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Influence of zeolite acidity on thiophene hydrodesulfurization activity

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Abstract

For H(x)NaY supported metal sulfide catalysts the intrinsic catalytic activity [thiophene hydrodesulfurization (HDS)] and the metal sulfide dispersion (dynamic oxygen chemisorption) are measured as a function of the acidity of the zeolite support (determined by ethylamine temperature-programmed desorption). The results show that the acidity can have a strong influence on both the conversion and the product selectivities. An increasing acidity results in an increase of the initial thiophene HDS activity. The increased activity is not caused by an increase in the metal sulfide dispersion, but, probably by a synergetic effect between the metal sulfide particles and the acidic zeolite support. The increase in initial thiophene HDS activity with increasing support acidity is also observed for cobalt, nickel and molybdenum sulfide catalysts prepared by impregnation using various zeolite supports (ZSM-5, Y, HUSY). The higher activity may be caused by an increase in thiophene adsorption in the zeolite pores, or by a direct effect of H^+ on the thiophene HDS reaction. Additionally, the acidic supports themselves also show a considerable initial HDS activity, indicating that the acid sites are able to desulfurize thiophene at reaction conditions.

Keywords: Acidity; Adsorption; Hydrodesulfurization; Metal sulfides; Oxygen chemisorption; Thiophene; Zeolites

1. Introduction

Hydrocracking is one of the major catalytic processes to convert residual feedstocks into distillate products. Modern hydrocracking catalysts often consist of a combination of a sulfidic Ni–Mo or Ni–W phase and an acidic zeolite [1,2]. Therefore zeolite-supported metal sulfide catalysts have been the subject of increasing research in recent years [3–15]. Fierro and co-workers [3–7] used several methods to prepare zeolite-supported transition metal sulfide catalysts. Catalysts

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prepared via impregnation with ammonium heptamolybdate (AHM) on Y zeolites showed loss of crystallinity and catalytic activity for the hydrodesulfurization (HDS) of thiophene with increasing calcination temperature. Addition of cobalt (via ion exchange or impregnation) to zeolite-supported molybdenum catalysts resulted in a higher stability of the zeolite structure. For these Co–Mo catalysts a small synergetic effect was observed [3]. Ion-exchanged NiNaY catalysts showed an increase in thiophene HDS and cracking activity with increasing nickel loading [5]. Kovacheva et al. [8] investigated zeolite Y supported cobalt, nickel and molybdenum sulfide catalysts. They found that efficient thiophene HDS catalysts could not only be obtained by adding a combination of sulfides (e.g. cobalt and molybdenum sulfide) to the zeolite support, but also via addition of a single sulfide (e.g. cobalt or nickel sulfide). Laniecki and Zmierzak [9,10] prepared catalysts via gas-phase deposition of $\text{Mo}(\text{CO})_6$ on Y type zeolites. These catalysts appeared to be more active for thiophene HDS than those prepared via impregnation with AHM. Protonated supports, due to the presence of strong Brønsted acid sites, cause fast deactivation and coking of the catalysts during the hydrodesulfurization of thiophene.

In the above studies several zeolite-supported metal sulfide catalysts (various preparation methods, metal sulfides and zeolite supports) are characterized and tested on their catalytic properties. For the latter usually the thiophene HDS reaction is used. Often Brønsted acid sites are present on the zeolite supports. On these acid sites high amounts of coke can be formed, resulting in a strong deactivation due to shielding of the metal sulfide phase by coke. Especially if the catalytic activities are compared at longer run time (steady-state activity), it is concluded that Brønsted acidity has a negative effect on the thiophene HDS activity [3,9]. Also on silica–alumina supports the presence of acid sites was found to have a negative influence on the thiophene HDS activity [16]. This negative influence is mainly caused by the coke formation. If we want to compare the intrinsic catalytic properties of the metal sulfide phase, activities measured at very short run time should be used, at which moment the influence of coke formation is still very small. Thus, in earlier work [14,15] it was concluded, based on measurements of the initial thiophene HDS activity (after 2 min run time), that a higher acidity of the support might just as well improve the HDS activity of zeolite Y supported nickel sulfide catalysts.

In the present study the question whether or not the acid sites can improve the HDS activity is examined further. Therefore, for HNaY-supported nickel sulfide catalysts the intrinsic catalytic activity and the nickel sulfide dispersion [characterized by dynamic oxygen chemisorption (DOC)] are measured as a function of the acidity of the zeolite support [determined by ethylamine temperature-programmed desorption (TPD)]. Additionally, cobalt, nickel and molybdenum sulfide catalysts prepared by impregnation using various zeolite supports with different acidities are tested on their thiophene HDS activity.

