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Investigation of CoNiMo/Al_2O_3 catalysts: Relationship between H_2S adsorption and HDS activity

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Abstract

Sulfidation of trimetallic CoNiMo/Al_2O_3 catalysts was studied by thermogravimetry at 400 °C under flow and pressure conditions. Results were compared with those obtained on prepared and industrial CoMo/Al_2O_3 and NiMo/Al_2O_3 catalysts. The amount of sorbed H_2S on the sulfided solids was measured at 300 °C in the H_2S pressure range 0–3.5 MPa at constant H_2 pressure (3.8 MPa). The adsorption isotherms were simulated using a model featuring dissociated adsorption of H_2S on supported metal sulfides and bare alumina. The amount of sulfur-vacancy sites could thus be determined under conditions close to industrial practice. A relationship with activity results for thiophene HDS and benzene hydrogenation was sought for.

Keywords: Hydrotreating catalysts; H_2S adsorption under pressure and flow conditions; Catalyst sulfidation; Thermogravimetric analysis; Sulfur-vacancy measurement; Relationship with activity

1. Introduction

Because of stringent regulations for fuels, more efforts have been focused in recent years to hydrotreatments [1,2]. To obtain cleaner fuels without changing drastically the processing conditions, refiners use more and more sulfided catalysts that combine both Ni and Co promoters with Mo/Al_2O_3 [3]. Enhanced activities may arise from the combination of benefits by using both the CoMo couple preferred for HDS and the NiMo couple for HDN and hydrogenation of aromatics. However, contradictory results have been reported in the literature, where trimetallic CoNiMo catalysts could exhibit either an increase or a decrease in activity with respect to model molecules [4–8]. For instance, we have reported that trimetallic CoNiMo/Al_2O_3 catalysts were less active than their analogous CoMo or NiMo for thiophene HDS performed at atmospheric pressure and benzene hydrogenation performed under pressure conditions [8]. We have concluded that the loss in activity was probably due to the formation of a separate mixed Co–Ni sulfide phase, which results by lowering the amount of promoted catalytic sites.

The number of reports about trimetallic CoNiMo/Al_2O_3 is limited [4–7] and the active sulfide phases were not cleared yet, while those of CoMo/Al_2O_3 and NiMo/Al_2O_3 have been very much investigated [3]. In spite of this, the number of active sites is still not precisely known although common understanding is emerging about the structure of the sulfided CoMo or NiMo catalyst.

In addition, we have established that industrial HDS activity of various CoMo/Al_2O_3 catalysts correlated with thiophene HDS activity under conditions where heteroring hydrogenation is rate limiting. It was concluded from kinetics that the amount of sulfur-vacancy sites controls the industrial activity [8,9].

Therefore, it seems necessary to determine the amount of vacancies on a sulfided catalyst for evaluation of catalytic activity under industrial conditions.

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So far, probe molecules such as O_2, NO, and CO, have been applied to quantify the number of active sites [10–13]. In many cases using such molecules, adsorptions were carried out at low temperature and pressure or under inert gas stream. For the purpose of estimating the amount of sulfur vacancies, measurements using a sulfur-containing molecule under high temperature and pressure must be much more pertaining.

In the present study, H_2S was used to appraise the amount of vacancies on several bi- and trimetallic CoNiMo/Al_2O_3 catalysts using a novel dynamic mass-measurement system [14,15]. The interaction between Ni, Co and Mo in the sulfided state was investigated and the amount of adsorbed H_2S was related to activity for thiophene HDS and benzene hydrogenation.

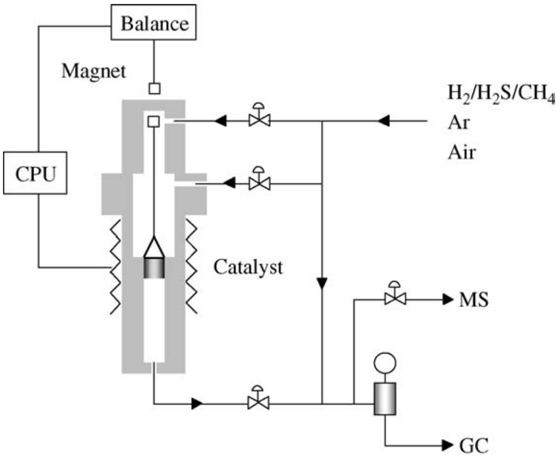

Fig. 1. Schematic diagram of high-pressure balance system.

