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HDS, HDN and HYD activities and temperature-programmed reduction of unsupported transition metal sulfides

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Several transition metal sulfides have been shown to exhibit high catalytic activities in various hydrotreating reactions. The simultaneous catalytic activities for hydrodesulfurization of dibenzothiophene, hydrodenitrogenation of indole and hydrogenation of naphthalene have been studied using high surface area bulk sulfides: NbS_2, MoS_2, ReS_2, RuS_2 and Co_9S_8. The metal–sulfur bond strengths have been assessed by temperature-programmed reduction of H_2S-pretreated sulfides, and it is demonstrated that this pretreatment is necessary to obtain reliable TPR data for the sulfides. The catalytic HDS activity is shown to follow the trend in the metal–sulfur bond strengths estimated by this improved method. Furthermore, the metal–sulfur bond strengths determined this way follow the trend estimated previously from theory. The TPR data suggest that a large number of sulfur vacancies exist in active catalysts under industrial reaction conditions. Such vacancies have recently been observed on model catalysts by use of STM.

Keywords: hydrotreating catalysis, unsupported sulfide, TPR, HDS, HDN, bond energy model

1. Introduction

Hydrotreating catalysis refers to a number of catalytic processes which serve to hydrogenate different petroleum streams in a refinery. The primary purpose is to remove organic sulfur, nitrogen and oxygen compounds as well as unsaturated hydrocarbons from the stream prior to its use as various fuels [1–5]. Hydrotreating catalysis is among the most important catalytic processes in operation worldwide and represents approximately 10% of the total world market for catalysts. Most present commercial hydrotreating catalysts contain a mixture of either nickel and molybdenum or cobalt and molybdenum. The active phase is typically supported on a high surface area alumina to maximize the accessible surface area of the sulfides. The structure of the active phase in these catalysts has been a matter of controversy for many years but today the so-called Co–Mo–S model [6] has gained general acceptance. Hydrodesulfurization (HDS) has been the most widely studied hydrotreating reaction and it has been suggested for many years that the active sites are sulfur vacancies [7]. More recently, this formed the basis for the bond energy model [8,9] which showed that there exists a correlation between the catalytic HDS activity and the estimated metal–sulfur bond strength. In principle, it should be possible to evaluate the metal–sulfur bond strength by temperature-programmed reduction (TPR) of the sulfide catalysts and such studies have been reported in literature [10–15]. However, often such data are influenced by the presence of the high surface area support materials and are incomparable due to differences in the experimental procedures. The use of pure (unsupported) high surface area transition metal sulfides minimizes secondary effects (such as adsorption, readsorption and diffusion) due to the support materials and also significantly eases characterization of fresh and spent catalysts. Therefore, we have prepared high surface area bulk sulfides: NbS_2, MoS_2, ReS_2, RuS_2 and Co_9S_8 and tested their HDS, hydrodenitrogenation (HDN) and hydrogenation (HYD) activities under industrially relevant conditions using a model feed. By using simultaneous measurements of all reactions it is ensured that the state of the catalyst is identical for all the reported reactivities. The metal–sulfur bond strengths have been assessed by TPR of H_2S-pretreated sulfides. In this way, it is possible to obtain reproducible TPR traces and to establish a correlation between the activities and the metal–sulfur bond strengths.

2. Experimental

2.1. Preparation of high surface area transition metal sulfides

All sulfide samples are passivated after their preparation by treatment with 1000 ppm O_2 in N_2 at room temperature prior to being exposed to the atmosphere.

Niobium sulfide. NbS_2 was prepared by a novel procedure. Under a protective atmosphere of N_2, 10 g of sulfur was added to a solution of 5 g of $Nb(OC_2H_5)_5$ in 200 ml of 99.9% ethanol. Hydrogen sulfide was bubbled through this solution for 2 h at room temperature. The resulting precipitate was isolated by filtration, washed with ethanol, dried under vacuum and heated at 10 °C/h to 400 °C under a flow of 10% H_2S in hydrogen.

Molybdenum sulfide. MoS_2 was prepared according to the previously described homogeneous sulfide precipitation (HSP) [16].

Rhenium sulfide. ReS_2 was prepared analogously to MoS_2 using the HSP method with ammonium perrhenate as a starting material. High surface area rhenium sulfide (>50 m^2/g) can also be easily prepared by sulfidation of tetraethylammonium tetrathioperrhenate(VII), $[NEt_4]ReS_4$, prepared according to Müller [17].

