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Zeolite Y type supported nickel and molybdenum sulfides. Relation between metal sulfide distribution and catalytic properties in thiophene hydrodesulfurization

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NaY supported Mo or Ni sulfide catalysts prepared by impregnation, ion exchange or gas phase deposition followed by various pretreatment procedures show different catalytic properties in thiophene hydrodesulfurization. These differences are discussed in terms of degree of sulfidation, metal sulfide distribution and dispersion.

1. INTRODUCTION

Zeolites have been extensively studied regarding their application as catalytically active compounds for various chemical reactions [1,2]. This is due to their specific properties such as the well defined micropore system in combination with a high specific surface area and the ability to act as a solid acid [3]. Therefore, they are also of interest as cracking active supports for transition metal sulfides in processes requiring simultaneous hydrocracking and hydrotreating reactions.

Several studies about zeolite supported nickel and/or molybdenum sulfides have been performed in recent years [4-9]. However, the results are not always consistent and sometimes even contradictory. Thus, more detailed knowledge about the influence of the preparation and sulfidation procedure on the location of the metal (sulfide) species (in- or outside the zeolite pore system) and their interaction with the zeolite is needed to understand the catalytic properties of these catalyst systems.

In the present study we report about NaY supported nickel or molybdenum sulfide catalysts with special emphasis on the pretreatment procedure and the resulting metal sulfide distribution throughout the zeolite. Most commonly, in industrial catalysts USY zeolite is used as support. In order to avoid influences arising e.g. from the extra framework alumina or the secondary pore system formed during dealumination by steaming, the original NaY zeolite is used for our model catalysts. Their catalytic activities are tested in atmospheric thiophene hydrodesulfurization (HDS). The activities are correlated with the results obtained from ¹²⁹Xe

NMR spectroscopy in combination with Xe adsorption and HREM/EDX measurements about the metal (sulfide) distribution.

2. EXPERIMENTAL SECTION

Catalyst preparation. Two different series of NaY supported catalysts with 2, 4, 6, and 8 wt.% Ni are prepared using ion exchange (IE) or pore volume impregnation (IMP). The experimental details are described elsewhere [9].

Part of the Mo catalysts containing different metal amounts (3.5, 5, 8, and 10.4 wt.%) is obtained by impregnation of NaY with $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ solutions of appropriate concentrations. The other part is prepared via gas phase deposition (GPD) of $\text{Mo}(\text{CO})_6$ on NaY in a purified He flow at 333 K for 16 h. Prior to this preparation step the NaY support is dried for to 2 h at 673 K in He (flow rate 3 l/h). The whole procedure provides full saturation of the zeolite, resulting in a loading of about 10.5 wt.% Mo. The catalysts are designated xMeNaY(P/p) with x representing the weight percentage of the transition metal Me. P/p stands for the applied preparation (IE, IMP, GPD) and pretreatment (fp; ox; d 423; d 573; su; dry su) procedure (vide infra).

Catalyst pretreatments. All catalysts are sulfided *in situ* (su) for 2 h at 673 K before testing, using a mixture of 10 % H_2S in H_2 (3,6 l/h, $\beta=6$ K/min). In order to investigate the influence of physisorbed H_2O one series of NiNaY(IE) samples is dried in purified He at 673 K prior to sulfidation (dry su). Before being sulfided, the MoNaY(IMP) catalysts are calcined (ox) at 673 K for 2 h. Three different *in situ* pretreatments are applied to the freshly prepared (fp) GPD-type Mo samples: decomposition of $\text{Mo}(\text{CO})_6$ to $\text{Mo}(\text{CO})_3$ at 423 K (d 423) or to metallic molybdenum at 573 K (d 523) in a He flow (flow and heating rate 3 l/h and 6 K/min, resp., in each case) and no pretreatment.

Chemical analysis. The samples are dissolved in aqua regia while carefully heating the mixture. During this process all metal sulfide species are converted to metal sulphate. Subsequently, the metal content is analyzed by AAS, while the amount of sulphate is determined by titration with barium perchlorate.

