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NOTES

Hydrodesulfurization and Hydrogenation Properties of Promoted MoS_2 and WS_2 Catalysts under Medium Pressure Conditions

Although industrial hydrodesulfurization (HDS) is a typical medium pressure process, carried out under continuous flow conditions, fundamental research has been performed for the most part by pulse and continuous flow experiments at atmospheric pressure. Another notable contrast between the technical process and fundamental studies is in the reactor feed used to characterize, for instance, catalytic activities, the nature of active sites involved, and the reaction mechanisms. In industrial processes the feed is usually very complex while for fundamental research often only a single model compound is used.

In order to check some structural aspects of the $CoO–MoO_3–\gamma-Al_2O_3$ catalyst system [discussed earlier (*1*)] for their relevance to more industrial application, three series of flow experiments have now been carried out at medium H_2 pressure. In addition to thiophene benzothiophene has also been used as a sulfur-containing agent, and, besides HDS activities, activities for benzene hydrogenation have also been measured. It should be stressed, however, that all measurements, in contrast to industrial practice, have concerned short run experiments.

A conventional stainless-steel apparatus was used. The fixed bed tube reactor, inner diameter $\phi = 13 \times 10^{-3}$ m, was fitted with a sintered plate (pore diameter 50×10^{-6} m). A micro-plunger pump was used for concurrent dosage of the feed. Composition of both the gas and light phase was analyzed on a squalane Chromosorb column (thiophene and benzene experiments) and on a polyphenyl-ether Diatoport S column (benzothiophene).

The various feed compositions were: (a) 92.5 mol% thiophene (Merck, "for synthesis") with 7.5 mol% cyclohexane (Fluka "for analysis"); (b) 34.7 mol% benzothiophene (Fluka, "pure grade") with 65.3 mol% dodecane (Phillips, purity > 95 mol%); and (c) 98.5 mol% benzene (Merck, "for analysis") with 1.5 mol% CS_2 (Merck, "for analysis"). Reaction conditions are given in Table 1.

The main reaction products were: (a) thiophene, butane, and H_2S (butenes were absent); (b) benzothiophene, dihydrobenzothiophene, ethylbenzene, and H_2S (*2*); and (c) benzene, cyclohexane, methylcyclopentane, methane, and H_2S.

For all experiments the catalyst particle size was $0.5–1.0 \times 10^{-3}$ m. Standard catalysts used were $MoO_3–\gamma-Al_2O_3$, Ketjen 120–1.5E (pore volume, 0.51×10^{-3} m^3 kg^{-1}; reactor density, 0.74 kg $liter^{-1}$) and $CoO–MoO_3–\gamma-Al_2O_3$, Ketjen 124–1.5E L.D. (pore volume, 0.70×10^{-3} m^3 kg^{-1}; reactor density, 0.67 kg $liter^{-1}$). Ketjen CK 300, pure grade $\gamma-Al_2O_3$ (pore volume, 0.53×10^{-3} m^3 kg^{-1}; reactor density, 0.62 kg $liter^{-1}$) was used for preparation of model catalysts according to methods described before (*1*).

These methods are indicated in Table 1, together with catalyst compositions and surface areas. All samples were sulfided in H_2S/H_2 (*1*) prior to the activity test.

Activities, measured after a 4-hr run time, are given in Table 1 and were calculated as follows: (a) [initial thiophene − remaining thiophene]/initial thiophene (both with reference to the thiophene/cyclohexane ratio); (b) [initial benzothiophene − remaining benzothiophene and dihydrobenzothiophene formed]/initial benzothiophene (both with reference to the fraction dodecane); (c) [methylcyclopentane + cyclohexane]/(methylcyclopentane + cyclohexane + remaining benzene); (c′) methylcyclopentane/[cyclohexane + methylcyclopentane].

All the results obtained are presented in Table 1. For an appropriate evaluation of these results it should be kept in mind that a number of important parameters were varied in catalyst preparation; these included purity as well as specific density and surface area of the γ-Al_2O_3 supports and concentration and degree of dispersion of the main active Mo- and W-compounds. Moreover, there were significant differences in the experimental conditions applied for the various reaction types. Therefore only the main effects will be discussed here.

A. *Thiophene desulfurization.* The catalyst preparation and promoter effects were qualitatively in very good agreement with those observed for activity measurements at atmospheric hydrogen pressure reported earlier (*1*).

B. *Benzothiophene desulfurization.* The results with respect to the effect of method of preparation were similar to those obtained for thiophene hydrogenolysis. Urimoto and Sakikawa (*3*), measuring the dibenzothiophene hydrodesulfurization activities for pure MoS_2 and WS_2 in batch experiments at 573 K and 50.65×10^5 N m^{-2}, have found a specific (per square meter) MoS_2/WS_2 desulfurization activity ratio of 1.49. From the data given in Table 1 (catalysts 1 and 4) a ratio of 2.66 can be calculated.