Ruthenium sulfide. RuS_2 was prepared according to the method of Lacroix et al. [18].

Cobalt sulfide. Co_9S_8 was prepared according to the HSP method using cobalt nitrate as a starting material.

2.1.1. X-ray powder diffraction

XRPD patterns were recorded in air from both fresh and spent catalysts by slow scanning on a Phillips vertical goniometer equipped with a θ-compensating divergence slit and a diffracted beam graphite monochromator utilizing Cu K-$L_{2,3}$ radiation. Crystal sizes were obtained using the Debye–Scherrer equation with correction for the θ-dependent instrumental response.

2.1.2. Surface area measurement

Surface areas of the sulfide catalysts were obtained from dinitrogen adsorption and desorption using a Quantachrome Autosorp analyser.

2.2. Preparation of catalyst particles for TPR and activity measurements

For TPR and catalytic testing, particles of ca. 0.60–0.85 μm were prepared by pressing tablets of the sulfide powder using an IR press. These tablets were crushed and sieved to the desired particle size range. The pore sizes of the unsupported sulfide catalysts are generally significantly larger than those of alumina-supported catalysts. Therefore, at the relatively low conversions achieved under the test conditions the particle size chosen eliminates diffusional limitations and ensures a sufficiently low pressure drop over the catalyst bed.

2.2.1. Temperature-programmed reduction

500 mg of the passivated sulfide catalyst was loaded into the TPR reactor and resulfided by heating to 400 °C in a 100 ml/min flow of 10% H_2S in Ar. After 2 h at this temperature the sample was cooled to room temperature. The sample was flushed with a flow of 100 ml/min He while being reheated to 400 °C and kept at this temperature for 2 h. After cooling to room temperature the TPR was initiated by heating at 10 °C/min in 1% H_2 in He. The composition of the exit gas was monitored by a mass spectrometer (Balzers QMG420).

2.2.2. Catalytic activity measurements

HDS of dibenzothiophene (DBT), HDN of indole (IN) and HYD of naphthalene (NAP) was carried out at 300–375 °C and 50 bar using the set-up previously described [19]. Basically, the conversion of DBT into sulfur-free products, IN into nitrogen-free products and NAP into hydrogenated products was measured from a feedstock containing 2 wt% DBT, 0.5 wt% IN and 1 wt% NAP in n-heptane. n-nonane was added as an internal reference to allow quantitative determinations of the conversion using gas chromatography and carbon disulfide was added to ensure a constant H_2S partial pressure of 0.1 bar. The reported conversions are obtained with 0.3 g of sulfide catalyst, a liquid feed flow of 0.3 ml/min and a hydrogen flow of 250 Nml/min.

3. Results and discussion

3.1. Synthesis

In table 1, the properties of the isolated sulfide catalysts are summarized. It is seen that samples with relatively high surface areas can be obtained by the reported methods. It is also seen that apparently there is no correlation between the crystal sizes determined from the XRPD patterns and the measured surface areas. This is probably due to to morphological and stoichiometric variations. Furthermore, it is not simple to consistently determine the active surface areas of the involved sulfide catalysts. Since several of the sulfides were pyrophoric when exposed to air after the sulfidation treatment, a passivation procedure was routinely used to allow handling of the sulfides under ambient conditions.

3.2. Temperature-programmed reduction

In figure 1, the TPR traces of the sulfide catalysts are shown, illustrating the consumption of H_2. A completely parallel production of H_2S was observed during the experiment, as shown for MoS_2 in figure 2. This suggests that all H_2S production is due to hydrogenation of the sulfide. The TPR traces of all sulfides contain a well-resolved peak at relative low temperature and broader features at higher temperatures. The well-resolved low-temperature peak is usually not observed when TPR is conducted after an ordinary sulfidation in a H_2S/H_2 mixture [12]. Apparently,

Table 1
Properties over the isolated sulfide catalysts.

Sulfide	Space group	Crystal size (Å)	BET surface area (m^2/g)
NbS_2	P6$_3$/mmc	$D^{020} = 16$	18
MoS_2	P6$_3$/mmc	$D^{020} = 46$	69
ReS_2[b]	Unknown[a]	$D^{020} = 63$	8
ReS_2	Unknown[a]	$D^{020} = 24$	40
RuS_2	Pa3	$D^{220} = 109$	27
Co_9S_8	Fm3m	$D^{331} = 450$	15

[a] From the XRPD pattern ReS_2 appears to be isostructural with MoS_2 and this is assumed in the determination of the crystal size.

