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Catalysis Today 45 (1998) 341–346

CATALYSIS TODAY

Sulfidation of an alumina supported CoMo hydrotreating catalyst: variation of the S/(Co+Mo) ratio with the sulfiding temperature

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Abstract

An alumina supported CoMo catalyst was activated in the temperature range 295–773 K with H_2/H_2S. At several temperatures, elemental analysis, EDX, XPS and TPO techniques were used to measure the degree of sulfidation, expressed as the S/(Co+Mo) atomic ratio. A particular attention was paid to EDX analysis. A remarkable agreement was obtained between elemental analysis, EDX and XPS. No quantitative information but qualitative ones could be obtained from TPO. An attempt was made to relate catalyst sulfidation with the catalytic activity in thiophene and tetralin model reactions of hydrotreatment.

Keywords: Sulfidation; Hydrotreatment; Sulfur analysis; XPS; EDX

1. Introduction

Recent environmental specifications concerning the diminution of sulfur and aromatics in gas oil impose a significant improvement of hydrotreating catalysts [1,2]. Industrial alumina supported Co(Ni)–Mo catalysts are commercially available in their oxidic form. These systems require a sulfidation step usually performed after loading the catalyst into the reactor unit. The activation procedure may significantly influence catalyst activity and stability. Therefore, a better understanding of the sulfiding process may improve its activity. The degree of sulfidation often expressed as the S/(Co(Ni)+Mo) atomic ratio is generally obtained using several physico-chemical techniques such as elemental analysis, energy dispersive X-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS) and temperature programmed oxidation (TPO). In this field, literature data are difficult to compare because of the different experimental conditions used by the authors and also because the results largely differ depending on the technique used for the determination of the sulfidation degree [3–8]. The aim of this work was to establish the validity of these various techniques for the determination of the sulfur stoichiometry of a CoMo based catalyst during a stepwise increase of the sulfidation temperature. An attempt was made to relate catalyst sulfidation with the catalytic activity in two model reactions.

2. Experimental

2.1. Catalyst and activation

The catalyst used was an alumina supported CoMo containing 12.3 wt% of Mo and 3.0 wt% of Co. Sulfidation was performed by treating the supported

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PII: S0920-5861(98)00244-2

oxide for 4 h at a given temperature (heating rate=5°C/min) with a mixture containing 85% H_2–15% H_2S. In these conditions it has been verified that the steady state equilibrium was reached. The sulfiding mixture was then replaced by a nitrogen flow at the activation temperature and the solid was quenched to room temperature. The solid was stored in an inert atmosphere in order to avoid its oxidation.

2.2. *Elemental analysis*

The elemental analysis of cobalt and molybdenum was achieved by inductively coupled plasma (ICP). The sulfur content was titrated in a CS-mat 5500 apparatus (Ströhlein Instrument) at Eurecat SA. The sample was oxidized in pure O_2 at 1473 K and the SO_2 production was analyzed with an IR detector previously calibrated with a solid sample of silver sulfate. An average value of S/(Co+Mo) was obtained from three analyses.

2.3. *EDX analysis*

EDX analyses were performed on a JEOL 2010 electron microscope equipped with a Link Isis microanalysis system. The H_2–H_2S activated catalyst was dispersed in an ethanol solution and a droplet of the suspension was deposited over a holey carbon film supported on a copper grid. The exposure of the catalyst to air was short enough to avoid the transformation of the sulfidic phase. The *K*-lines of S, Co, O, Al and the *L*-line of Mo were selected for quantitative analyses. However, as the Mo $L_{\alpha 1}$, $L_{\beta 1}$ and $L_{\beta 2}$ lines, respectively, at 2.293, 2.395 and 2.518 keV overlap the S $K_{\alpha 1}$, $K_{\alpha 2}$ and $K_{\beta 1}$ lines situated at 2.308, 2.307 and 2.464 keV, peaks decomposition was done after calibrating the detector with MoO_3 and $MnSO_4$ as reference samples which provide the Mo and S profiles. For each sulfidation temperature, an average value of the S/(Co+Mo) ratio was obtained from at least 20 analyses.

2.4. *XPS*

XPS analyses were carried out with an ESCALAB 200 R (Fisons Instruments) using an aluminium (Al K_α=1486.6 eV) X-ray source. The samples were prepared in a glove box under argon atmosphere. The powder was deposited and fixed on a sample holder, and transferred into the spectrometer without exposure to air. Calibration of binding energies was done with the C1s signal at 284.5 eV coming from the contaminating carbon. This correction was in agreement with the position of Al at 74.1 eV coming from alumina. The charge effect was precluded in some cases with flood gun. The XPS signals were analyzed by using the program Eclipse. The S/(Co+Mo) ratio was determined after subtracting the non-linear Shirley background and correcting the Mo3d peak area from the S2s contribution.