2. Experimental

2.1. Catalyst preparation

A CaY zeolite ($\text{Ca}_{25}\text{Na}_4(\text{AlO}_2)_{54}(\text{SiO}_2)_{138}$) was prepared from NaY (PQ, CBV-100, $\text{Na}_{54}(\text{AlO}_2)_{54}(\text{SiO}_2)_{138}$) by repeated ion exchange with CaCl_2 aqueous solutions.

$\text{NH}_4(x)\text{NaY}$ zeolites (x is the percentage of Na exchanged by NH_4^+) were prepared via ion exchange of the NaY zeolite with aqueous solutions of NH_4NO_3 of appropriate concentration. A Na-ZSM-5 zeolite was prepared from a H-ZSM-5 zeolite (Exxon Chemical AT281-C, $\text{Si}/\text{Al} = 40$) by repeated ion exchange with NaCl aqueous solutions. The metal contents of these zeolites after ion exchange were determined using atomic adsorption spectroscopy (AAS).

Nickel, cobalt and molybdenum catalysts supported on NaY, CaY, Na-ZSM-5, H-ZSM-5 and also stabilized Y (HUSY, Katalistics, $\text{Si}/\text{Al} = 5.6$) were prepared by pore volume impregnation with aqueous solutions of NiCl_2 , CoCl_2 and AHM, respectively. All catalysts contained 0.75 mmol metal per gram of catalyst (4.0, 4.0 and 6.5 wt.-% of nickel, cobalt and molybdenum, respectively), calculated on the basis of the water-free zeolite. A series of $\text{Ni}/\text{H}(x)\text{NaY}$ catalysts ($\text{Ni}/\text{H}(0)\text{NaY}$ is the same catalyst as Ni/NaY) was prepared by impregnation of the $\text{NH}_4(x)\text{NaY}$ supports with a NiCl_2 solution of appropriate concentration. After impregnation, the samples were dried in air overnight at 383 K, and subsequently calcined at 673 K for 2 h. During this treatment the $\text{NH}_4(x)\text{NaY}$ zeolites were converted into $\text{H}(x)\text{NaY}$. All the $\text{Ni}/\text{H}(x)\text{NaY}$ catalysts contained 4 wt.-% nickel (calculated on the basis of the water-free zeolite).

A series of $\text{Mo}/\text{H}(x)\text{NaY}$ catalysts was prepared by gas-phase adsorption of $\text{Mo}(\text{CO})_6$ on the zeolite supports. Prior to the adsorption the $\text{NH}_4(x)\text{NaY}$ zeolite was activated for 2 h at 673 K in a helium flow, during which the zeolite was converted to $\text{H}(x)\text{NaY}$. After cooling to 333 K the zeolites were saturated with molybdenum hexacarbonyl vapour passing through the support in a helium stream. This procedure provided full saturation of the zeolite with $\text{Mo}(\text{CO})_6$, leading to a concentration of about 2 $\text{Mo}(\text{CO})_6$ per supercage (about 11 wt.-% Mo). After saturation the samples were cooled to room temperature, and subsequently exposed to air. All samples were stored in a desiccator over a saturated CaCl_2 solution.

2.2. Catalytic activity

Thiophene HDS activity measurements were carried out in a micro flow reactor under standard conditions (673 K, 1 bar pressure, 4.0 vol.-% thiophene in hydrogen, 50 std $\text{cm}^3 \text{min}^{-1}$). Catalyst samples of 0.25 g (particle size 0.125–0.425 mm) were sulfided in situ using a gas mixture of 10% H_2S in hydrogen (60 std $\text{cm}^3 \text{min}^{-1}$, 6 K min^{-1} from 293 to 673 K, 2 h at 673 K). After sulfidation the flow was switched to the thiophene/ H_2 flow. Reaction products were analyzed by on

line gas chromatography (GC) analysis (HP 5890, Chrompack CP Sil 5 CB Capillary Column). The first sample was taken after 2 min reaction time and the following ones at intervals of 35 min.

Due to the presence of acid sites considerable polymerization (of unsaturated products) and cracking (of butenes and polymerized products) took place resulting in a large variety of products and coke formation. Therefore, thiophene converted to any of the reaction products including coke was taken into account for the determination of the conversion (calculated from the amount of unconverted thiophene) and the reaction rate constant (k_{HDS}) assuming the reaction to be first order in thiophene [17].

