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Hydrodesulfurization Catalysis by Small Metal Sulfide Particles

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ABSTRACT

Monometallic (Mo, Co and Ni) sulfide particles dispersed in the micropores of zeolites can have a very high initial activity for the hydrodesulfurization of thiophene. Catalyst characterization, using ¹²⁹Xe NMR, HREM and Mössbauer Emission Spectroscopy (MES), shows that the location (in- or outside the zeolite pores) and size of the sulfide particles depends strongly on catalyst preparation conditions.

The kinetics of thiophene HDS has been studied on metal (Mo, Co, Rh and Pt) sulfides dispersed on a carbon support. The order of thiophene in the HDS reaction appears to be a strong function of metal sulfide and temperature. The catalysts show a large compensation effect.

INTRODUCTION

A fundamental question in hydrodesulfurization (HDS) catalysis is the nature of the catalytically active sulfide site [1]. Whereas studies of highly dispersed cobalt sulfide particles on carbon [2] indicated a high activity for single sulfide particles, research on CoMoS phases indicated the importance of the interaction of combined sulfide phases [3]. Nørskov et al [4] have suggested a relation between the Me-S bond energy and HDS activity and predicted a maximum activity for metals with the weakest Me-S bond strength.

Zeolites provide an interesting support material to investigate more closely the question of particle size as well as sulfide-support interaction. Characterization of metal sulfide zeolites shows that the application of conventional impregnation techniques results in a significant fraction of the sulfide phase external of the zeolite crystallite [5]. We will report on synthesis procedures to prepare sulfide particles specifically inside the zeolite micropores. Such catalysts enable the comparison of

the relative activity of small sulfide particles. As main characterization techniques, Xe-NMR, HREM and Mössbauer Emission Spectroscopy (MES) have been used.

Kinetic studies have been done for highly dispersed carbon supported materials, because of the rapid decline of the zeolite catalysts when tested in the HDS reaction. The kinetic studies have a particular aim to elucidate the relation between the reaction rate and the sulfide particle-thiophene interaction energy. A recent theoretical study [6] has shown that the overall kinetics depends on :

- 1) The rate of C-S bond rupture that requires a strong interaction between the catalyst and sulfur of thiophene.
- 2) The rate of surface sulfur removal, that requires a low sulfur-catalyst interaction energy.
- 3) The rate of dissociative hydrogen adsorption.

EXPERIMENTAL

CoNaY (3.1 wt% Co) and NiNaY (3.5 wt% Ni) catalysts are prepared by ion exchange of NaY with aqueous solutions of CoCl_2 or NiCl_2 followed by washing and drying in air (16 h, 383 K). Two different sulfidation procedures have been applied for in situ sulfidation:

- 1) Dry sulfidation, by first drying the freshly prepared material in He to remove physisorbed water present in the zeolite (in 1 hour from 298 K to 673 K), followed by 2 h atmospheric sulfidation in 10% $\text{H}_2\text{S}/\text{H}_2$ at 373 K or 673 K.
- 2) Wet sulfidation, by treating the freshly prepared materials with 10% $\text{H}_2\text{S}/\text{H}_2$ at 1 bar according to the following temperature program: in 1 h from 298 K to 373 K or 673 K and 2 h at this temperature.

MoNaY (11.8 wt% Mo) is prepared by gas phase deposition of molybdenum hexacarbonyl on dry NaY (16 h, 333 K) followed by in situ sulfidation (10 % $\text{H}_2\text{S}/\text{H}_2$, 1 bar, in 1 h from 298 K to 373 or 673 K and 2 h at this temperature). For the preparation of the carbon supported catalysts we refer to [2].

The catalytic activity of the in situ sulfided catalysts is measured by thiophene HDS (micro flow reactor, 200 mg catalyst, 673 K, 1 bar, 60 ml/min 4 % thiophene/ H_2). Comparison of the zeolite activities is based on initial conversion (after 2 minutes run time) because of rapid deactivation due to coke formation. The kinetic measurements are carried out after in situ sulfidation (10 % $\text{H}_2\text{S}/\text{H}_2$, 1 bar, in 1 h from 293 K to 673 K, 3 h at 673 K) in a microflow reactor (1 bar, 54 ml/min 1-6% thiophene/ H_2 , 6 ml/min 10% $\text{H}_2\text{S}/\text{H}_2$). Kinetic measurements are carried out in a differential plug flow reactor.

The Xe NMR experiments are described in [7]. For the MES measurements we refer to [8]. HREM measurements are carried out at a Philips CM 30 ST microscope.

