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Journal of Catalysis 215 (2003) 353–357

JOURNAL OF CATALYSIS

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Research Note

On the sulfur tolerance of supported Ni(Co)Mo sulfide hydrotreating catalysts

E.J.M. Hensen,* V.H.J. de Beer, J.A.R. van Veen, and R.A. van Santen

Schuit Institute of Catalysis, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

Received 19 June 2002; revised 17 October 2002; accepted 3 December 2002

Abstract

This research note describes the sulfur tolerance in hydrodesulfurization for a set of CoMo and NiMo catalysts on various supports. The activity decrease with increasing H_2S concentration is diminished by supports with enhanced Brønsted acidity. The sulfur tolerance for NiMo catalysts increases in the order activated carbon < alumina < titania < amorphous silica-alumina. A direct interaction between Brønsted acid sites and the active sites is proposed. Complexing agents decrease the sulfur tolerance for a given support due to stacking of MoS_2 slabs. Clearly, CoMo catalysts are less prone to sulfur poisoning than NiMo catalysts. NiMo is the preferred metal combination for desulfurization under sulfur-lean conditions.

Keywords: Hydrodesulfurization; CoMo; NiMo; Thiophene; Sulfur tolerance; Support; Brønsted acidity

1. Introduction

Supported metal sulfide catalysts constitute the most important class of refinery catalysts for the production of clean motor fuels. Ever-tightening fuel specifications necessitate the conversion of the most refractory sulfur components. The pivotal property of these Co(Ni)Mo sulfide catalysts is their ability to convert organosulfur compounds to clean hydrocarbons in the abundant presence of fouling molecules such as H_2S and NH_3 [1]. Hydrogen sulfide generally decreases reaction rates due to competitive adsorption with sulfur-containing molecules. However, the behavior is more complex as dissociative adsorption may alter the nature of the active sites. For instance, Leglise et al. [2] pointed out that sulfhydryl species play a positive role in the catalytic mechanism of thiophene conversion at very low hydrogen sulfide partial pressures. High conversion levels imply high hydrogen sulfide partial pressures necessitating sulfur-tolerant catalysts. Generally, CoMo catalysts are preferred when a high hydrodesulfurization (HDS) duty is required whereas NiMo-based materials are used when nitrogen removal is the major goal.

Most research is focused on alumina-supported catalysts, since alumina is the preferred support for hydrotreating applications [1]. The use of other supports can be instructive, because new insights into the influence of the metal–support interaction on the functioning of the active phase can be acquired. Carbon has been widely studied [3–7] as a potential commercial support material, since it allows easy metal recovery. A major drawback is its low density. From a fundamental point of view, the absence of strong metal–support interactions in carbon–supported catalysts, resulting in the formation of type II Me–Mo–S phases (Me = Co, Ni) [8–10], is interesting. On the contrary, titania-based catalysts exhibit a strong Mo–support interaction [11]. Interestingly, titania-supported Mo sulfide, which exhibits a high HDS activity, is difficult to promote by Co or Ni [12,13]. Amorphous silica-aluminas (ASA) are of interest due to their improved HDN activities [14], although HDS activities are generally low [12,14]. This last observation is mostly explained by a low MoS_2 dispersion [11,12].

The effect of the support on the sulfur tolerance of CoMo, NiMo, and Mo catalysts was noted by several authors [15–20]. For instance, Farag et al. [15] recently compared DBT and 4,6-DMDBT activities for CoMo supported on carbon and alumina and found a much higher H_2S tolerance in the latter case. A beneficial effect of ASA compared to conventional alumina on the sulfur tolerance was also

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* Corresponding author.
E-mail address: e.j.m.hensen@tue.nl (E.J.M. Hensen).