Coke formation which often causes strong deactivation due to shielding of the metal sulfide phase can severely hamper the evaluation of the intrinsic catalytic properties. Therefore, the catalysts were mainly compared on the basis of their activity at very short run time (2 min). This initial thiophene HDS activity was assumed to be representative for the intrinsic catalytic properties of the catalysts. Due to the sometimes very strong deactivation at short run times, the reproducibility of the initial thiophene HDS activity was less than for steady state activities, but still quite sufficient to compare the intrinsic activities of catalysts with each other (the initial HDS activity was reproducible within 10%).

2.3. *Dynamic oxygen chemisorption*

DOC measurements [18–21] were used to determine the relative nickel sulfide dispersions for a series of Ni/H(*x*)NaY catalysts. For this purpose catalysts were sulfided in situ following the same procedure as for the activity measurements. After sulfidation, the catalysts were flushed for one hour at 673 K in helium (oxygen and water-free to levels lower than 1 ppm), and then cooled to 333 K, at which temperature the oxygen chemisorption was performed. At this temperature the support did not adsorb oxygen. According to Bachelier et al. [18–20], side reactions (SO₂ and COS formation) are avoided, and the oxygen is chemisorbed irreversibly on the sulfide catalyst. Pulses of 5% oxygen in helium were injected in the helium carrier gas flow and passed over the catalyst and a thermal conductivity detector. When effluent peaks had increased to constant size (less than 1% difference between successive peaks) the total oxygen uptake was calculated.

2.4. *Temperature-programmed desorption of ethylamine*

The number of acid sites present after sulfidation was determined by ethylamine TPD [22,23]. Ethylamine was adsorbed on the in situ dried sample (673 K in helium flow) until full saturation. After adsorption, first an isothermal desorption of ethylamine was carried out at 323 K, and then the TPD procedure was started. During TPD the weight loss was measured by thermogravimetric analysis (TGA) using a Seteram TG 85-16-18 balance, while the desorbed products were identified

by mass spectrometry. The physisorbed ethylamine will desorb in the temperature range between 323 and 600 K, while the ethylamine adsorbed on Brønsted acid sites only desorbs after decomposition to ammonia and ethene between 650 K and 750 K [22,23]. The amount of ethylamine adsorbed on Brønsted acid sites can be calculated from the weight loss at high temperature. This amount is a good indication for the number of Brønsted acid sites.

3. Results and discussion

For sulfided Me/H(x)NaY catalysts the influence of the acidity on the thiophene HDS activity can be examined by varying the degree of Na⁺ exchange. A higher degree of exchange of Na⁺ against H⁺ results in a higher acidity of the zeolite support. In Fig. 1 the influence of the increasing acidity on the initial thiophene HDS activity (after 2 min run time) is given for sulfided Ni/H(x)NaY (prepared by impregnation) and Mo/H(x)NaY (prepared by gas-phase adsorption of Mo(CO)₆) catalysts. Also the initial activity of the sulfided pure H(x)NaY supports is given. These acidic zeolites show a substantial HDS activity without the presence of a metal sulfide phase. For all three series of catalysts the HDS activity increases linearly with increasing acidity. But for the nickel and molybdenum sulfide catalysts the increase is much stronger than for the zeolite support itself.

The number of acid sites on the sulfided zeolite support and Ni/H(x)NaY catalysts are measured by ethylamine TPD [22,23]. The results of these measurements are given in Table 1. The pure NaY support showed no desorption of ethylamine around 700 K, which is to be expected as NaY does not contain any acid sites. The number of acid sites increases almost linearly with increasing degree of Na⁺ exchange, and is slightly lower than the theoretical number of acid sites calculated from the degree of Na⁺ exchange. This is in line with previous results

Fig. 1. Thiophene HDS activity versus acidity of the support, expressed as the percentage of Na⁺ exchanged against H⁺. (○) H(x)NaY, (□) Ni/H(x)NaY, (●) Mo/H(x)NaY.

Table 1

Acidity of sulfided H(*x*)NaY and Ni/H(*x*)NaY zeolites measured by ethylamine TPD between 575 and 725 K

Degree of Na ⁺ exchange (%)	Ethylamine desorption (mmol/g zeolite)	
	H(<i>x</i>)NaY	Ni/H(<i>x</i>)NaY
0	0	0.3
10	0.4	0.5
22	0.8	0.7
30	1.2	1.2
46	1.8	1.7

from ethylamine desorption experiments [22,23], which are usually somewhat lower than the theoretical values.