2. Experimental

Conventional γ-alumina, GFS-C from Rhône-Poulenc, was used as a support. Active metals were successively loaded by the incipient wetness technique [8]. Promoter and molybdenum contents were close to those of industrial CoMo/Al_2O_3 (HR306C-1.2) and NiMo/Al_2O_3 (HR346) catalysts from Axens (Table 1), which were used for comparison. Three trimetallic CoNiMo-x samples have been prepared, where x represents the molar percentage of Ni among promoters.

After crushing and sieving (0.2–0.5 mm), a mass of 1–3 g of sample was filled in a small basket, following introduction into the high-pressure reactor (Fig. 1). At first, the sample was calcined at 400 °C under air stream at atmospheric pressure for 1 h to remove adsorbed water. The temperature was then decreased to 100 °C, and an Ar flow was introduced in the system. The temperature was then decreased to 40 °C. Ar was switched to H_2, when air was no longer present in the reactor, and pressure was raised to 4 MPa. Finally, the H_2 stream was switched to the sulfiding mixture of H_2S (10 mol%), CH_4 (10 mol%) and H_2. The catalyst was in situ sulfided at 400 °C for 10 h in the gas phase.

The basket was lifted up every 2 min to measure sample mass. Mass measurements were corrected from buoyancy effect according to the method described in previous reports [14,15]. It is worth to point out that the basket sits on the internal bottom walls of the pressure reactor, so that the gas flowed entirely through the catalysts bed. The composition of gas stream was analyzed by using an on-line mass spectrometer and a chromatograph to monitor compounds produced and consumed throughout the experiment. After the sulfidation stage, the H_2S pressure was adjusted in the range 0–0.35 MPa at various temperatures (40, 80, 130, 220, and 300 °C). Hence, adsorption isotherms were determined from H_2S isobars at constant H_2 pressure (3.8 MPa). Only results obtained at 300 °C, a temperature relevant to catalysis, are reported in this study.

Table 1
Tested samples

Catalyst	Mo (wt.%)	Co (wt.%)	Ni (wt.%)
Mo	9.62	0	0
HR306	9.39	2.42	0
CoMo	9.26	2.93	0
CoNiMo-26	9.27	2.11	0.73
CoNiMo-50	9.28	1.39	1.39
CoNiMo-74	9.28	0.73	2.07
NiMo	9.30	0	2.63
HR346	9.34	0	2.75

3. Results and discussions

3.1. Sulfidation behavior

Fig. 2 shows the variation of mass of sample Mo/Al_2O_3 and that of an CoNiMo/Al_2O_3 during the sulfidation stage. The profiles were found to be similar for all investigated solids and to match that observed for the industrial CoMo/Al_2O_3 [15]. When the H_2S mixed stream was introduced in the system, the mass increased due to adsorption of H_2S on the supported Co–Ni–Mo oxides and on bare alumina. The mass decreased during the temperature ramping period, and then it increased slightly during the isothermal stage at 400 °C and more markedly when the sulfided solid was cooled down (Fig. 2).

Following the study about CoMo/Al_2O_3 [15], sulfidation was found to proceed through three stages: i.e., H_2S adsorption with partial replacement of metallic oxygen atoms by sulfur atoms (region I, Fig. 2), complete sulfidation of the supported oxides (II), and removal of the water formed (III). The phenomena were identified from the derivatives of mass change. The first inflexion point around 70 °C shows the highest rate of mass loss. From gas phase and chemical analyses, it was inferred that H_2S adsorbed on the catalyst, and that sulfur atoms partly replace oxygen atoms of the