2.5. *TPO*

The TPO experiments were performed at atmospheric pressure in an open flow reactor. In a typical run, 0.1 g of sulfided catalyst was heated (5°C/min) up to 823 K into a flow (50 ml/min) of O_2(4.45%)/Ar gas mixture. Gas phase composition (SO_2, O_2 and H_2O) was determined with a mass spectrometer (Fisons Instruments) equipped with a VG quadrupole analyser working in a Faraday mode. A silica capillary tube heated at 453 K continuously bled off a small fraction of the gas phase into the spectrometer. The amount of SO_2 was determined by calibrating the mass spectrometer with a known stoichiometric mixture of SO_2/Ar.

2.6. *Catalytic tests*

The catalytic activity was determined using both thiophene hydrodesulfurization (HDS) and tetralin hydrogenation (HYD) reactions. These reactions were carried out in an open flow microreactor working under atmospheric and medium high pressure, respec-

Table 1
Experimental conditions for the catalytic tests

Reactions	Reactants	Temperature (K)	Total pressure (10^5 Pa)	Reactant pressure (10^2 Pa)	Added H_2S pressure (10^2 Pa)
HYD	Tetralin	573	30	60	720
HDS	Thiophene	573	1.1	28	—

tively. Products distribution was analyzed by an online gas chromatography. The experimental conditions are detailed in Table 1.

3. Results and discussion

3.1. Optimization of EDX analysis conditions

The influence of experimental EDX variables on the stability of the sulfided phase has been first studied because it was observed that sulfur content depends on the operating conditions used for EDX measurements, i.e. probe size, beam focusing and beam convergence. Various probe sizes (25, 15, 10 and 3 nm) have been tested. The beam was either focused (diameter=probe size) or defocused (diameter=100 nm) in order to reduce the electron intensity. Different beam convergence angles α (α=1, 2, 3) have been also used, knowing that α=1 corresponds to a parallel beam and α=3 corresponds to a convergent beam. For selected conditions, a series of three successive analyses of the same catalyst area was achieved on a sample sulfided at 673 K. Acquisition time was in the range 0.5–2 min depending on the acquisition rate. The results are presented in Fig. 1.

It was noticed that the S/(Co+Mo) atomic ratio decreases after the first analysis upon beam exposure, particularly for a small probe size. This effect is even more pronounced when a focused beam is used