After impregnation with NiCl₂, calcination and sulfidation the acidity of the catalysts is hardly changed, except for the Ni/H(0)NaY catalyst. On this catalyst some Brønsted acid sites are present after sulfidation. Possibly, these sites are generated by the replacement of some Na⁺ ions by Ni²⁺ via ion exchange during impregnation. Upon drying, the Na⁺ ions will form NaCl. After sulfidation, the Ni²⁺ are converted into nickel sulfide [14,15], and their position in the zeolite lattice is probably taken by protons resulting in a somewhat acidic catalyst. ²³Na-DOR NMR measurements have proven the presence of NaCl both in the calcined and the sulfided Ni/NaY catalysts [24], indicating that some ion exchange has occurred during impregnation. On the other Ni/H(*x*)NaY catalysts the preparation has no measurable influence on the zeolite acidity. Apparently, no significant amounts of NaCl are formed. The Cl[−] ions probably leave the zeolite as HCl either during calcination or during sulfidation.

Besides the HDS activity also the product selectivities are changed by the increasing acidity of the support. In Fig. 2 the initial product selectivities (at 2 min run time) of the Ni/H(*x*)NaY catalysts are plotted as a function of the degree of Na⁺ exchange of the support. The extent of polymerization and cracking increases immediately if the acidity is increased by ion exchange of Na⁺ against H⁺, resulting in a far lower amount of C₄ products. When the acidity is further increased the change in product selectivities is less pronounced. Apparently, only a few acid sites are needed to obtain a high degree of polymerization and cracking of the C₄ products.

Ni/H(0)NaY shows already a high selectivity for cracked (C₁–C₃) and polymerized (> C₄) products, in spite of the fact that on the original zeolite support no acid sites are present. The cracking and polymerization is probably caused by the acid sites formed during impregnation and sulfidation. Besides the product selectivity, these acid sites can also influence the HDS conversion (Fig. 1 clearly shows an increasing HDS activity with increasing acidity). However, the amount of acid sites on the sulfided Ni/H(0)NaY catalysts is probably too low to cause a strong HDS activity effect.

Fig. 2. Product selectivity for thiophene HDS versus the acidity of the zeolite support (expressed as the percentage of Na^+ against H^+) for sulfided $\text{Ni}/\text{H}(x)\text{NaY}$. (○) C_4 products, (□) C_1 – C_3 products, (●) products $> \text{C}_4$.

The increasing thiophene HDS activity with increasing support acidity might be due to an improvement of the nickel sulfide dispersion. Possibly, the support acidity can influence the nickel sulfide dispersion. Therefore, the relative nickel sulfide dispersions of the $\text{Ni}/\text{H}(x)\text{NaY}$ catalysts are compared by measuring the amounts of oxygen chemisorbed on the freshly sulfided catalysts [18–21]. From the results given in Table 2 it can be concluded that all sulfided $\text{Ni}/\text{H}(x)\text{NaY}$ catalysts chemisorb similar amounts of oxygen. Apparently, the dispersion of the nickel sulfide phase is hardly influenced by the acidity of the $\text{H}(x)\text{NaY}$ support. The amounts of chemisorbed oxygen found for these catalysts are comparable to that of a sulfided 4 wt.-% nickel containing Ni/CaY catalyst [14,15]. There are no significant differences in dispersion for impregnated zeolite Y supported nickel sulfide catalysts. The nickel sulfide dispersion is probably determined by the impregnation procedure, and not by the composition of the zeolite Y support.

For the $\text{Ni}/\text{H}(x)\text{NaY}$ catalysts the initial thiophene HDS activity increases with increasing acidity, while the nickel sulfide surface area remains constant. Thus, the

Table 2
Dynamic oxygen chemisorption on sulfided $\text{Ni}/\text{H}(x)\text{NaY}$ zeolites

Degree of Na^+ exchange (%)	Oxygen chemisorption ($\text{mmol O}_2/\text{kg}$)
0	25
10	22
22	24
30	28
46	25

Fig. 3. Thiophene HDS activity versus run time for different zeolite supported nickel sulfide catalysts. (□) Ni/NaY, (■) Ni/CaY, (▽) Ni/HUSY, (○) Ni/Na-ZSM-5, (●) Ni/H-ZSM-5.

activity increase is not caused by an improved nickel sulfide dispersion, but by the increased support acidity. The fact that for the Ni/H(x)NaY the activity increase with growing acidity is much stronger than for the pure H(x)NaY support, indicates that the higher activity of the acidic catalysts is not caused by the additional activities of Ni/H(0)NaY and pure H(x)NaY, but that a synergetic effect occurs between the nickel sulfide phase and the acidic support.