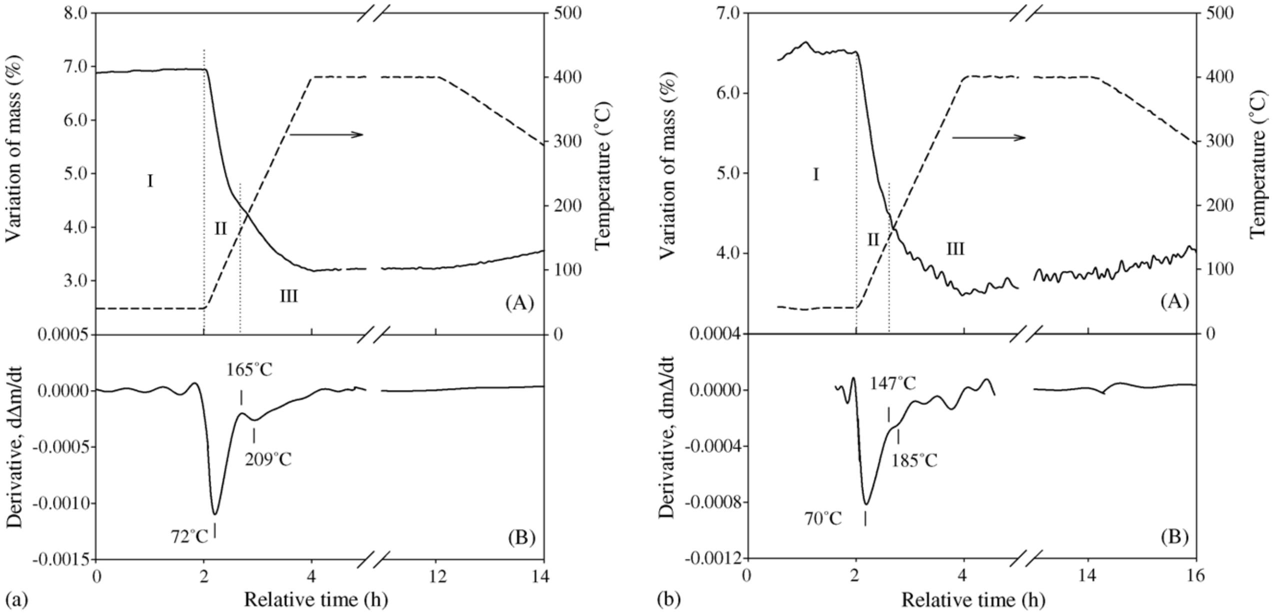

Fig. 2. Mass profiles during sulfidation: (a) Mo and (b) CoNiMo-50.

supported oxides. The O–S exchange was accelerated at 140 °C, as evidenced by the second peak around 200 °C; reduction to MoS_2-like species was completed at 300 °C. The replacement of the adsorbed water formed by the adsorption of H_2S was a slow process, as shown by the slight increase in mass observed during the isothermal stage at 400 °C. Since the peaks at high temperature were not large, differences between samples were hardly seen or buried in experimental errors. However, temperatures of the inflexion points were not so different from one catalyst to the other, which indicates that the sulfidation mechanism is barely affected by promoter Co or Ni. Although the sulfidation step is said to be important for activity [16–18], major differences in sulfidation profiles were hardly observed in this study.

3.2. H_2S adsorption isotherms

The 300 °C isotherms of sorbed H_2S were simulated using model Eq. (1), which features dissociative adsorption of H_2S on both metal sulfides (M) and bare alumina (A) [14]. Among fifteen rival models [14], this model was found to be the most suitable to fit the experimental adsorption data:

$$m = m_\infty\left[\frac{(1-f)\sqrt{K_A P}}{1+\sqrt{K_A P}} + \frac{f\sqrt{K_M P}}{1+\sqrt{K_M P}}\right] \tag{1}$$

Table 2
Adsorption parameters at 300 °C derived from simulations

Catalyst	m_∞ (g/g sulfide)	f	K_A (MPa^{-1})	K_M (MPa^{-1})
Mo	0.0224	0.475	105	6599
HR306	0.0290	0.550	107	7348
CoMo	0.0270	0.514	104	7342
CoNiMo-25	0.0271	0.492	105	7499
CoNiMo-50	0.0247	0.467	106	6532
CoNiMo-75	0.0276	0.440	105	7174
HR346	0.0297	0.404	104	7198

m_∞ (g/g sulfided catalyst): mass of H_2S adsorbed at saturation; f: fraction of coverage on metal sulfides; K_A (MPa^{-1}): adsorption constant on alumina surface; K_M (MPa^{-1}): adsorption constant on metal sulfide surface.

The comparison of the parameters suggests that combining Co and Ni lowers the H_2S adsorption capacity (Table 2); the mass m_∞ of H_2S adsorbed at the monolayer was found to be the lowest in the case of CoNiMo-50. It could mean that a different structure was formed when Co and Ni were co-loaded with Mo, which cannot emerge in the case of bimetallic CoMo and NiMo catalysts.

The tendency in adsorption parameters was fairly coincident with activities (Table 3), trimetallic CoNiMo samples exhibited lower activities for thiophene HDS and benzene hydrogenation than their bimetallic counterparts. It implies that the number of sulfur-vacancies, i.e. active sites, was lower on CoNiMo catalysts than on CoMo or NiMo catalyst. The configuration of active site of supported Co(Ni)–Mo–S phase is well-known [3]. Thus, in CoNiMo samples, some Co and Ni ions could form a mixed sulfide phase on alumina surface, which would result in a decrease in the amount of active sites.

Besides, the coverage fraction f of H_2S on metal sulfides decreases with Ni content (Table 3); it indicates that the morphology of promoted MoS_2 particles differs between Co- and Ni-containing solids. This deserves to be considered, since activity is generally affected by the size and stacking of MoS_2 slabs [3].