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doi:10.1016/S0021-9517(03)00012-5

noted by Robinson et al. [17]. Borque et al. [19] stressed that the ranking of hydrotreating catalysts is influenced by the type of feedstock and reaction conditions including the hydrogen sulfide partial pressure. Finally, Kasahara et al. [20] observed that the use of Co and Ni as promoters to alumina-supported Mo catalysts resulted in less inhibition by H_2S than in unpromoted ones. However, CoMo catalysts showed a much better sulfur tolerance than NiMo catalysts in the HDS of (di)benzothiophene. Despite these reports, no systematic effort to study the support effect on the sulfur tolerance for one particular model reaction under one particular set of reaction conditions has been made. In this contribution we describe such inhibition effects in atmospheric thiophene HDS for a set of NiMo and CoMo catalysts supported on activated carbon, alumina, amorphous silica-alumina, and titania.

2. Experimental

A suite of NiMo sulfide catalysts was prepared on the support materials activated carbon (Norit RX-3 extra, p.v. 1 ml/g, s.a. 1190 m^2/g), alumina (Ketjen CK-300, p.v. 0.66 ml/g, s.a. 263 m^2/g), amorphous-silica-alumina (Shell, p.v. 0.67 ml/g, s.a. 455 m^2/g, 45 wt% silica), and titania (Degussa P-25, p.v. 0.32 ml/g, s.a. 50 m^2/g, anatase:rutile = 75:25). Carbon- and alumina-supported CoMo catalysts were included for comparison. Prior to use, the support materials were calcined at 573 K for 2 h with the exception of the activated carbon which was dried at 383 K overnight. All catalysts were prepared by coimpregnation of ammoniacal solutions of ammoniumheptamolybdate (Merck, > 97%) and nickel (cobalt) nitrate (Merck, p.a.). If indicated, the impregnation solution contained the complexing agent nitrilotriacetic acid (NTA) according to the procedure by Van Veen et al. [8]. The catalysts were dried in air at 383 K for 16 h and with exception of those prepared with NTA calcined in static air at 723 K for 2 h. Catalysts are denoted as follows: MeMo(-NTA)/S with Me the promoter ion, (NTA) indicating the use of NTA, and S the support material (C for activated carbon, Al for alumina, Ti for titania, and ASA for amorphous silica-alumina).

Atmospheric gas-phase thiophene hydrodesulfurization experiments were carried out in a single-pass quartz microflow reactor with an internal diameter of 4 mm. Gasified thiophene was obtained by passing hydrogen through the liquid in a saturator (293 K). The required thiophene concentration was obtained by diluting this flow with pure hydrogen and a H_2S/H_2 mixture. All flows were regulated by thermal mass flow controllers. The reactor bed consisted of an amount of catalyst (sieve fraction: 125–250 μm) with inert carbon of the same sieve fraction. The reactor was operated in differential mode. Reaction products are analyzed by gas chromatography (CP-Sil 5 CB column).

Prior to reaction, catalysts were sulfided in situ in a H_2S/H_2 mixture (10 vol% H_2S). The gas flow was kept at 60 ml/min (standard temperature and pressure) while heating at a rate of 6 K/min to 673 K (in the case of NTA: 2 K/min). The temperature was kept at this temperature for 2 h. Subsequently, the catalyst was exposed to a mixture of 3.33 kPa thiophene and 1 kPa H_2S in hydrogen at a total flow rate of 100 ml/min (standard temperature and pressure) at 673 K. After a stabilization period of 13 h, kinetic measurements were started at 623 K.