Combined ^{129}Xe NMR spectroscopy and Xe adsorption measurements. The principle as well as the main experimental conditions are explained in [10, 11]. In the present study the spectra of the ^{129}Xe adsorbed at different Xe pressures are taken at 303 K with a Bruker MSL 400 spectrometer at 110.7 MHz.

High Resolution Electron Microscopy (HREM) and Energy Dispersive X-ray Analysis (EDX). To estimate qualitatively and quantitatively the metal (sulfide) phase formed on the outer surface of the zeolite particles both HREM and EDX are performed using a Philips CM 30 ST apparatus. The sample preparation is described in [9].

Catalysis. Thiophene HDS activity measurements are carried out in a micro flow reactor (673 K; 0.1 MPa; 4.0 % thiophene in H_2 , 3 l/h; 0.25 g cat., particle size: 0.125 - 0.425 mm). Reaction products are analyzed by on line GC. Because of deactivation during the reaction which is probably caused by coke formation or metal sulfide sintering the catalysts are compared on the basis of their *initial* activities.

3. RESULTS AND DISCUSSION

3.1. Nickel containing catalysts

For the sulfided NiNaY(IE) samples the initial HDS activity increases almost linearly with increasing transition metal content (Figure 1). This confirms the observations by Cid et al.[4]

Figure 1. HDS activities of NiNaY(IE/su)-● and NiNaY(IMP/su)-▲ catalysts.

Figure 2. HDS activities of NiNaY(IE/su)-● and NiNaY(IE/dry su)-▼ catalysts.

for such catalysts. The sulfided NiNaY(IMP) samples show only a small activity increase at low loadings but at higher loadings the activity levels off. The pure NaY is not active in thiophene conversion. The clear contrast between the two catalyst series demonstrates the strong influence of the preparation method on their catalytic behaviour. This is mainly due to the large differences in nickel sulfide distribution and dispersion [11]. However, the acidic sites created during the sulfidation of the ion exchanged samples can also have a considerable effect on the HDS activity [4, 9].

Figure 2 shows the initial HDS activities of the NiNaY(IE/su) and NiNaY(IE/dry su) catalyst series. It is clear that additional drying before sulfidation significantly increases the initial HDS activity. This increase is the strongest at low metal loadings. The influence of drying before sulfidation is negligible for the corresponding NiNaY(IMP) samples.

There might be several reasons for the observed drying effect. Chemical analysis as well as temperature programmed sulfidation measurements show complete sulfidation of Ni for both types of catalyst precursors [9]. Concerning 4NiNaY(IE/dry su), the nickel sulfide phase consists mainly of Ni₃S₂ while in the case of 4NiNaY(IE/su) besides Ni₃S₂ a certain amount of NiS is formed. This is in line with the HREM results. For the latter catalyst they reveal large nickel sulfide particles on the outer surface of the zeolite going along with the appearance of NiS lattice distances. Unlike the non-dried catalyst, the external nickel sulfide particles present in 4NiNaY(IE/dry su) are considerably smaller and more numerous. These findings point to a better distribution and/or dispersion of the nickel sulfide phase in the case of the dried catalysts.

This could be confirmed by combined ¹²⁹Xe NMR spectroscopy and Xe adsorption measurements. In Figure 3 the Xe adsorption isotherm of the reference NaY is compared with

Figure 3. Xe adsorption isotherms of NaY-■, NiNaY(IE/su)-● and NiNaY(IE/dry su)-▲.

Figure 4. Chemical shift for Xe adsorbed on NaY-■, NiNaY(IE/su)-● and NiNaY(IE/dry su)-▲.

those of the samples 4NiNaY(IE/su) and 4NiNaY(IE/dry su). It appears that the slopes of the linear part of the isotherms of both Ni containing samples are smaller than that of the NaY to almost the same extent. This indicates a lower Xe adsorption capacity for the Ni loaded catalysts compared with NaY due to the presence of nickel sulfide inside the zeolite pore system. In addition, this internal amount of nickel sulfide must be approximately the same. This conclusion is supported by the data obtained from EDX analysis. Comparing the average Ni/Si ratio in the EDX spectra of a large number of zeolite particles with the ratio of a spot on a zeolite particle, hardly containing any Ni at its outer surface, fractions of about 35 % of the nickel sulfide phase, being present inside the zeolite cavities, could be estimated.