The effect of the acidity on the thiophene HDS activity can also be examined by varying the zeolite support. The thiophene HDS activities of nickel, cobalt and molybdenum sulfide supported on various zeolites are given in Figs. 3, 4 and 5. Clearly there are large differences in activity. The CaY-supported nickel, cobalt and molybdenum catalysts show a higher initial activity compared with their NaY-supported counterparts. However, they deactivate significantly stronger, especially in the case of molybdenum sulfide. The HUSY-supported catalysts show by far the highest initial thiophene HDS activity, but their deactivation is very strong. In spite of this strong deactivation the activity is still relatively high after 2.5 h reaction.

On the CaY support acid sites are formed by hydrolysis of water molecules on the Ca^{2+} ions at high temperatures [25,26], for instance during sulfidation at 673 K. From ethylamine TPD the number of Brønsted acid sites on sulfided Ni/CaY can be estimated to be 0.8 mmol g^{-1} [14,15]. These acid sites are probably less strong than those present on the H(x)NaY supports. Consequently, the initial activity of the Ni/H(22)NaY is significantly higher than that of Ni/CaY, in spite of the fact that the number of Brønsted sites is almost the same on both catalysts.

The number of acid sites on the HUSY support can be calculated from the framework Si/Al ratio, and amounts to 1.9 mmol g^{-1} . Compared to H(x)NaY the

Fig. 4. Thiophene HDS activity versus run time for different zeolite supported cobalt sulfide catalysts. (□) Co/NaY, (■) Co/CaY, (▽) Co/HUSY, (○) Co/Na-ZSM-5, (●) Co/H-ZSM-5.

HUSY zeolite contains somewhat stronger acid sites due to the higher Si/Al ratio of the zeolite framework (5.6 vs. 2.6) [27]. Nevertheless the Ni/H(46)NaY catalyst shows a slightly higher initial activity compared to Ni/HUSY (both catalysts have a comparable number of acid sites).

Fig. 5. Thiophene HDS activity versus run time for different zeolite supported molybdenum sulfide catalysts. (□) Mo/NaY, (■) Mo/CaY, (▽) Mo/HUSY, (○) Mo/Na-ZSM-5, (●) Mo/H-ZSM-5.

The amounts of coke deposited on Ni/NaY, Ni/CaY and Ni/HUSY after 2.5 h reaction, as determined by temperature-programmed oxidation are 7, 12 and 14 wt.-%, respectively. The coke formation is most likely due to the presence of acid sites. The amounts of coke are high on all catalysts, also on Ni/NaY. As described above, on this catalyst some acid sites are formed during impregnation and sulfidation. This small amount of acid sites is responsible for a high degree of polymerization and cracking reactions and a high amount of coke. On the Ni/CaY and Ni/HUSY catalysts higher amounts of acid sites are present. Consequently, on these catalysts coke formation is significantly stronger compared to Ni/NaY. Probably, the stronger deactivation of these catalysts is to a large extent caused by this coke formation. Also sintering of the metal sulfide phase may influence the deactivation behaviour of the catalysts [14,15], but this effect will probably be the same for all nickel sulfide catalysts, and will not cause any differences in deactivation.

The Na-ZSM-5-supported catalysts show activities which are slightly higher (Ni and Co) or comparable (Mo) with those of the NaY-supported counterparts. The smaller pore size of the ZSM-5 zeolite compared to the NaY zeolite (5.6 vs. 7.4 Å) apparently has no negative effect on the thiophene HDS activity. The higher activity of the Na-ZSM-5-supported catalysts may be the result of a somewhat higher metal sulfide dispersion or a different distribution of the metal sulfide through the pores of the zeolite [14,15], but it is also possible that different thiophene adsorption properties of the zeolite influence the HDS activity. When H-ZSM-5 is used as a support the initial activity increases significantly. Apparently, the small amount of acid sites present on the H-ZSM-5 support (0.4 mmol/g) have a considerable influence on the thiophene HDS activity. Also these catalysts show a substantial deactivation, which again may have been caused by coke formation. For ZSM-5 zeolites, studies have shown that due to steric constraints coke formation is relatively low compared to Y zeolites [28–30]. This is probably the reason why the deactivation on the H-ZSM-5-supported nickel and cobalt sulfide catalysts is relatively low compared to for instance the HUSY type catalysts. The overall picture emerging from Figs. 3, 4 and 5 is that the highest initial activities are obtained by combining the metal sulfides with acidic zeolites. This supports the conclusion, that besides a negative effect (coking), the zeolite acidity also has a significant positive effect on the thiophene HDS activity.