3. Results and discussion

The composition of the various catalysts, information on their morphology, and their thiophene HDS activities are collected in Table 1. Activities are steady-state reaction rates expressed per mol Mo. Clearly, carbon is the preferred support in both NiMo and CoMo. The activity differences between CoMo–NTA/C on the one and CoMo–NTA/Al and CoMo/Al on the other hand cohere well with differences observed by Van Veen et al. [8] and Hensen et al. [21]. The activity trends for the NiMo analogues are similar and in agreement with results of Van Veen et al. [9]. The use of NTA results in fully sulfided type II Me–Mo–S phases for alumina-supported catalysts with higher activities than found for catalysts prepared by conventional coimpregnation, which mainly leads to type I Me–Mo–S phase with residual Mo–O–Al linkages at reasonable Mo loadings [8]. The alumina-supported NiMo–NTA catalyst has a somewhat higher stacking degree than $NiMo/Al_2O_3$ in accordance with more complete sulfidation. The values for the average slab length of both catalysts are close. In contrast to alumina-supported catalysts, there is hardly any NTA effect on the activities of titania- and ASA-supported NiMo sulfide. Here, we find that titania-supported catalysts are somewhat more active than NiMo–NTA/Al. This difference stems from the somewhat higher Ni/Mo ratio for the titania-based catalysts. Strikingly, there is only a small NTA effect for the titania-supported catalysts as already described by Vissenberg et al. [13]. Further investigations [13,22] showed that this effect is only apparent. While the active phase in NiMo/Ti is strongly anchored to the support [12,22,23], NiMo–NTA/Ti has a higher initial activity which strongly decreases due to sintering in the initial stages of the reaction. This is most probably induced by sulfidation of the TiO_2 surface. Vissenberg et al. [13] reported difficulties in determining slab lengths and stacking degrees for titania-supported catalysts, although it is clear that the morphologies do not differ to a large extent from alumina-supported catalysts. There is also no clear NTA effect for the ASA-supported NiMo catalysts. Our TEM investigation indicated pronounced stacking for both ASA-supported catalysts and a higher averaged slab length compared to alumina-supported ones in line with recent results for ASA-supported MoS_2 [24]. A recent Mo adsorption study [25] showed that molybdate anions preferentially adsorb on alumina patches of the ASA surface. Since alumina makes up a rather small part of the total ASA surface area,

Table 1
Metal loading[a] of catalysts, averaged slab length (L), stacking degree (s), thiophene HDS reaction rate, and sulfur tolerance (ρ) of the various catalysts

Catalyst	Mo (wt%)	Me (wt%)	Me/Mo	L (nm)[b]	s[b]	Reaction rate[c]	ρ[d]
NiMo–NTA/C	6.2	1.2	0.31	1–2[e]	1.2[e]	28.6	0.34
NiMo/Al	9.6	1.4	0.25	2.8	1.7	10.4	0.39
NiMo–NTA/Al	6.2	1.1	0.28	2.9	1.9	15.6	0.36
NiMo/Ti	3.9	0.9	0.38	–[e]	–[e]	20.4	0.45
NiMo–NTA/Ti	3.9	0.9	0.36	–[e]	–[e]	18.4	0.41
NiMo/ASA	8.0	1.5	0.30	n.d.	2.4	15.0	0.48
NiMo–NTA/ASA	8.0	1.5	0.30	n.d.	2.6	15.6	0.48
CoMo–NTA/C	6.0	1.1	0.30	1–2[e]	1.2[e]	41.0	0.65
CoMo/Al	10.9	2.0	0.30	3.1	1.3	12.8	0.75
CoMo–NTA/Al	6.7	1.1	0.26	n.d.	n.d.	22.4	0.71

n.d., not determined.

[a] Checked by atomic absorption spectroscopy.

[b] Average slab lengths and stacking degree partly taken from Refs. [13,34].

[c] Reaction rate in mol thiophene/mol Mo h (conditions: $T = 623$ K, partial pressures: 3.33 kPa thiophene and 1 kPa hydrogen sulfide, total flow rate 100 ml/min).

[d] Sulfur tolerance defined as the ratio of the reaction rates corresponding to 2.0 kPa H_2S and 0.1 kPa H_2S. The accuracy in the sulfur tolerance is better than 0.01.

[e] Quantitative analysis of the slab length of carbon-supported [24] and of slab length/stacking of titania-supported MoS_2 particles [13] proved to be very difficult. From a more detailed analysis [24] an averaged slab length in carbon-supported MoS_2 of 1–2 nm with a stacking degree between 1 and 1.4 was derived.

the catalysts are composed of type II MoS_2 even without the use of NTA.

