Unsupported NiMoAl hydrotreating catalysts prepared from NiAl-terephthalate hydrotalcites exchanged with heptamolybdate

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A B S T R A C T

Unsupported NiMoAl hydrotreating catalysts were prepared starting from NiAl-terephthalate layered double hydroxides (LDHs) with x values (Al/(Al + Ni) ratios) in the 0.3–0.8 range by ion exchange with ammonium heptamolybdate, followed by calcination at 723 K. Mixed oxides containing ca. 33–43 wt% molybdenum and Ni/Mo atomic ratios in the 0.5–1.4 range were obtained. There was loss in the long-range ordering of the LDHs in the c direction during the ion-exchange, but the local structure of the brucite layers was maintained. The calcined mixed-oxides had surface areas ranging from 26 to 122 m^2 g^{-1}. The catalysts were sulphided in situ and subsequently tested in the simultaneous dibenzothiophene (DBT) HDS and tetralin (THN) hydrogenation reactions in a high pressure batch reactor at 613 K and 70 bar. The catalysts had higher specific activity for both the HDS and the HDA reactions and much higher selectivity for the ring hydrogenation (HYD) route in the HDS of DBT than a conventional NiMo/Al$_2$O$_3$ catalyst. Their activities in both reactions were similar to those of an Al-free unsupported NiMo catalyst, but their preference for the HYD route was higher than that of the latter.

1. Introduction

There is nowadays a global and growing concern about environmental protection. In terms of energy for transportation, this is reflected increasingly stringent environmental in terms of sulphur content, giving rise to the need of producing the so-called ultra-low sulphur diesel (ULSD), containing less than about 10 ppm sulphur [1]. In several countries, cetane number and aromatic hydrocarbons content are also specified [2].

In petroleum refineries, the main process used for improving the quality of diesel with respect to these properties is hydrotreating (HDT). In this process, unwanted components present in petroleum fractions are removed by reaction with hydrogen at high pressures [3]. For many decades, alumina-supported mixed sulphides comprised of a group 6 element (Mo and/or W) together with an element of groups 9 (Co) and/or 10 (Ni) of the periodic table, have been used in HDT.

The principal organosulphur components in diesel belong to the family of condensed-ring aromatic compounds, such as dibenzothiophenes (DBTs). However it has been observed that the most refractory compounds towards HDS are condensed-ring

organosulphur compounds with alkyl groups in the vicinity of the sulphur atom, such as in 4,6-dialkyldibenzothiophenes [3]. For the HDS of these compounds the so-called hydrogenation (HYD) route is required [4], where the previous hydrogenation of one of the condensed aromatic rings has to occur before the sulphur atom is removed. With the conventional alumina-supported catalysts, severe temperature and pressure operating conditions are necessary for this route to be significant, impairing process economics.

Recently, unsupported mixed sulphides of the same family as the supported ones have come into commercial use [5]. They are reported to have higher selectivity for the HYD route in the HDS of DBTs and therefore higher activity for ULSD production than the alumina-supported catalysts. Furthermore, due to their stronger hydrogenating function, they are also reported to be useful for hydrodenitrogenation (HDN) and hydrodearomatisation (HDA), which leads to cetane improvement under appropriate operating conditions [5]. This opens promising lines of research for new formulations and preparation methods of this type of catalysts and also for understanding the reasons for their improved hydrogenation performance.

The present work is focused on the use of layered double hydroxides (LDHs), also known as hydrotalcite-type materials, as precursors for unsupported NiMo mixed-sulphide catalysts. The structure of LDHs is based on the stacking of brucite-like (Mg(OH)$_2$) layers with an excess positive charge that is

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compensated by interlayer anions [6]. Their general formula is $[(M^{2+})_{1-x}(M^{3+})_x(OH^-)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} is a divalent cation (Ni, Mg, Cu, Zn, etc.), M^{3+} is a trivalent cation (Al, Cr, Fe, V, etc.) and A^{n-} a charge compensation anion (commonly NO_3^-, Cl^-, SO_4^{2-}, CO_3^{2-}). This subject has been reviewed several times [6–8].

LDHs are widely used as catalyst and support precursors due in part to the possibility of preparing homogeneous mixed oxides from them [6,9,10]. Furthermore, different interlayer metal oxy-anions, such as vanadates [7,11], molybdates [12,13] and tungstates [14,15], may be used to obtain useful catalysts for many applications, such as hydrotreating of oil fractions [15,16] or selective oxidations [17]. Recently Wang et al. have reported on the activity for 4,6-dimethyldibenzothiophene HDS of NiMoWAl catalysts obtained by direct sulphidation of LDH-containing materials obtained by ion exchange of a NiAl-nitrate LDH with isopolymetallate salts of Mo and W, in the presence of a surfactant and ethylene glycol [16].