Although the activity trends described above are generally the same for all three metal sulfide catalysts, there are also some small differences in catalytic behaviour between the different metal sulfide catalysts. The activities of the nickel and cobalt catalysts are similar except when NaY and Na-ZSM-5 are used as support in which case the cobalt catalysts are slightly but significantly more active than the nickel catalysts. The molybdenum catalysts show somewhat lower activities than the nickel and cobalt catalysts, especially the acidic ones. The deactivation of the CaY and H-ZSM-5-supported molybdenum catalysts is relatively strong compared to that of the corresponding cobalt and nickel sulfide catalysts.

Table 3

Initial (at 2 min run time) product selectivities for zeolite supported nickel sulfide catalysts (4 wt.-% Ni)

Catalyst	Product selectivities (%)							
	C ₁ /C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	>C ₈
Ni/NaY	2.2	8.2	75.9	0.7	3.8	3.5	4.7	1.0
Ni/CaY	4.7	18.4	49.7	3.6	2.8	9.6	10.4	0.8
Ni/HUSY	22.5	19.2	38.9	8.2	3.0	3.2	4.3	0.7
Ni/Na-ZSM-5	8.0	17.7	50.6	0.4	3.0	11.6	8.4	0.3
Ni/H-ZSM-5	12.7	28.3	16.0	2.5	5.6	18.8	15.5	0.5

The fact that the activity differences between the three metal sulfides (compared per zeolite) are not very large is in contrast with Al₂O₃-supported catalysts, viz. sulfided Co/Al₂O₃ or Ni/Al₂O₃ are far less active than sulfided Mo/Al₂O₃ [31,32]. As in the case of carbon-supported catalysts [33,34], the sulfided zeolite-supported cobalt and nickel catalysts show a considerable thiophene HDS activity. The interaction between cobalt or nickel and the zeolite support is not as strong as on the Al₂O₃ support, in which case sulfidation of cobalt or nickel is partly prevented [31,32], causing clearly lower activities for these metal sulfides compared to carbon or SiO₂. The zeolite support behaves more like these inert supports. Therefore we assume that the interaction between the zeolite support and the metal sulfide has no influence on the HDS activity nor on the degree of sulfidation of the metal sulfide.

The relative activities of the zeolite-supported cobalt, nickel and molybdenum catalysts are somewhat different from those measured for carbon or unsupported catalysts. The almost equal activities of cobalt and nickel sulfide and the lower activity of molybdenum sulfide for the zeolite-supported catalysts is in contrast with the relatively high activity of Co/C compared to Ni/C or Mo/C [33], while for unsupported catalysts molybdenum sulfide is usually slightly more active than cobalt or nickel sulfide [35,36]. The differences in relative activities are probably caused by differences in dispersion of the metal sulfide phase. For instance, the relatively low activity of the zeolite-supported molybdenum sulfide catalysts may be due to a somewhat lower dispersion of the molybdenum sulfide [14,37]. Also the location of the metal sulfide phase on the zeolite-supported catalysts might have some influence on the relative activities. After all, the presence of acid sites improves the thiophene HDS activity, and nearly all acid sites are located in the zeolite pores. Thus, especially for the acidic catalysts, the metal sulfide inside the zeolite pores might be more active than the sulfide located on the outside of the zeolite particles [14,15]. If the amount of nickel sulfide inside the zeolite pores is higher than the amount of molybdenum sulfide, this may cause a relatively low activity of the zeolite-supported molybdenum sulfide catalysts, especially for the acidic ones.

Also the product selectivities are strongly influenced by the acidity of the zeolite support, as is shown in Table 3 for nickel sulfide catalysts. In this table not all

products are taken into account, since particularly for the catalyst systems containing acidic supports some chromatographic peaks could not be identified. This fraction of non-identified compounds is, however, very small and it will therefore have no significant influence on the product distribution. Additionally, part of the thiophene HDS products are converted into coke. These products are of course not detected by GC analysis and are also not included in the product selectivities shown in Table 3. Especially, at short run time a large part (up to 50%) of the converted thiophene is not detected by GC analysis, and will probably be converted into coke. None of the identified products contained sulfur. Compounds such as tetrahydrothiophene or *n*-, *sec*-, or *tert*-butylmercaptane are not present. Although there may be some sulfur-containing molecules among the non-identified products, apparently most of the products are desulfurized before they are polymerized and cracked. For Ni/NaY a large fraction of C₄ products is observed mainly existing of butenes with only small amounts of *n*-butane and *i*-butane. Similar to carbon-supported catalysts [33] also NaY-supported nickel sulfide show poor hydrogenating properties for butenes formed during thiophene HDS. Besides C₄ molecules some polymerized and cracked products are formed, again indicating that also on this catalyst acid sites are present in spite of the supposedly non-acidic character of the NaY support. For Ni/CaY and Ni/HUSY the C₄ fraction decreases as, due to the higher acidity of these catalysts, more polymerization and cracking occurs. The Ni/Na-ZSM-5 shows a high degree of polymerization and cracking, in spite of the fact that the zeolite support itself is not acidic. Probably, also on this catalyst some exchange of Na⁺ ions against Ni²⁺ ions has occurred during impregnation, resulting in an acidic catalyst after sulfidation. For the Ni/H-ZSM-5 the degree of polymerization and cracking has strongly increased.