[b] This low surface area ReS_2 was prepared by sulfidation at 650 °C and represents the sample used in the activity measurements.

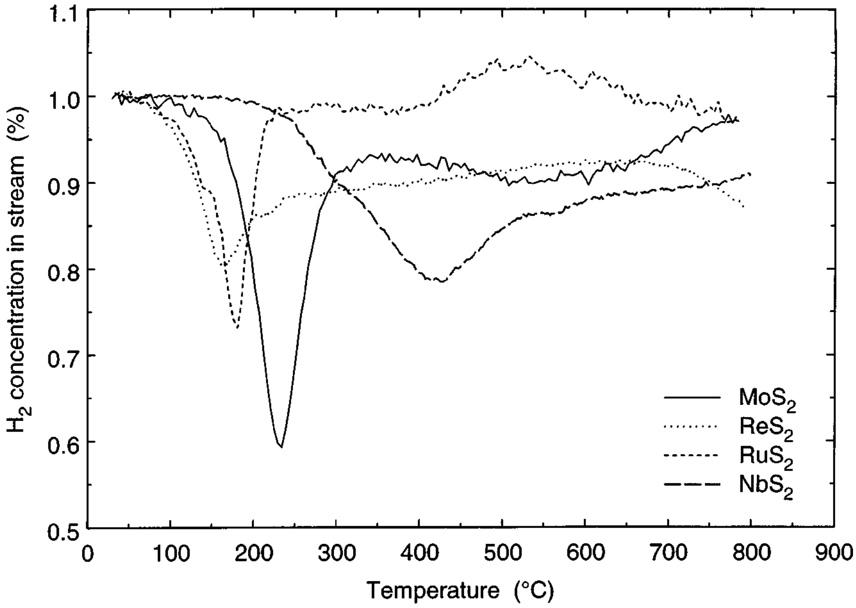

Figure 1. H_2 consumption during temperature-programmed reduction of H_2S-pretreated high surface area transition metal sulfides.

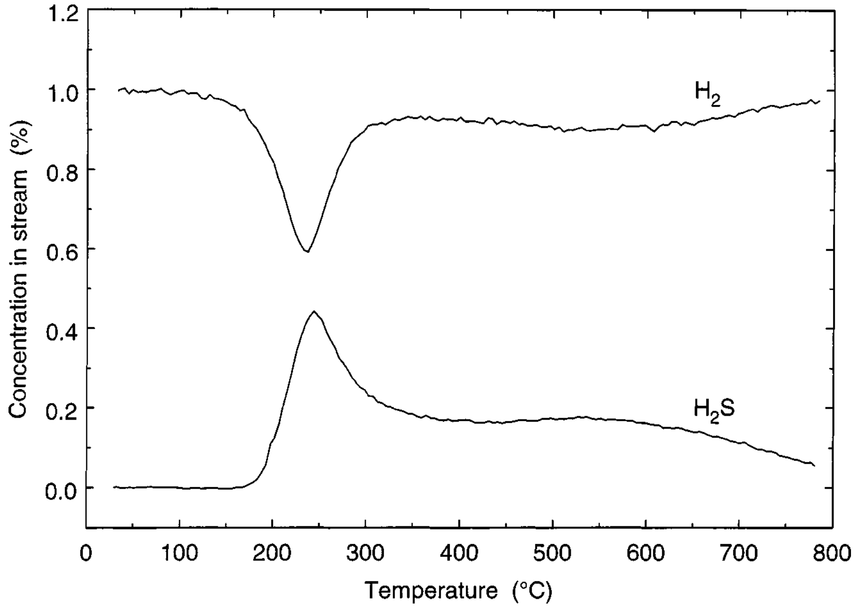

Figure 2. H_2S production and H_2 consumption during temperature-programmed reduction of H_2S-pretreated MoS_2.