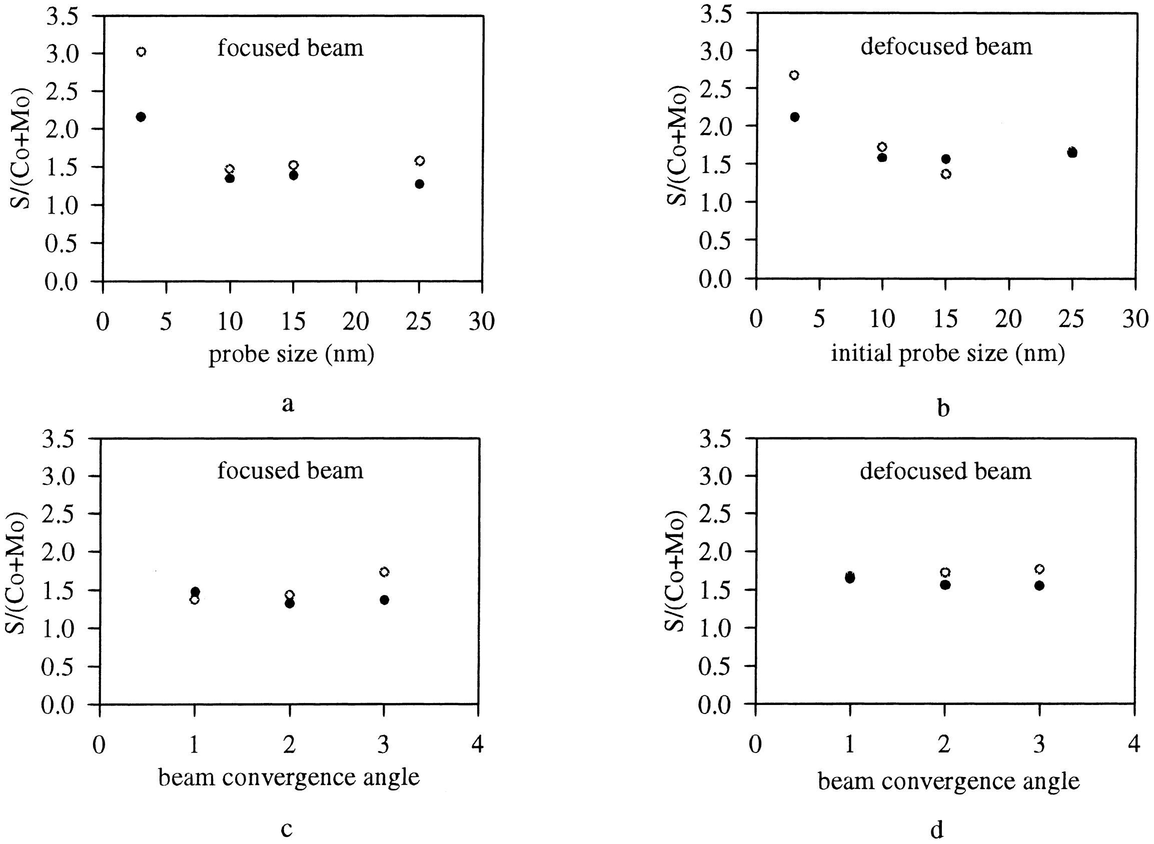


Fig. 1. S/(Co+Mo) atomic ratio versus: (a) the probe size for a focused beam; (b) the initial probe size for a defocused beam; (c) the beam convergence angle for a focused beam; (d) the beam convergence angle for a defocused beam. The blank spots represent the first analysis and the dark spots represent average values of the three measurements.

(Fig. 1(a) and (b)). For instance, small probes below 10 nm, which require a quite long acquisition time, provoke a reduction of the solid i.e. partial removal of sulfur due to prolonged illumination which creates a local overheating of the area under investigation. Moreover, for a probe size of 3 nm, the poor analysis yield leads to an erroneous S/(Co+Mo) ratio. From Fig. 1(c) and (d), it is also observed that the S/(Co+Mo) ratio decreases systematically between the first and the latter analyses. This phenomenon seems to be more important for a focused beam. These results have allowed to optimize the operating conditions in order to maintain the stability of the solid during EDX measurements. A defocused beam, a low beam convergence and a probe size above 10 nm are required.

3.2. *Evolution of the sulfidation state with the temperature*

The CoMo/Al_2O_3 catalyst was analyzed at each step of sulfidation from room temperature until 773 K. The sulfidation state of the catalyst was followed using several physico-chemical techniques including elemental analysis, EDX analysis, XPS and TPO. Obtained data are illustrated in Fig. 2.

Chemical analyses show that the S/(Co+Mo) ratio increases from 0.75 up to 1.70 for a sulfiding temperature of about 573 K and then remains roughly constant for higher sulfidation temperatures. These results are in good agreement with those obtained by de Beer et al. [6] and Kim and Woo [7] using sulfur analysis. While, Prada-Silvy et al. [8] have reported lower values. The observed plateau corresponds to a complete sulfidation of the catalyst assuming S/Mo=2 and S/Co=8/9. Interestingly, a significant amount of sulfur representing 44% is already incorporated into the solid at room temperature. Proper EDX analysis gives results which corroborate those determined by chemical analysis. XPS measurements confirm likewise the above results. These data show that chemical analysis, EDX and XPS are in fairly good agreement. Furthermore, the sulfidation state of the catalyst is homogeneous because the overall or the local stoichiometries are similar.

Only the S/(Co+Mo) ratio determined by TPO deviates from the data determined by the other techniques. This discrepancy may be ascribed to the partial solubilization of SO_2 into the desorbed H_2O condensed at the reactor outlet. Moreover, the presence of Co may cause an increase of the residual amount of sulfur (10%) remaining on the catalyst after oxidation [10]. The TPO cannot be considered as a quantitative technique.

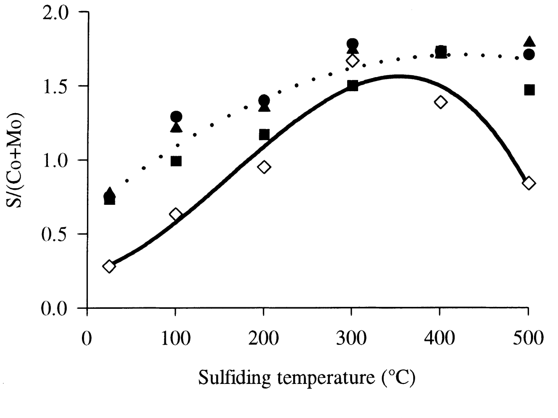


Fig. 2. Atomic ratio S/(Co+Mo) versus the sulfiding temperature, determined by the elemental analysis (dark circles), EDX analysis (dark squares), XPS (dark triangles) and TPO (blank diamonds and dark line).