Ni/CaY and both the ZSM-5-supported catalysts produce large amounts of C₇ (mainly toluene) and C₈ products (mainly ethylbenzene and *p*-xylene). The C₈ products are probably the result of polymerization of butenes. Larger polymerization products are formed as well, but most of these products will not be able to leave the zeolite pore system, and will finally be converted into coke. Due to cracking of these large molecules C₇ or smaller products are formed. For Ni/HUSY the amount of polymerized products (> C₄) is relatively small. Probably, most of the polymerized products formed are either immediately cracked into very small molecules, or converted into coke. This results in a relatively low product selectivity for C₇ and C₈ products, and a high selectivity for C₁/C₂ and C₃. The zeolite-supported cobalt catalysts show product selectivities similar to those of the nickel catalysts. The molybdenum catalysts, especially those supported on NaY and Na-ZSM-5, show a higher C₄ product selectivity (95 and 90%, respectively). In contrast to the nickel and cobalt catalysts, hardly any ion exchange has occurred during impregnation with AHM, and thus only a very few acid sites have been formed after impregnation and sulfidation, resulting in very low amounts of cracking and polymerization products on the NaY and Na-ZSM-5-supported molybdenum catalysts.

Fig. 6. Thiophene HDS activity versus run time for the pure zeolite supports. (○) CaY, (●) HUSY, (□) H(46)NaY.

The acidic zeolite supports also show a thiophene HDS activity in the absence of a metal sulfide phase, as can be observed for instance on the H(*x*)NaY supports (Fig. 1). With increasing acidity an increasing initial thiophene HDS activity is measured. The non-acidic zeolites are not active for thiophene HDS. In Fig. 6 the HDS activities of pure CaY, HUSY and H(46)NaY are given. The catalytic activities of these acidic zeolites are however far lower than those of their metal sulfide containing counterparts. The CaY and HUSY zeolites deactivate slowly, and are still active after 2.5 h reaction. The H(46)NaY zeolite shows a surprisingly high initial activity, followed by a rapid deactivation. After 2.5 h run time the catalyst has lost its activity completely. Lopez Agudo et al. [6,38] and Cid et al. [39] also reported thiophene HDS conversions on zeolites containing strong Brønsted acid sites (H-ZSM-5, HUSY and HNaY zeolites). Their catalysts also showed a rapid deactivation caused by coking.

For the CaY, HUSY and HNaY catalysts only very small amounts of products from the HDS reaction could be detected. Apparently, most of the products are converted into coke. The amounts of coke as analyzed by temperature-programmed oxidation are 13, 13 and 22 wt.-% for the CaY, HUSY and H(46)NaY zeolite, respectively. Among the small quantity of products detectable by on line GC analysis are hardly any C_4 's. Mainly aromatics (benzene, toluene, ethylbenzene, *p*-xylene and *o*-xylene) and small molecules (C_1 – C_2 – C_3 products) are observed. No S-containing hydrocarbon products can be detected. On the colder parts of the glass reactor tube elemental sulfur is deposited during the HDS reaction, indicating that at least a part of the reacted thiophene is desulfurized.

