂	26	26	1.0
V ₂ S ₃	60	21	0.35
V ₂ S ₃	38	12.3	0.32
Rh ₂ S ₃	55	135.5	2.5
Rh ₂ S ₃	19	57	3
Rh ₂ S ₃	11	26	2.4

tivities are very low in the previous study and similar to Mo sulphide in the present work. The reason for this discrepancy is probably the existence of several sulphide compositions, some of them being active and others less so. For instance, a detailed study of the properties of the Nb-S system has shown that NbS₃ is more active than NbS₂, which has been used by Pecoraro and Chianelli (1, 11). Similarly V₅S₈ and V₂S₃ can be obtained under different atmospheres, V₂S₃ being more active than V₅S₈ (13) and no indication was given about the stoichiometry of the catalyst used in Ref. (1).

In the case of BP HN, the most active catalysts are always Rh and Ru sulphides. Some others are particularly efficient for this reaction, e.g., V and Nb sulphides. However, in the latter case the conversion of BP leads mainly to benzene and cyclohexane. These cracking properties are

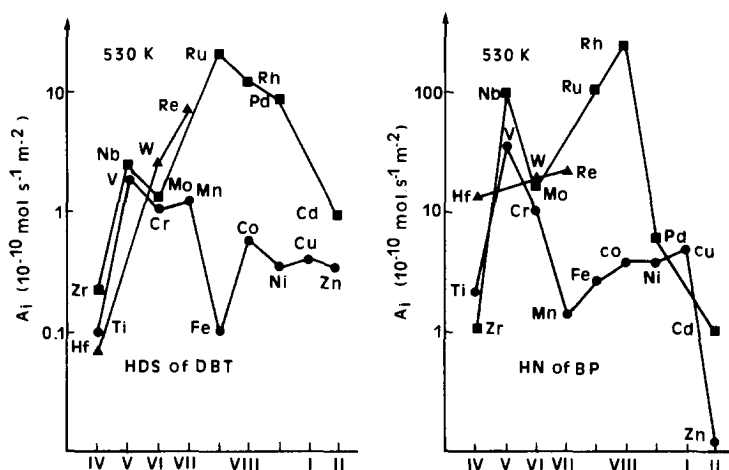


FIG. 1. Intrinsic activities (A_i) of transition metal sulphides for the hydrodesulphurization of dibenzothiophene (HDS of DBT) and the hydrogenation of biphenyl (HN of BP) at 530 K.

not observed for the other sulphides which transform biphenyl into phenylcyclohexane and dicyclohexyl.

No clear relationship can be found with the crystal structure (cubic for RuS_2 , fibrous for NbS_3 , lamellar for MoS_2 and WS_2). On the other hand, Ledoux *et al.* (3) ascribed a high activity in HDS to elements which may exhibit various possibilities of coordination with sulphur. However, this hypothesis is not corroborated for one of the most active sulphides, viz., RuS_2 . It has also been proposed that the presence of $(\text{S})_2^{2-}$ is favorable for the catalytic activity (14, 15). This hypothesis can explain the high activity of Ru and Nb sulphides but not the activity of V, Mo, and Rh sulphides.

The relative activities defined by $\alpha = A_s(\text{HN})/A_s(\text{HDS})$ have been calculated for the most active catalysts. Under the experimental conditions used in this work, the observed value of α is close to 10 for Mo, Cr, Ni, and Cu sulphides and reaches 20 for V, Nb, and Rh sulphides, whereas for Co, Ru, Pd, Cd, W, and Re chalcogenides α lies between 1 and 6. The comparable α value observed for most of the samples suggests that the active sites involved in both reactions are similar. However, the nature of the HN and HDS sites may differ by the

number of anionic vacancies associated with a metal ion. For instance, Tanaka (16) has presented evidence that hydrogenation reactions can be related to three anionic vacancies whereas two or four vacancies are needed for performing isomerization reactions. The number and the distribution of such anionic vacancies drastically depend on experimental conditions (e.g., $\text{H}_2\text{S}/\text{H}_2$ ratio, temperature, etc.) and on the chemical nature and structure of the chalcogenide (17).

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