RESULTS AND DISCUSSION

Mössbauer Emission Spectroscopy of CoNaY catalysts

Two Co^{2+} ion exchanged NaY samples (4 wt % Co) were compared, a dry and a wet sulfided catalyst. The doublet with largest quadrupole splitting is due to a non sulfidic Co^{2+} high spin contribution.

For the wet sulfided catalyst this spectral contribution rapidly vanishes at increasing sulfidation temperature, whereas it remains for the dry sulfided catalyst up to 673 K due to incomplete sulfidation. The quadrupole splitting for the other major doublet (which is due to cobalt sulfide) decreases slowly at increasing sulfidation temperature for the dry sulfided catalyst, whereas it

declines rapidly for the wet sulfided system [9]. This indicates that the cobalt sulfide dispersion of the dry sulfided catalyst remains higher than for the wet sulfided one [8]. HREM measurements of CoNaY show no cobalt sulfide on the outer surface of the zeolite for the dry 373 K sulfided sample, while large cobalt sulfide particles are found for the wet 673 K sulfided sample.

The Mössbauer signal of the dispersed cobalt sulfide phase present in the low temperature sulfided sample (especially the dry sulfided ones) is remarkably similar to that of the CoMoS

phase on carbon and Al_2O_3 supported systems [8]. The HDS activity of the wet sulfided catalysts is lower than the activity of the dry sulfided catalysts. The sulfidation temperature has also an influence, the activity of CoNaY is decreasing with increasing sulfidation temperature. (Table 1).

Xe NMR measurements of MoNaY catalysts

The Xenon adsorption capacity of the molybdenum containing zeolite increases with increasing sulfidation temperature. This phenomenon is accompanied by a decrease in chemical shift of the ^{129}Xe NMR signal (Figure 2). Hence the amount of sulfide in the zeolite pores decreases when the sulfidation temperature is increased. This agrees with HREM results. The molybdenum sample sulfided at 373 K shows no molybdenum sulfide at the outer surface of the zeolite while for the

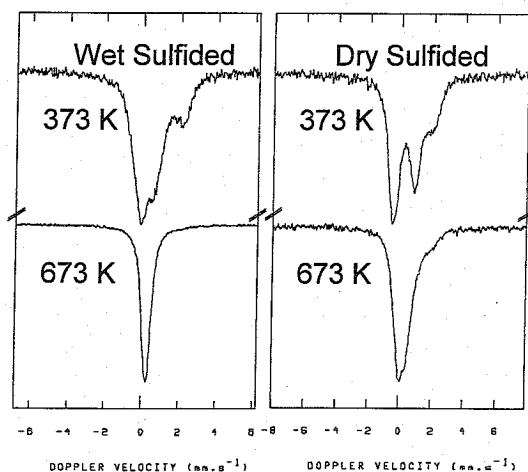


Figure 1. MES spectrum of CoNaY after different sulfidation procedures

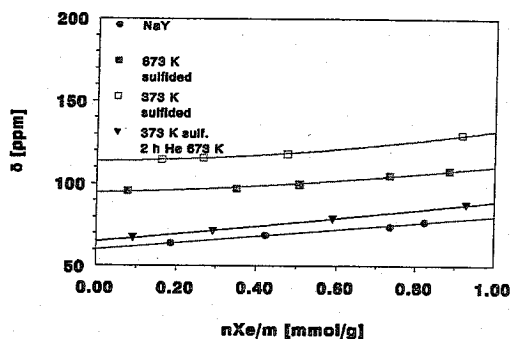


Figure 2. ^{129}Xe NMR signal as function of the Xe adsorption for CoNaY at different temperatures sulfided.

sample sulfided at 673 K an inhomogeneous distribution of molybdenum sulfide at the outer surface is found.

The chemical shift of MoNaY sulfided at 373 K is strongly decreasing (Figure 2) after heating in He at 673 K for 2 h. This phenomenon is accompanied by an increasing Xe adsorption capacity. Probably, the molybdenum sulfide inside the zeolite pores is mobile and accumulates at the outer surface of the zeolite. The effect

of the different sulfidation temperatures of MoNaY on the overall thiophene HDS activity is shown in Table 1.

Comparison of initial thiophene HDS activities

Table 1 summarizes initial conversions for Ni sulfide/NaY, Co sulfide/NaY and Mo sulfide/NaY. Data are shown for wet and dry sulfided catalysts. Whereas the overall activity is significantly affected by sulfidation conditions one finds:

$\text{Ni sulfide/NaY} > \text{Co sulfide/NaY} \cong \text{Mo sulfide/NaY}$

Table 1. Initial conversion (%) in thiophene HDS after different sulfidation procedures

Catalyst	CoNaY (3.1 wt% Co)		NiNaY (3.5 wt% Ni)		MoNaY (11.8 wt% Mo)
	wet	dry	wet	dry	
373 K	46.2	62.2	53.2	82.5	62.6
673 K	28.7	45.2	55.6	84.5	44.1

On carbon supported catalysts small cobalt sulfide particles gave significantly higher activity than the molybdenum sulfide particles [2]. Earlier data [10] for bulk sulfides indicated much smaller differences between the sulfides, probably due to significant differences in dispersion.