For both WS_2 and MoS_2 the promotion effects of Co and Ni on benzothiophene desulfurization seemed to be significantly higher than for thiophene desulfurization. In addition, it was observed during all experiments that, with decreasing HDS activity as a function of run time, the concentration of dihydrobenzothiophene in the reaction products increased much faster than the benzothiophene concentration. This indicates that, in contrast to thiophene HDS (*4*, *5*), benzothiophene is partly hydrogenated (dihydrobenzothiophene) prior to desulfurization (ethylbenzene). No aromatic ring saturation was observed, indicating that this is not a necessary prelude for scission of the bond between sulfur and aromatic carbon. The last two observations are in agreement with the findings of Givens and Venuto (*2*).

C. *Benzene hydrogenation.* Again the same qualitative effects of catalyst preparation as for thiophene and benzothiophene hydrodesulfurization were found. The extent of promotion by Co and Ni seems to be relatively high.

Catalysts containing WS_2 showed far better benzene hydrogenation properties than those based on MoS_2, and, for both catalyst types, Ni was found to be the most effective promoter. This is in fairly good agreement with the findings reported by Ahuja *et al.* (*6*). As far as the catalysts based on WS_2 are concerned there is a discrepancy with the data reported by Farragher and Cossee (*7*) who found Co to be a much more effective promoter for benzene hydrogenation than was Ni.

C′. *Isomerization.* From the results given in Table 1, it is very likely that we are dealing here primarily with a carrier effect, although unsupported sulfide catalysts also have some isomerization activity (*8*). Samples (*1–6*) supported on a pure grade γ-Al_2O_3 (Ketjen CK 300) showed a higher isomerization activity than those sup-

TABLE 1

List of Catalysts Tested and Reaction Conditions

Catalyst		Composition (mol% balanced by the support)					Surface area ($m^2 g^{-1}$)	Preparation method (see Ref. (*1*))	Activities at 4-hr run time (% conversion)			
No.	Notation[a]	WS_2	CoO	NiO	MoS_2	MoO_3			HDS		Benzene hydrogenation	Cyclohexane isomerization
									Thiophene	Benzothiophene		
1	WS_2 + Al[b]	19.4					118	D	8	3	7	54
2	Co-(WS_2 + Al)	18.0	7.1				111	E	22	41	41	23
3	Ni-(WS_2 + Al)	18.0		7.1			108	E	26	45	79	6
4	MoS_2 + Al[b]				19.4		129	D	15	15	2	45
5	Co-(MoS_2 + Al)		6.9		18.0		117	E	24	46	16	22
6	Ni-(MoS_2 + Al)			6.9	18.0		123	E	27	47	20	18
7	Mo-Al					9.9	235	Ketjen 120	35		15	7
8	Co-Mo-Al		6.7			9.3	226	A	58		84	7
9	Ni-Mo-Al			6.7		9.3	223	A	55		90	4
10	Co-Mo-Al		5.4			9.0	241	Ketjen 124	57	100	76	10
	Reaction conditions											
	Total liquid feed rate (10^{-3} liter hr^{-1})								4.1	5.0	3.8	
	H_2 pressure (10^5 N m^{-2})								101.3	101.3	101.3	
	H_2 flow rate (liters hr^{-1})[c]								7.2	7.2	3.6	
	Mole ratio H_2/reactant								6.4	25.7	3.5	
	Reactor temperature (K)								523	523	673	
	Reactor charge (10^{-3} liter)								15	10	15	

[a] γ-Al_2O_3 is abbreviated by Al. Impregnation and mechanical mixing are indicated by a hyphen and a plus sign, respectively.

[b] Surface area of WS_2 and MoS_2 is, respectively, 2.6 and 7.8 $m^2 g^{-1}$.

[c] Measured at 295 K and 1.013×10^5 N m^{-2}.

ported on a HDS base γ-Al_2O_3. This phenomenon correlates inversely with the Na_2O content of these supports which were, respectively, 0.0004 and 0.086–0.14 wt% according to the manufacturer. It is well known that sodium reduces the acid properties of γ-Al_2O_3. In addition to this, the isomerization activity was decreased by the introduction of Co and even more effectively by Ni. Similar observations are reported by Ahuja *et al.* (*6*). An influence of Co and Ni on the isomerization of promoted catalysts can be explained by noting that, after presulfiding, some Co^{2+} still remained in the support (*9*). Preliminary experiments with sulfided NiO–γ-Al_2O_3 samples showed Ni to be less sulfidable than Co, suggesting a stronger interaction with the support.

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