The influence of hydrogen sulfide on the reaction rate was determined by varying the H_2S partial pressure (0.1–2.0 kPa) at the reactor inlet. The reactions were carried out under differential conditions implying a constant H_2S partial pressure along the reactor axis. Fig. 1 shows the influence of the hydrogen sulfide partial pressure on the HDS activity of NiMo sulfide catalysts. The sulfur tolerance (ρ) is defined as the ratio of the reaction rates at 2.0 and 0.1 kPa H_2S. The values of this parameter for the various catalysts are listed in Table 1. Although the differences in ρ are subtle there is a clear dependence on the choice of the support and the addition of NTA in the catalyst preparation. Here we stress that the accuracy in the sulfur tolerance is better than 0.01. Carbon-supported catalysts are most prone to H_2S poisoning, while catalysts supported on the refractory oxides retain much more of their activity under H_2S-rich conditions. The sulfur resistance appears to be a function of the support acidity, that increases in the order: C < Al_2O_3 < TiO_2 < ASA. Moreover, it is observed that the application of NTA reduces ρ. NiMo–NTA/Ti shows a lower ρ than NiMo/Ti in accordance with the difference between NiMo–NTA/Al and NiMo/Al. This latter finding gives substance to the thought of different Ni–Mo–S phases being present in NiMo–NTA/Ti and NiMo/Ti. On the contrary, the absence of such an effect for ASA agrees well with the occurrence of a type II Ni–Mo–S phase, irrespective of the use of NTA. The main conclusion is that support materials with a high Brønsted acidity and a strong metal-support interaction result in catalysts less prone to H_2S poisoning in thiophene HDS. A comparison with the work of Robinson et al. [17] indicates that this is also valid for gas-phase HDS of (substituted) DBT. An explanation of these intriguing results is not straightforward. First, the interaction of the support with the MoS_2 phase may indirectly influence the electronic state of the promoter ions, thus affecting their activity. In alumina-supported catalysts, the MoS_2 phase is strongly bound to the subjacent support by Mo–O–Al linkages, whereas it is proposed that only a weak Van der Waals interaction with the support remains when NTA is used [8,9,21]. This does not tally with the observation that there remains a significant support effect on ρ for the NTA-prepared catalysts. On the other hand, the very fact that there is a support effect observed for these NTA catalysts may indicate that there is a more direct physical interaction between the active sites and some groups of the adjacent support. An appealing picture is the interaction of the support acidic groups with sulfur atoms nearby the active sites influencing their electronic state. A higher Brønsted acidity of such groups then results in a high sulfur tolerance. Generally, MoS_2-based catalysts have a low stacking degree

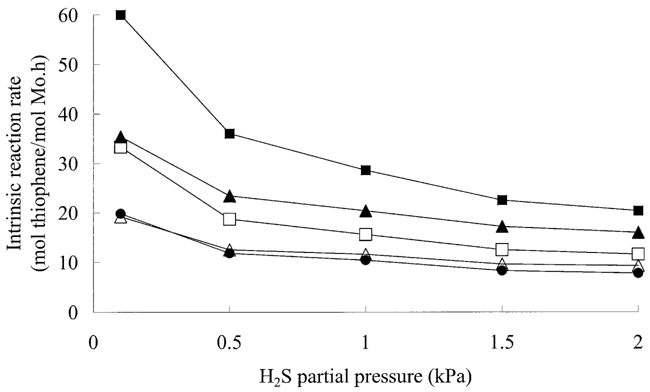

Fig. 1. Reaction rate vs hydrogen sulfide partial pressure ($T = 623$ K, thiophene partial pressure: 3.33 kPa): (■) NiMo–NTA/C; (□) NiMo–NTA/Al; (▲) NiMo/Ti; (●) NiMo/Al, and (△) NiMo/ASA.