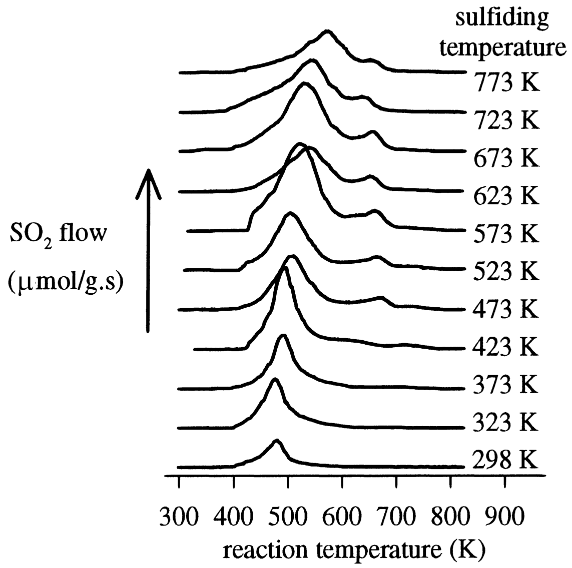
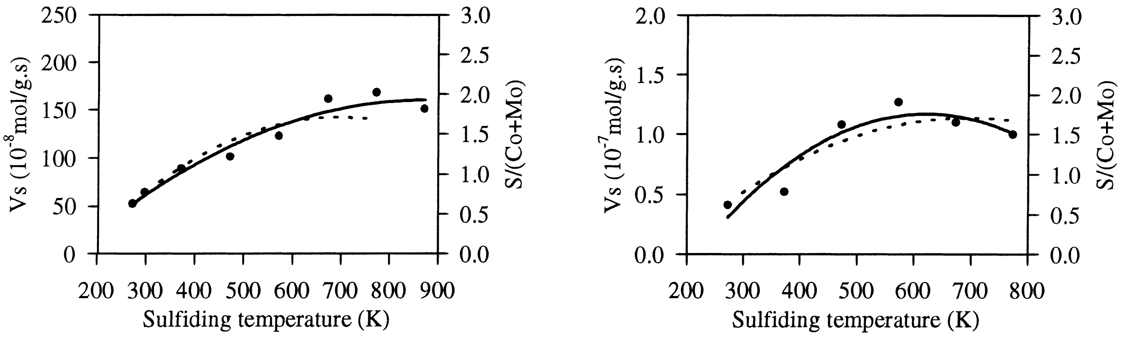


Fig. 3. SO_2 flow produced by TPO versus the reaction temperature, for different sulfiding temperatures.



a b

Fig. 4. Atomic ratio S/(Co+Mo) (dotted line) and specific activity (line and dark spots) versus the sulfiding temperature in: (a) thiophene HDS, and (b) tetralin HYD.

3.3. TPO qualitative results

Fig. 3 represents the TPO profiles of various catalysts sulfided at different temperatures. These profiles exhibit two distinct peaks as already observed for different MoS_2-like catalysts [3,9,10]. The first peak exists whatever the sulfiding temperature is. Its maximum is situated at 478 K when the sulfidation is achieved at room temperature. When the sulfiding temperature increases, this peak, which is mainly caused by oxidation of Mo sulfides, is progressively shifted to higher temperatures suggesting a stronger Mo–S bond. The second sulfur species appears at 658 K only for a sulfiding temperature of 473 K. According to [10], this species could be related to unoxidized sulfides which are most attributed to MoS_2-like structures remaining in the bulk phase.

3.4. Catalytic activity

As evidenced in Fig. 4((a) and (b)) the HDS and HYD catalytic activities increase with the sulfiding temperature up to 673 K and then remain almost constant. The comparison of these data with those reported in Fig. 2 shows that both the catalytic properties and the catalyst stoichiometry follow the same evolution with respect to the sulfiding temperature. Therefore, the catalytic activity could be related to the sulfidation state of the catalyst [8,11]. The amount of sulfur incorporated into the solid plays a primordial role in the ability of the catalyst to catalyze the HDS and HYD reactions.

4. Conclusion

This study points out the importance of a careful use of each technique in order to precisely determine the sulfur content of hydrotreating catalysts. Our results report self consistent S/(Co+Mo) ratio measures using different physico-chemical techniques. The evolution of the S/(Co+Mo) atomic ratio shows that the catalyst has reached a total sulfidation already at 573 K. Moreover, the same trend is observed for the activity in both thiophene HDS and tetralin HYD suggesting that the sulfidation state plays a primordial role in the catalytic activity.

Acknowledgements

CG greatly acknowledges EURECAT SA and the ADEME for a Ph.D. grant and, ChG and ML thank ECOTECH–CNRS program for financial support.

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