As can be seen from Figure 4, the chemical shift δ of the NMR signals for ^{129}Xe adsorbed on 4NiNaY(IE/dry su) is markedly higher than the shift for 4NiNaY(IE/su). This large difference together with the completely changed curve shape can be only explained considering a second parameter influencing the chemical shift (besides the mean free path for the Xe atoms inside the micropores). According to Fraissard et al. [10] the presence of strong adsorption sites causes a deviation from the linear dependence of δ on the amount of Xe adsorbed. Particularly at low amounts of Xe adsorbed each Xe atom will have a relatively long residence time on the strong adsorption sites, resulting in an increased chemical shift compared with samples having only weaker adsorption sites. If the Xe concentration increases the exchange of strongly adsorbed Xe atoms with those adsorbed on other sites of the zeolite will become faster, and the influence of the strong adsorption on δ will become smaller. Consequently, the chemical shift at first decreases and then, if the number of Xe - Xe collisions becomes predominant, increases. As a result the curvature is concave. The drying step before sulfidation of NiNaY(IE) leads to smaller nickel sulfide particles, most likely also inside the zeolite pores. Probably, both the number and/or the adsorption strength of these smaller particles is higher, causing an increased δ compared with NiNaY(IE/su), especially at low Xe pressures. The difference of δ between NaY and NiNaY(IE/su) corresponds well with the lower adsorption capacity for the latter.

Thus, as could be shown by ^{129}Xe NMR spectroscopy in combination with Xe adsorption

and HREM/EDX measurements the application of a drying step prior to sulfidation enables the formation of small nickel sulfide particles. The presence of physisorbed water during the sulfidation increases the mobility of the Ni species and facilitates the formation of bulky nickel sulfide particles. The higher HDS activity of the NiNaY(IE/dry su) samples is caused by the higher nickel sulfide dispersion.

3.2. Molybdenum containing catalysts prepared by impregnation

Figure 5 shows the initial thiophene HDS activities for the sulfided IMP- and GPD- type MoNaY catalysts. Concerning the MoNaY(IMP/su) samples, the catalytic activity increases with Mo loading. This indicates an enlargement of the available active molybdenum sulfide sites. In order to understand the catalytic behaviour, the degree of sulfidation as well as the distribution of the oxidic and sulfided Mo species have to be studied.

In Figure 6 the chemical shifts for ^{129}Xe adsorbed on both the oxidic and sulfided forms of MoNaY(IMP) and NaY at zero xenon density are summarized. With increasing Mo loading the δ values for the oxidic precursors and for the sulfided catalysts become gradually larger. In addition, at all metal loadings the extrapolated chemical shift is slightly higher for the sulfided samples. These NMR spectroscopy results are in good agreement with those obtained from the Xe adsorption capacity measurements [12]. The decrease of the adsorption capacity and the increase of the chemical shift found for the MoNaY(IMP/ox) samples relative to NaY show that after calcination at 673 K part of the oxidic Mo species are located inside the zeolite pores. Nevertheless, considering the magnitude of the changes it must be assumed that the majority of the Mo species remains external. The evidence for such a distribution is taken from EDX measurements carried out on 10.4MoNaY(IMP/ox). It could be estimated that at most 25 % of the Mo is located inside the zeolite pores. This is in line with the results published by Laniecki et al. [6].

Subsequent sulfidation does not substantially change the distribution of the oxidic Mo species. The slope of the adsorption isotherms and, consequently, the adsorption capacities of

Figure 5. Initial HDS activities of various xMoNaY(IMP) and 10.5MoNaY(GPD) catalysts.

