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Unsupported trimetallic Ni(Co)-Mo-W sulphide catalysts prepared from mixed oxides: Characterisation and catalytic tests for simultaneous tetralin HDA and dibenzothiophene HDS reactions

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ABSTRACT

Unsupported A-Mo-W (A = Ni or Co) sulphide catalysts were obtained from mixed oxides containing different W:Mo ratios. An in situ liquid-phase sulphidation of the mixed oxides in a batch reactor was followed by catalytic tests in a liquid-phase reaction (at 613 K and 70 bar), using a mixture of dibenzotiophene (DBT) and tetralin (THN) as the feed. After the catalytic tests, the bulk sulphide catalysts were characterised by nitrogen physical adsorption, XANES/EXAFS, SEM and HR-(S)TEM. The HR-TEM images showed randomly oriented, stacked-layer particles typical of Mo (W) sulphides and an elemental HR-STEM mapping evidenced Mo/W homogeneous distribution in the trimetallic sulphides. The EXAFS results for the trimetallic catalysts are consistent with the presence of nickel or cobalt sulphide domains, and $Mo_{1-x}W_xS_2$ solid solutions. The intralayer Mo:W solid solutions were confirmed to be thermodynamically stable with respect to phase separation by DFT calculations, which were also used to aid in the interpretation of the EXAFS results. The effect of the W:Mo ratio on the catalytic properties of the Ni- and Co-containing series was found to be different. For the Ni series, increasing the W content caused an activity increase in THN hydrodearomatization (HDA) relative to DBT hydrodesulphurization (HDS), while it had little influence on the relative contribution of the *direct desulphurisation* (DDS) route with respect to the *previous hydrogenation* (HYD) route for DBT HDS. In contrast, for the Co series, the activities and selectivities were essentially insensitive to the W content. Both the Ni and Co series of unsupported sulphides were more selective for the HYD route in DBT HDS than a supported $NiMo/Al_2O_3$ catalyst.

1. Introduction

Hydrotreating processes are used in oil refineries for reducing the content of unwanted components (such as sulphur, nitrogen and metal compounds, as well as aromatic hydrocarbons) in oil fractions and products, by reaction with hydrogen. Due to the tightening of air-quality legislation in many countries [1], there is a continuing effort to develop more efficient catalysts and processes for the production of ultralow-sulphur fuels, especially diesel (USLD). Although great progress has been made in the development of efficient catalysts for these processes, major challenges remain, for example, their modest aromatic hydrocarbons saturation activity. Improving the aromatics saturation activity of hydrotreating catalysts has become a research priority since recent environmental restrictions establish minimum values for cetane number and lower limits for polyaromatic contents in diesel cuts.

Unsupported catalysts have emerged as a promising commercial alternative to fulfil tighter diesel specifications, without the need for an extensive revamp of existing refinery hydrotreating units [2,3]. This is due to their higher hydrogenating power, even if they are generally more expensive than conventional supported catalysts because of their larger metal content. In the last decade, since the first patents for their use in hydrotreating were published (e.g. [4]), the interest in the study of trimetallic (NiMoW) sulphides has considerably increased [2,5].

Previous research [6–11], using thiosalts for the preparation of unsupported bimetallic sulphide catalysts, has led to significant progress in the understanding of their structure and catalytic activity. Thomazeau et al. [12] synthesised bulk $Mo_{1-x}W_xS_2$ compounds from thiosalts, and used EXAFS to show that Mo and W cations were present in every sulphide layer, *i.e*, intralayer solid solutions

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were formed. Later work by the same authors [13] showed that the $Mo_{0.5}W_{0.5}S_2$ system kept the intralayer solid solution structure when it was supported on alumina (by a co-precipitation method) and subsequently nickel-doped. The catalytic activity of these samples was evaluated in gas-phase thiophene hydrodesulphurization (HDS) and in liquid-phase HDS of a hydrotreated gasoil [14]. Based on DFT calculations of (unsupported) cluster systems, the ternary $NiMo_{1-x}W_xS_2$ compounds were expected to be more active than the bimetallic NiW and NiMo sulphides, in contrast with the $CoMo_{1-x}W_xS_2$ system where no Mo/W synergy was predicted. The catalytic activities of the promoted $NiMo_{1-x}W_xS_2$ unsupported systems were not reported in that work.

Unfortunately, the preparation of hydrotreating catalysts from thiosalts is difficult to scale up [15], due to the costs involved and the use of toxic ammonium sulphide or hydrogen sulphide in the preparation of the precursors. It is therefore surprising that little attention has been paid to the preparation of trimetallic unsupported hydrotreating catalysts from oxide precursors [16,17], which is a relatively cheaper and easier method.

Well-characterised Ni-promoted $Mo_{1-x}W_xS_2/Al_2O_3$ catalysts with different Mo to W ratios were synthesised by pore volume impregnation of γ-Al_2O_3 with the metal salts in a recent work by van Haandel et al. [18]. There was no synergy from the simultaneous presence of Mo and W in ternary Ni-based $Mo_{1-x}W_xS_2$ materials under the reported conditions of the model reactions, either in the gas-phase thiophene HDS or in the liquid-phase dibenzothiphene (DBT) HDS activity. The effect of pressure and temperature in the gas-phase catalyst activation was followed by XPS and EXAFS. The mixing of W and Mo in the $Mo_{1-x}W_xS_2$ slabs was found to be dependent on the activation pressure in those supported systems. At higher activation pressures a Mo-W solid solution was formed whereas, for lower activation pressure, EXAFS gave evidence of Mo-W-S sulphide particles with a core-shell structure.