From the above results it can be concluded that the presence of acid sites improves the thiophene HDS conversion. The activity differences between the metal sulfide catalysts supported by different zeolites (Figs. 3, 4 and 5), or between series of Ni/NaY, Ni/CaY (both prepared by impregnation) and NiNaY (prepared by ion exchange) catalysts [14,15] indicate that higher initial thiophene HDS conversions can be obtained on acidic zeolite supports. [It is relevant to note that changes in the preparation method (impregnation or ion exchange) effect the nickel sulfide dispersion, the distribution of the nickel sulfide over the zeolite particle and the acidity. However, DOC measurements and comparison of the NiNaY (ion exchange) and Ni/NaY (impregnation) catalysts with other catalysts such as Ni/CaY revealed that the high initial activity of NiNaY (ion exchange) is not only caused by the dispersion or the slightly higher amount of nickel sulfide in the zeolite pores, but also to a large extend by the differences in acidity between these catalysts.] For USY-supported tungsten catalysts [39], HNaY-supported molybdenum catalysts [38] and ion-exchanged sulfided NiNaY catalysts [5] it is also shown that an increasing acidity can result in higher thiophene HDS activities. For sulfided Me/H(x)NaY catalysts the initial HDS activity increases with increasing acidity, suggesting that a synergetic effect occurs between the metal sulfide phase and the acidic zeolite. There are several ways in which this synergetic effect can be explained: (I) a higher concentration of thiophene in the pores of the zeolite, (II) acceleration of the rate determining step in the thiophene HDS reaction, or (III) changes in the catalytic properties of the metal sulfide phase.

(I) The presence of acid sites may result in an increased adsorption of thiophene in the pores of the zeolite. Consequently, the local thiophene concentration around the metal sulfide particles in the zeolite pores will be higher which, assuming that the reaction is first order in thiophene, will result in an enhanced reaction rate. Most likely, only the sulfide particles located inside the zeolite pores will participate in this synergetic effect.

(II) There are many possibilities for H^+ ions to interfere with the thiophene HDS reaction. For instance, it is possible to describe the desulfurization of thiophene on a metal sulfide particle as a four electron reduction process [32,40,41] leading to the formation of H_2S and butadiene:

The electrons in the first reaction may be provided by the metal sulfide. Protons are always available at the surface of the metal sulfide in the form of SH groups, but possibly the high concentration of protons in the close vicinity of the metal sulfide particles can lead to an acceleration of the first reaction, leading to a higher overall reaction rate. The protons may also directly accelerate the C–S bond scission, for instance by destabilization of the aromatic structure of the thiophene ring.

(III) The protons of the zeolite support may be able to change the catalytic properties of the metal sulfide clusters located in the zeolite pores. For instance, the interaction between the metal sulfide particles and the acid sites may lead to the formation of a larger number of acidic SH groups on the sulfide surface. As these SH groups are probably involved in the thiophene HDS reaction (see for instance II), a higher concentration of SH groups can result in a higher activity.

None of the above mentioned explanations for the synergetic effect can explain the desulfurization activity of the pure zeolite supports. The reactions of thiophene on these zeolites (without the presence of a metal sulfide phase) can not be explained by the usual thiophene HDS mechanism which occurs on a metal sulfide catalyst. The reactions with thiophene over the acidic zeolites will most probably take place at the Brønsted acid sites. Thiophene may adsorb on these sites, followed by the removal of H_2S via β -elimination [42].

The diacetylene will subsequently polymerize over the acid sites. The thiophene may also decompose into two acetylene molecules and a sulfur atom. Presumably, under reaction conditions (673 K, 4% thiophene in hydrogen, atmospheric pressure) many other acid catalyzed reactions with thiophene are possible. Due to the absence of a hydrogenation function these will mainly result in unsaturated products (which will polymerize quickly over the acid sites) and H_2S or elemental sulfur. Also direct polymerization of thiophene may be possible, resulting in large sulfur containing molecules trapped in the pores of the zeolite.

Apparently, two effects of the presence of acid sites can be distinguished: (I) the acid sites show a desulfurization activity themselves and (II) a synergetic effect occurs between the metal sulfide phase and the acid support. The synergetic effect will most likely only be observed if the acid sites and the metal sulfide are in close vicinity of each other. As almost all acid sites are located in the zeolite pores, only the metal sulfide particles in the zeolite pores will contribute to the synergetic effect. So, probably the metal sulfide particles located inside the zeolite pores contribute significantly to the HDS activity.

4. Conclusions

The thiophene HDS activity and product selectivity of zeolite-supported metal sulfide catalysts are not only dependant on the type of metal sulfide and the pore structure of the zeolite support, but also on the acidity. A higher acidity leads to an increase of the initial thiophene HDS activity. Interestingly, this acidity effect is not due to an increase in metal sulfide dispersion but most likely results from a

synergy between the small metal sulfide particles and the acidic support. Only the metal sulfide particles located inside the zeolite pores will contribute to this effect. Further improvement of these catalysts may thus be obtained by developing preparation methods which result in higher amounts of metal sulfide particles inside the zeolite pores. Studies specifically aiming at the intrinsic catalytic properties of small metal sulfide particles in zeolite pores are only meaningful in the absence of acid sites, or after inactivation of acid sites by selective poisoning or application of sufficiently low reaction temperatures.

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