Part of the larger activity of Ni and Co zeolites may be due to the larger acidity compared to that of the Mo catalysts prepared from the carbonyl [5].

Kinetic measurements

Table 2 summarizes kinetic data for carbon supported sulfided catalysts. The reaction order in thiophene appears to be a strong function of temperature. One notes the large differences in activation energy for the four catalysts and also large differences in pre exponents (v_{overall}). This corresponds to a large compensation effect.

Table 2. Kinetic data for carbon supported sulfided catalysts

	Mo/C	Co/C	Rh/C	Pt/C
thiophene reaction order (583 K)			0.39	
thiophene reaction order (613 K)	0.62	0.54	0.44	0.43
thiophene reaction order (673 K)	0.68	0.77		0.65
$E_{\text{overall}}^{\text{act}}$ (kJ/Mol)	75	60	104	98
v_{overall} [$\text{m}^3/(\text{kg cat s})$]	$2.9 \cdot 10^5$	$3.9 \cdot 10^4$	$3.3 \cdot 10^8$	$1.6 \cdot 10^7$
Conversion at 673 K (%) (50 mg catalyst, $P_T = 6 \cdot 10^3$ Pa)	4.2	22	65	14.4

The Rh catalyst is most active. The Rh and Pt catalyst have the highest activation energy. Both catalysts compensate this by a large pre-exponent (v_{overall}). Comparing the Mo and Co data one notes

the striking temperature dependence in the reaction order of the Co catalyst compared to that of the Mo catalyst. An increase in reaction order implies a decrease in surface coverage. The larger change with temperature for Co indicates that the interaction energy with the sulfur containing

species is larger than for molybdenum. This is consistent with the lower overall activation energy of Co and with the computed (Table 3 [11]) metal-sulfur interaction energies.

In the case a dissociation reaction is rate limiting one can use equation (1) for the overall activation energy

$$E_{\text{overall}}^{\text{act}} = E_{\text{reac}}^{\text{act}} + \Delta E_{\text{ads}} (1 - \Theta) \quad \{ E_{\text{overall}}^{\text{act}} > 0, \Delta E_{\text{ads}} < 0 \} \quad (1)$$

$E_{\text{overall}}^{\text{act}}$	overall activation energy	ΔE_{ads}	heat of adsorption
$E_{\text{reac}}^{\text{act}}$	activation energy of rate limiting step	Θ	surface coverage

Hence, at constant $E_{\text{reac}}^{\text{act}}$, the larger the adsorption energy the lower the overall activation energy. The higher activity of the Co catalyst compared to the Mo catalyst is consistent with a stronger interaction

of adsorbed molecules with sulfidic particles. On the other hand the high activation energy measured for Rh and Pt indicates a difference in rate limiting step. The lower metal-sulfur interaction energy would imply a higher $E_{\text{react}}^{\text{act}}$. The low reaction order implies a relatively high surface coverage, further increasing the overall activation energy. The large pre-exponent indicates a large gain in activation entropy, as would occur in the C-S bond rupture due to the desorption of butadiene ($\text{Thiophene}_{\text{ads}} \rightarrow \text{S}_{\text{ads}} + \text{Butadiene}$). Apparently, on cobalt sulfide and molybdenum sulfide, with low overall pre-exponents, the transition state complex is tightly bonded to the surface with low activation entropy. Possibly thiophene hydrogenation ($\text{Thiophene}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{dihydrothiophene}$) or dissociative hydrogen adsorption ($\text{H}_2 \rightarrow 2 \text{H}_{\text{ads}}$) with little entropy change is now rate limiting instead of C-S bond rupture.

CONCLUSION

Small metal sulfide particles are active in hydrodesulfurization catalysis. The larger activity of nickel sulfide and cobalt sulfide particles compared to molybdenum sulfide supports the earlier proposals [8] that CoMoS and NiMoS phases obtain their activity due to the dispersion of active small Co and Ni sulfide particles along the edges of molybdenum sulfide.

The high activity of cobalt sulfide versus molybdenum sulfide appears to be related to a larger interaction of thiophene with cobalt sulfide phase compared to molybdenum sulfide resulting in a lower overall activation energy. A hydrogenation step is probably rate limiting. The large activity of noble metal sulfides relates to large overall pre-exponents, indicating of C-S bond breaking to be rate limiting in a step that produces desorbed products as butadiene.

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