Table 3
Sulfur contents, structural parameters, and catalytic rates

Catalyst	S_{chem}[a] (g/g sulfide)	S_{ads}[a] (g/g sulfide)	S_{ads}/Mo (at.%/at.%)	*n*[b] (atom)	*d*[b] (nm)	R_{Thio}[c] (mol/h g)	R_{Be}[c] (10^{-1} mol/h kg)
Mo	0.0631	0.06310.0	0.240	8.7	4.84	–	–
HR306	0.0727	0.0150	0.468	5.2	2.62	61.6	62
CoMo	0.0742	0.0131	0.412	6.0	3.13	64.8	69
CoNiMo-25	0.0738	0.0125	0.395	6.2	3.28	40.3	44
CoNiMo-50	0.0736	0.0108	0.342	7.2	3.92	36.9	39
CoNiMo-75	0.0737	0.0114	0.360	6.8	3.68	44.2	41
HR346	0.0739	0.0113	0.353	7.0	3.76	92.7	76

[a] Sulfur content from chemical analysis adjusted to DS = 100; S adsorbed on metal sulfides at saturation = $f \times m_\infty$.

[b] *n*: number of Mo atoms on a slab edge; *d*: diameter of MoS_2 slab. $d = 2 \times 0.315 \times (n - 1)$.

[c] Thiophene HDS measured at 400 °C and 0.1 MPa; benzene hydrogenation, 300 °C and 8 MPa H_2 [8].

3.3. Distribution of metal sulfides and sulfur vacancies

From chemical analyses, the degree of sulfiding DS (as MoS_2, Co_9S_8 or Ni_9S_8) ranged between 99 and 105, suggesting that all catalysts were fully sulfided in the experiments. However, the amount of free edge sites is important in all cases. The S_{ads}/Mo ratios, shown in Table 3, measure the relative amounts of sulfur vacancies in sulfided catalysts. Results show that promoted catalysts have 1.5–2.0 times more sulfur vacancies than Mo/Al_2O_3 under high pressure and temperature conditions relevant to catalysis. Since it is known that H_2S adsorbs competitively with the organic reactant on the active site, we can infer that the amount of H_2S sorbed on metal sulfide allows to estimate the maximum amount of active sites.

Using adsorption parameters, information about the structure of the supported MoS_2 particles at 300 °C could be attained (Table 3). Firstly, we assume that all vacancies, located on the edges of hexagonal-shaped MoS_2 slabs, were filled by sulfur atoms at the monolayer. Thus, the total amount of structural sulfur in metal sulfide could be easily calculated as the sum of adsorbed sulfur S_{ads} and chemical sulfur $S_{chem.}$ (Table 3). Secondly, assuming that one sulfur atom is bounded to Co or Ni atoms at saturation, the structural S/Mo ratio could be estimated for each catalyst. Values were found to equal 2.25 for Mo/Al_2O_3 and 2.30–2.44 for Co–Ni–Mo samples. This gives an average slab diameter ranging from 2.6 to 3.9 nm (Table 3), in line with TEM measurements [3].

In fact, the sizes of MoS_2 slab are not so different for all catalysts. It means that Co or Ni promoters have little effect on the diameter of MoS_2 particles. Nothing, however, could be said at this stage about their influence on stacking. Furthermore, we could deduce that about 60% of the total edge sites in all Co–Ni–Mo samples are free to adsorb H_2S, compared to 53% in the case of the Mo sample. This demonstrates that active sites are easily accessible to reactants.

4. Conclusion

Several Co–Ni–Mo catalysts have been sulfided at 400 °C and 4 MPa using a novel system with a reactor coupled to an analytical balance. Similar sulfidation profiles were found for all catalysts; this suggests that the sulfidation mechanism was not affected by the presence of Co or Ni promoter. Adsorption isotherms of H_2S on the sulfided catalysts have been determined at 300 °C under flow and pressure conditions. Modeling indicates that H_2S adsorbs dissociatively on both metal sulfides and bare alumina. The amount of sorbed H_2S on sulfided particles was evaluated, and consequently the amount of sulfur vacancy under conditions relevant to catalysis. It was found that 60% of the edge molybdenum sites are free of sulfur, and that the presence of Co or Ni promoter has little effect on MoS_2 particle size.

Differences in adsorption properties were revealed for trimetallic $CoNiMo/Al_2O_3$. Rates for thiophene HDS and benzene hydrogenation were lower with the catalyst with an equal amount of Co and Ni. This can be explained by the presence of a mixed Co and Ni sulfide, as it was previously proposed [8].

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