in the case of alumina [24,26,27], titania [13], and even carbon [24] due to its high surface area. Most of the edge sites are thus in close proximity to the support. The effect of NTA is to increase stacking to some degree resulting in active sites that do not interact with support acidity groups. These have a lower sulfur tolerance in line with the observation for the carbon-supported catalysts and thus result in a lower average ρ. An alternative effect of the use of NTA as chelating ligand could be inhibition of Brønsted acid sites by adsorption of nitrogen-containing components deriving from the decomposition of NTA. However, detailed XPS studies on hydrotreating model catalysts containing chelating agents [28] indicated that no nitrogen species are left after standard sulfidation. This is further underpinned by the absence of an NTA effect in the ASA-supported catalysts. In this case, stacking is significant irrespective the use of NTA [24]. We envisage that the strength of the OH groups of the ASA support, which interact with the MoS_2 edge sites, increases the overall sulfur tolerance to such a degree that the effect of a decreased number of active sites interacting with such surface groups is less important.

The positive effect of H_2S in the hydrogen–deuterium exchange rate between deuterium species adsorbed on the metal sulfide and hydrogen atoms of the support was also explained by such a direct interaction [29], although this interpretation is not conclusive [30]. Alternatively, support acidic groups may serve as anchoring centers for thiophene which would result in an increased local reactant concentration and enhanced activity. Although Brønsted acid sites of zeolite strength are necessary for thiophene cracking [31], Brønsted sites of lower strength may also lead to thiophene adsorption [32].

Fig. 2 displays the difference in sulfur tolerance between CoMo and NiMo catalysts. The decrease in HDS activity with increasing H_2S partial pressure is more pronounced for NiMo catalysts than for CoMo catalysts. This is also reflected in the values for the sulfur tolerance which are much higher for the CoMo catalysts. While at H_2S partial pressure above 0.5 kPa, the CoMo combination is the preferred catalyst, the situation is totally different under sulfur-lean conditions. Interestingly, this means that the Ni-promoted catalyst outperforms the Co-promoted one, the latter one being traditionally used in industry when a large HDS duty is required. A similar behavior was reported for benzothiophene and DBT HDS by Kasahara et al. [20] and for (substituted) DBT by Robinson et al. [17]. In industrial practice, this different response on hydrogen sulfide can be made use of, especially in two-stage operations where in the second bed a lower H_2S partial pressure is allowed by countercurrent flow [33].

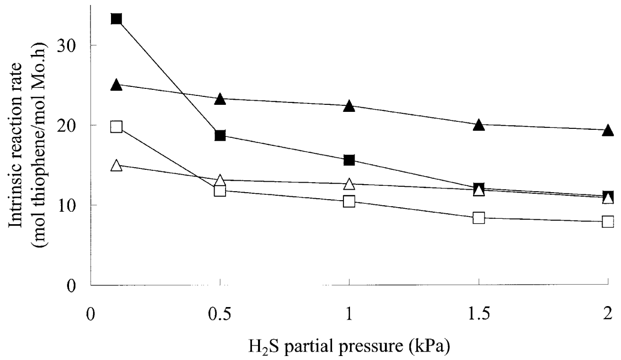

Fig. 2. Reaction rate vs hydrogen sulfide partial pressure ($T = 623$ K, thiophene partial pressure: 3.33 kPa): (■) NiMo–NTA/Al; (□) NiMo/Al; (▲) CoMo–NTA/Al; (△) CoMo/Al.

4. Conclusions

The sulfur tolerance of CoMo and NiMo sulfide catalysts strongly depends on the applied support material. The decrease in HDS activity with increasing hydrogen sulfide partial pressure is less pronounced for supports with enhanced Brønsted acidity. The sulfur tolerance for NiMo catalysts increases in the order activated carbon < alumina < titania < amorphous silica-alumina. A direct interaction between Brønsted acid sites and the active sites is proposed. The use of NTA decreases the sulfur tolerance for a given support due to stacking of the MoS_2 slabs. This results in a lower number of MoS_2 edge sites in direct interaction with Brønsted sites due to the separation of the support and active sites in slabs other than the one attached to the support.

A fundamental difference in sulfur tolerance between CoMo and NiMo catalysts is noted, the latter one having a lower sulfur tolerance making it the preferred catalyst under sulfur-lean conditions.

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