There is clearly a lack of information in the open literature about the physicochemical and catalytic properties of bulk trimetallic NiMoW sulphides prepared from mixed oxides and virtually no information on the related CoMoW system. Furthermore, most model compound studies reported for unsupported catalysts involve only the HDS reaction (DBT and/or 4,6-dimethyldibenzothiophene) [15,19–24]. However, as mentioned earlier, there is currently much interest in the HDA function of hydrotreating catalysts [25], so it is important to make catalytic measurements in the simultaneous HDS of sulphur compounds and the HDA of aromatic hydrocarbons [26–29].

Hein et al. [30] studied unsupported bimetallic catalysts with Ni/Mo = 1.2 and Ni/W = 0.9, and an unsupported trimetallic catalyst with Ni/(Mo + W) = 1.3. These Ni-based precursors, not characterised in that work, were sulphided in the gas phase without previous thermal treatment. The catalysts activities were evaluated for the hydrodenitrogenation (HDN) of *o*-propylaniline and HDS of DBT. The trimetallic catalyst had both greater HDN and HDS activities than the bimetallic ones. The authors explained this result by the preferential incorporation of Ni in the perimeter of the mixed trimetallic $Mo_{1-x}W_xS_2$ slabs. Only the trimetallic catalyst with Mo/W = 1.3 was studied, no other Mo/W ratios were considered. Co-based catalysts were not studied in that work.

Recently Licea et al. [31] have investigated the properties of NiMo bulk sulphide catalysts obtained from mixed oxides. The mixed oxides were obtained by calcining a synthesised lamellar precursor with the so-called ϕ_y phase, whose crystal structure has been determined by Ying et al. [31], with general formula $(NH_4)H_{2x}Ni_{3-x}(OH)_2(MoO_4)_2$ $(0 \leq x \leq 3/2)$. Ni atoms can fractionally occupy the octahedral sites, which allows the synthesis of compounds with Ni/Mo ratios in the range from 0.75 to 1.5. Layered structures containing Co, Cu or Zn as the divalent metal have also been reported [32] but despite the chemical similarity between W and Mo [33], W-containing ϕ-y structures have not been reported so far in the open literature.

It is well known that DBT undergoes HDS by two parallel paths, namely the *direct desulphurization* (DDS) and the *previous hydrogenation* (HYD) routes [34]. In the work of Licea et al. [31] the mixed oxides were in situ sulphided and the catalytic activity of the mixed sulphides was evaluated in the simultaneous dibenzothiophene (DBT) HDS and tetrahydronaphthalene (THN) HDA reactions. The NiMo bulk sulphide displayed pronounced selectivity for the HYD pathway in DBT HDS, when compared to a conventional NiMo alumina-supported catalyst. This is known to be the pathway that benefits the HDS reaction of the most refractory organo-sulphur molecules (alkyl-dibenzothiophenes) under hydrotreating conditions [25,35].

In the present work, Ni-Mo-W catalysts and Co-Mo-W bulk sulphides were prepared from liquid-phase sulphidation of mixed-oxide precursors. The activity and selectivity of the catalysts were evaluated in the sulphided state in the simultaneous HDS of dibenzothiophene (DBT) and HDA of tetralin (tetrahydronaphtalene, THN) and were further characterised by several physicochemical techniques. A combination of EXAFS and density functional theory calculations was employed to investigate the mixed MoW sulphides, in particular to establish whether or not solid solutions were obtained by the preparation method used, and if formed, whether the solid solutions were ordered or disordered.

2. Experimental

2.1. Synthesis

Two series of AMoW (A = Ni or Co) precursors were synthesised by a co-precipitation method as described elsewhere [31]. Ammonium heptamolybdate and ammonium metatungstate aqueous solutions were prepared each containing quantities of Mo and W to obtain 1:0, 2:1, 1:1, 1:2 and 0:1 molar Mo:W solutions. A Ni (or Co) nitrate aqueous solution was also prepared so to obtain equimolar A: (Mo + W) compounds. By the slow addition of NH_4OH, the pH of the solution was increased to 8. The solution was then transferred to a closed bottle, where a treatment was carried-out for 4 h at 353 K. The Ni-based green (yellowish for some compounds) and Co-based pink (brown for some compounds) precipitates obtained were then washed with enough water to reach neutral pH and then dried for 24 h. The synthesised ammonia-containing materials were nominated A_z-Mo_y-W_x-am, where “am” stands for ammonia, A = Ni or Co, *z* is the A/(W + Mo) molar ratio, *x* is the W/(Mo + W) molar ratio, and *y* = 1-*x* is the Mo/(Mo + W) molar ratio. The values of *z* and *x* were obtained from the X–ray fluorescence (XRF) chemical analysis of the samples (*c.f* Table 1). In order to simplify the notation, the materials not containing W were denominated $Ni_{1.6}$-Mo-am and $Co_{1.1}$-Mo-am, whereas the materials not containing Mo were denominated $Ni_{1.6}$-W-am and $Co_{1.2}$-W-am.

In order to obtain the mixed oxides, the Ni-based and Co-based precursors were heated under static air at a rate of 5 K min^{-1} up to 673 K and 623 K, respectively, and maintained at the final temperature for 3 h. The calcination temperatures were chosen as low as possible to maximise the surface areas, while also guaranteeing that all volatile compounds (H_2O and NH_3) were evolved, based on the thermogravimetric analysis of the precursors. The corresponding calcined materials were named A_z-Mo_y-W_x-ca (“ca” stands for calcined). The sulphidation was performed in-situ, immediately before the catalytic tests, as described under Section 2.8, and the sulphide catalysts were named A_z-Mo_y-W_x-s (“s” stands for sulphide). It should be emphasised that in all cases the subscripts *x*, *y*, *z* represent the overall compositions of the samples and do not imply the existence of single phases with the given stoichiometry.

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