Figure 6. Chemical shift at zero Xe density for various xMoNaY(IMP) catalysts.

the MoNaY(IMP/su) samples are only somewhat smaller than those for the nonsulfided precursors. The slightly higher chemical shift for the sulfided catalysts observable in Figure 6 might be caused by the larger size of the MoS₂ than for parent oxidic Mo species. This results in a diminished pore volume and, consequently, in a shortened mean free path for the Xe atoms. However, a small increase of the amount of Mo species inside the pores is also possible.

From the combined HREM/EDX investigations it can be concluded that the distribution of the oxidic and sulfided Mo species between the internal and external zeolite surface is inhomogeneous. On some zeolite particles high amounts of Mo can be discerned, while on others the concentration is far lower. In the case of 10.4MoNaY(IMP/su) well developed MoS₂ layers widely covering the outer surface of the zeolite particles are observed whereas other areas exhibit only a few small MoS₂ slabs. In addition, some very large Mo particles (50nm) are found on the exterior which are probably not fully sulfided. This assumption is derived from the results of the chemical analysis showing a decreasing degree of sulfidation with increasing Mo content (S/Mo ratio changes from 2.2 for 3.5MoNaY(IMP/su) down to 1.3 for 10.4MoNaY(IMP/su)). High Mo loadings obviously enhance the probability to form large molybdenum oxide particles which are much more difficult to sulfide down to their core [13]. EDX analysis shows the presence of both sulfur and molybdenum inside the pores demonstrating at least a partial sulfidation of the Mo species.

Despite its low sulfidability, 10.4MoNaY(IMP/su) shows the highest HDS conversion among the IMP-type Mo samples. Therefore, the degree of sulfidation seems to be less important for the catalytic activity. On the other hand, ¹²⁹Xe NMR spectroscopy shows that the amount of Mo inside the zeolite pores increases with enhanced Mo content. On the external zeolite surface higher Mo loadings will mainly result in bulky Mo particles, and not in a significant increase of the active molybdenum sulfide surface. Thus, the increase in activity with increasing Mo loading should be most likely ascribed to higher amount of smaller MoS₂ species located in the zeolite cavities.

3.3. Molybdenum containing catalysts prepared by gas phase deposition

From Figure 5 it can be seen that the initial HDS activities of the sulfided, but differently pretreated 10.5MoNaY(GPD) catalysts vary significantly. The samples directly sulfided after Mo(CO)₆ adsorption (10.5MoNaY(GPD/su)) or after heating up to 423 K (10.5MoNaY(GPD/d 423, su)) have a similar activity (the latter is not shown in Figure 5). Only the 10.5MoNaY(GPD/d 573, su) catalyst is clearly less active. According to the experience with the IMP-type catalysts it is reasonable to assume that their catalytic properties are again dominated by the metal sulfide distribution. Hence, ¹²⁹Xe NMR spectroscopy in combination with Xe adsorption and HREM measurements should show whether this assumption is true.

Unlike the pore volume impregnation the gas phase deposition of Mo(CO)₆ on NaY results in precursor catalysts in which all Mo is located in the zeolite pores. This is convincingly demonstrated in Figure 7. It can be seen that the δ value for 10.5MoNaY(GPD/fp) sample is extremely high. This is line with its very low Xe adsorption capacity indicating that the pores are almost completely filled (Figure 8). Subsequent thermal treatment at 423 K or 573 K leads to the formation of less voluminous Mo(CO)₃ complexes or metallic Mo, respectively. The shape and the slope of the isotherms for these samples changes distinctly denoting higher adsorption capacities. Consistently, this is accompanied by a marked decrease of the

Figure 7. Chemical shift at zero Xe density of various 10.5MoNaY(GPD) samples.

Figure 8. Xe adsorption isotherms of various 10.5MoNaY(GPD) samples.

corresponding δ values. For 10.5MoNaY(GPD/d 573) HREM reveals that the preponderant part of the zeolite particles is partly covered with dark spots of metallic Mo. In addition, from EDX analysis could be estimated that only about 10 % of the Mo remains in the supercages. Sulfidation of this sample leads to a small decrease of its adsorption capacity and, unexpectedly [10], to a large decrease for the chemical shift (Figure 7). Probably, the volume of the MoS_2 formed in the pores is slightly larger while the interaction between MoS_2 and Xe is much less strong than between Mo and Xe. However, the combined methods point to the majority of Mo present on the exterior, also after sulfidation. Referring to the conclusion drawn for the IMP-type Mo catalysts that the HDS activity is most likely linked to the amount of small MoS_2 species in the pores, it is not surprising that the activity found for this sample is rather low.