this peak originates from sulfur atoms that are too weakly bound to be present at the catalyst surface after sulfidation in a standard hydrogen-containing gas mixture. This was proven by conducting a temperature-programmed sulfidation in 10% H_2S/Ar of a MoS_2 sample initially sulfided in 10% H_2S/H_2. It was observed that during this sulfidation H_2S was consumed and H_2 produced correspondingly. Therefore, it appears that the surface sulfidation/reduction reaction is reversible,

$$^*S + H_2 \rightleftharpoons H_2S + ^*$$

As a consequence of this equilibrium, the TPR trace of a sulfide catalyst is expected to be very dependent on the pretreatment of the catalyst. If the catalyst is sulfided in a H_2/H_2S mixture both the ratio of hydrogen to hydrogen sulfide as well as the cooling ramp may influence the subsequent TPR experiment. Obviously, this dependence on the pretreatment is expected to be most pronounced for the most active catalysts, i.e., those with the weakest metal–sulfur bond strengths. By conducting the TPR of H_2S-pretreated catalysts this dependence is eliminated and a quantitative determination of the surface sulfur atoms is possible. In order to verify that the well-resolved low-temperature peak could conclusively be attributed to surface sulfur atoms we conducted a TPR experiment with two samples of ReS_2 prepared similarly, but sulfided at 400 and 650 °C to yield surface areas of 40 and 8 m^2/g. The TPR traces are shown in figure 3 and it is easily seen that the sample with the lower

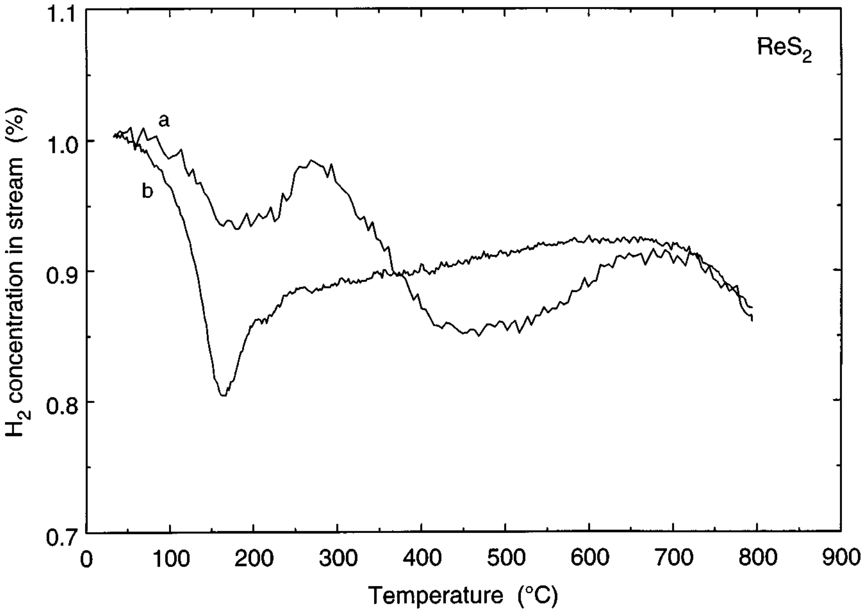

Figure 3. H_2 consumption during temperature-programmed reduction of H_2S-pretreated ReS_2 with surface areas of 8 (a) and 40 m^2/g (b).

Table 2
Conversions of DBT, IN and NAP over the sulfide catalysts at the test temperatures.

Catalyst	T (°C)	X^a DBT	IN	NAP
NbS_2	372	2.8	6.7	2.1
MoS_2	332	19.7	44.6	18.6
ReS_2	312	25.4	62.1	6.1
RuS_2	302	78.3	32.6	31.8
Co_9S_8	372	3.1	4.5	1.5

[a] Conversion of DBT into sulfur-free products, IN into nitrogen-free products and NAP into hydrogenated products.

surface area has a much less pronounced low-temperature peak but a significant feature at higher temperature. The relative areas of the low-temperature peaks are in satisfactory agreement with the ratio of the surfaces areas of the two samples. Thus, it appears that the low-temperature peak can be assigned to surface sulfur atoms. Previously, it has been found for MoS_2 catalysts prepared similarly to those in the present study that the TPR trace is dependent on the pretreatment of the catalyst [20].