Sulfidation of 10.5MoNaY(GPD/fp) and 10.5MoNaY(GPD/d 423) samples produces almost equal catalysts. Both, the shape of their isotherms as well as the corresponding δ values at zero xenon density are very similar. This allows the conclusion that the distribution of the MoS_2 phase is also comparable. HREM results show well developed MoS_2 layers on the outer surface of 10.5MoNaY(GPD/su). The degree of sulfidation is almost the same (S/Mo ratio: 2.0 and 1.9, resp.) for both catalysts. Most likely, the thermal treatment at 423 K has no influence on the sulfidation of these two catalysts. Consequently, their HDS activities are equal.

Interestingly, the two catalysts with similar Mo loadings but prepared via various procedures (IMP and GPD) gives slightly different activities. It can be derived from the Xe adsorption measurements that their adsorption capacities are not much different. Therefore, the amount of MoS_2 located inside the zeolite pores should be much the same. The slightly higher HDS activity of xMoNaY(GPD/su) is probably caused by the presence of smaller MoS_2 particles inside the zeolite pores.

4. CONCLUSIONS

The thiophene HDS activity of sulfided NiNaY and MoNaY catalysts is strongly

determined by the distribution (in - or outside the zeolite pores) and the dispersion of the Ni or Mo species. Both distribution and dispersion depend on the preparation method and treatment of the catalyst prior to sulfidation. The more Ni or Mo present as small sulfide particles in the zeolite pores the higher the HDS activity.

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REFERENCES

1. J.A. Rabo (ed.), Zeolite Chemistry and Catalysis, ACS Monograph, Washington, 1974
2. W.F. Hölderich, in: Stud. Surf. Sci. Catal., Vol.49 (P.A.Jacobs, R.A. van Santen, eds.) p. 69, Elsevier, Amsterdam, 1989
3. A. Corma, NATO ASI Series, Ser.C, Vol. 352 (1992) 373
4. R. Cid, J.L.G. Fierro, A. Lopez Agudo, Zeolites 10 (1990) 95
5. A. Ezzamarty, E. Catherine, D. Dornet, J.F. Hemidy, A. Janin, J.C. Lavalley, J. Leglise, P. Meriaudeau, in: Stud. Surf. Sci. Catal., Vol. 49 (P.A. Jacobs, R.A. van Santen, eds.) p. 1025, Elsevier, Amsterdam, 1989
6. M. Laniecki, W. Zmierczak, Zeolites 11 (1991) 18
7. Y. Okamoto, A. Maezawa, H. Kane, T. Imanaka, J. Mol. Catal. 52 (1989) 337
8. J.A. Anderson, B. Pawelec, J.L.G. Fierro, P.L. Arias, F.Duque, J.F.Cambra, Appl. Catal. A: 99 (1993) 55
9. W.J.J. Welters, G. Vorbeck, H.W. Zandbergen, V.H.J. de Beer, R.A. van Santen, submitted to J. Catal.
10. J. Fraissard, T. Ito, Zeolites 8 (1988) 350
11. T.I. Korányi, L.J.M. van de Ven, W.J.J. Welters, J.W. de Haan, V.H.J. de Beer, R.A.van Santen, Catal. Lett. 17 (1993) 105
12. G. Vorbeck, W.J.J. Welters, E.M. van Oers, L.J.M. van de Ven, J.W. de Haan, V.H.J. de Beer, R.A. van Santen, 1stEurop. Conf. Catal., B. of Abstr., p. 308, Montpellier, 1993
13. P. Arnoldy, J.A.M. van den Heykant, G.P. de Bok, J.A. Moulijn, J. Catal. 92 (1985) 35