3.3. Catalytic activity measurements

In table 2, the conversions of DBT, IN and NAP at the test temperatures are shown. In all cases, the XRPD patterns of the catalysts prior to and after the catalytic activity tests were almost indistinguishable. Since the sulfide catalysts exhibit activities which vary dramatically it was not possible to test them all at the same temperature and obtain reasonable conversions. Such an approach would have allowed a more direct comparison of both activities and selectivities. However, there is no doubt that the HDS activity ranking can be summarized as $RuS_2 > ReS_2 > MoS_2 > NbS_2 \approx Co_9S_8$. This ranking is similar to that reported by Pecoraro and Chianelli [21] and in agreement with the ranking of the metal–sulfur bond strengths found in the TPR studies above. However, rhenium sulfide and ruthenium sulfide appear to have very similar metal–sulfur bond energies in agreement with expectations from the theoretical considerations [8,9]. The fact that ruthenium sulfide is more active than rhenium sulfide could therefore be related to a difference in the number of active sites since only a relatively small fraction of the total surface area of the anisotropic ReS_2 structure is expected to exhibit activity. In comparison, RuS_2 has a cubic structure and possibly all surface area is available for catalysis. This difference in the number of active sites is substantiated by the lower area under the low-temperature H_2 consumption peak of ReS_2 relative to RuS_2. Alternatively, these catalysts have sulfur atoms that are so weakly bound that formation of the vacancy is no longer the sole rate-determining step. It appears that the selectivies vary significantly among the different sulfides but without detailed information about the relevant activation energies it is not possible to make quantitative comparisons. However, in figure 4 we have shown the HDS conversion vs. the HDN conversion to give an impression of the activity and selectivity variations. In previous comparisons of HDS, HDN and HYD selectivities, the acitivities for HDS, HDN and HYD have often been compared although they were measured individually under different reaction conditions (pressure, temperature, model feed stock, H_2S and NH_3 partial pressures). In these studies high HDN selectivities of ReS_2 [22], MoS_2 [22] and NbS_2 [23] have been observed. The very low HYD selectivity of ReS_2 observed here is conspicuous but was also found for a supported ReS_2/alumina catalyst. In comparing the present selectivities to those previously reported it should be emphasized that those obtained here are measured simultaneously.

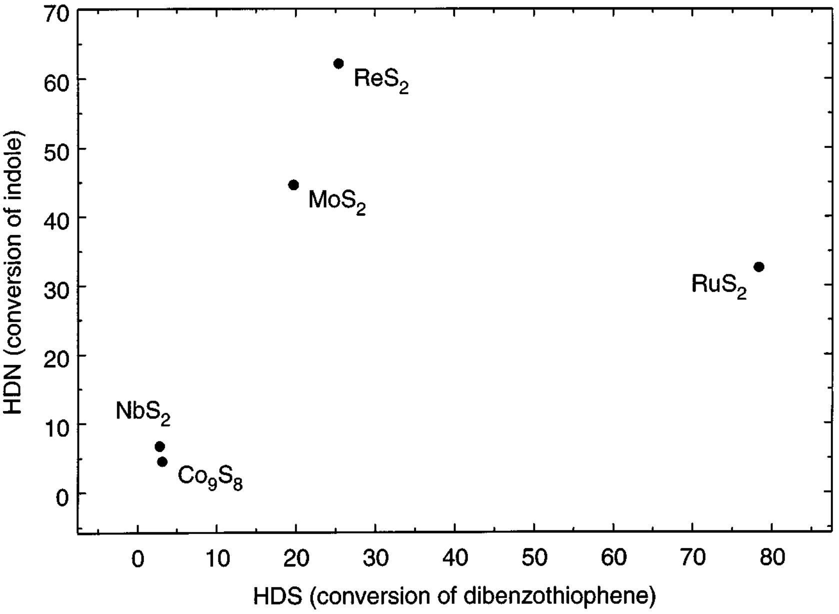

Figure 4. HDS conversion vs. HDN conversion for RuS_2 (302 °C), ReS_2 (312 °C), MoS_2 (332 °C), Co_9S_8 (372 °C) and NbS_2 (372 °C).

4. Conclusion

The simultaneous catalytic HDS, HDN and HYD activities of the unsupported transition metal sulfides NbS_2, MoS_2, ReS_2, RuS_2 and Co_9S_8 are reported. It is seen that the catalytic activities vary over a wide range and the following ranking is found: $RuS_2 > ReS_2 > MoS_2 > NbS_2 \approx Co_9S_8$. This activity variation can be rationalized in terms of the bond energy model when the metal–sulfur bond strengths are assessed by TPR of H_2S-pretreated catalysts. This pretreatment is necessary to populate all surface sites with sulfur. It is shown that these sulfur atoms cause a well-resolved low-temperature H_2 consumption peak during TPR. The results suggest that a large number of sulfur vacancies are present during industrially relevant conditions in accordance with recent scanning tunneling microscopy results [24]. It appears plausible that these sites are responsible for the catalytic activity of sulfide catalysts. In principle, the temperature-programmed reduction of H_2S-pretreated sulfide catalysts should allow a determination of *both* the total number of sites and the strength of these sites or alternatively indicate the number of active sites present at various H_2S/H_2 ratios. Such studies are in progress on supported catalysts.

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