In the present work, NiMoAl catalysts were prepared by sulphidation of mixed-oxides obtained by calcination of NiAl-heptamolybdate HDLs. The latter were, in their turn, obtained by ion-exchange with ammonium heptamolybdate (AHM) of NiAl-terephthalate HDLs. Terephthalate was chosen as the initial compensation anion partly because, due it is length, it facilitates the diffusion of bulky anions such as heptamolybdate into the interlayer gallery and is easily replaced by this anion [13,18,19], but an even more important factor is that it allows the obtention of LDH phases with high aluminium content. It is frequently said in the literature that the maximum possible x value in the formula of LDHs is 0.33 due to the so-called cation avoidance rule, which states that the second coordination sphere of a 3+ cation cannot contain another 3+ cation, due to electrostatic repulsion [6,8]. We have recently found, however, that it is possible to prepare LDHs with x values around 0.5 with terephthalate as the compensation anion [20].

The sulphided catalysts were tested in the simultaneous HDS of dibenzothiophene and hydrogenation of tetrahydronaphthalene (THN) and their behaviour in these reactions was compared to those of a conventional, alumina-supported NiMo catalyst and an aluminium-free NiMo unsupported catalyst.

2. Experimental

2.1. Preparation of the materials

The preparation of the NiAl-terephthalate LDH starting materials was described in detail elsewhere [20]. Briefly, they were prepared by simultaneous dropwise addition, to a water-containing beaker, of an aqueous solution of the metal nitrates and another containing terephthalic acid dissolved in sodium hydroxide, so as to maintain the pH at 6.5 ± 0.3. The precipitation was carried-out at 323 K and the precipitate obtained was aged in the mother-solution for 16 h at room-temperature. The resulting solid was recovered by vacuum filtration, abundantly washed with previously boiled de-ionized water until neutral pH and finally dried in an oven at 373 K. Materials with nominal x values in the LDH formula $Ni_{1-x}Al_x(OH)_2TA_{x/2}\cdot mH_2O$, where TA represents the terephthalate anion, in the 0.3–0.8 range were prepared. The nomenclature of these materials follows the scheme HTXTA, where X is an integer equal to approximately $10\times$ the nominal x value.

The terephthalate anion was exchanged with heptamolybdate by contacting 1 g of the NiAl-TA LDH with a $0.07\,mol\,g^{-1}$ ammonium heptamolybdate (AHM) solution for 24 h under continuous stirring in a closed Nalgene bottle heated to 353 K, aiming to obtain materials with the general formula $Ni_{1-x}Al_x(OH)_2(Mo_7O_{24})_{x/6}\cdot mH_2O$. The exchanged material was recovered by vacuum filtration, abundantly washed with deionised water until neutral pH and dried in an oven at 373 K for 4 h. The heptamolybdate-exchanged materials were named HTXMo, where X has the same meaning defined before.

NiMoAl mixed-oxides were obtained by heating the molybdenum-exchanged LDHs at a $10\,K\,min^{-1}$ heating rate to a final 723 K temperature, which was kept for 3 h. The final temperature was chosen with basis on a study of the calcination temperature dependence of the BET surface area with one of the samples. The calcined materials were named TAXMo-ca.

The calcined mixed-oxides were sulphided in situ, before the catalytic tests, under a CS_2/n-hexadecane mixture, in a batch $500\,cm^3$ Parr reactor. A careful sulphidation procedure was used, in order to avoid catalyst reduction before or after sulphidation. First, 0.6 g catalyst was dried under nitrogen flow at 393 K for 2 h. A $200\,cm^3$ amount of a 5 vol% solution of carbon disulfide in n-hexadecane was added to the reactor. The amount of CS_2 added was calculated to be 5 times the stoichiometric one required to completely sulphide the unsupported mixed-oxides. Next, the reactor was pressurized to 40 bar with hydrogen, heated to 503 K under constant pressure and kept at this temperature for 2 h. It was then heated to 613 K under constant pressure and kept at this temperature for 16 h. Finally, it was cooled to 593 K and vented to atmospheric pressure, in order to remove the water and hydrogen sulphide formed during the sulphidation. X-ray absorption data, to be discussed elsewhere, showed that this protocol led to essentially complete sulphidation of the catalysts. The sulphided mixed-oxides were named HTXMo-s.

2.2. Characterization

Quantitative analysis of the metals in the NiAl-terephthalate LDHs was performed by X-ray fluorescence spectroscopy (XRF), as described elsewhere [20] after calcination at 773 K. Metal analysis in the molybdenum-exchanged LDHs was carried-out, also after calcination at 773 K, by atomic absorption spectroscopy (AAS), using a Thermo Scientific ICE Series 3000 instrument. Carbon analyses were performed in both the terephthalate and in the heptamolybdate-exchanged LDHs, using a Perkin-Elmer 2400CHN instrument.

Powder X-ray diffraction (XRD) patterns were obtained in a Rigaku Ultima IV apparatus using CuKα radiation ($\lambda = 0.15418$ nm), operated at 40 kV and 20 mA. Scans were performed at $2°\,min^{-1}$ in the $3°$ to $70°$ range (2θ values).

FTIR spectra were obtained in a Spectrum One Perkin Elmer instrument with the samples dispersed in a ca. 1% proportion in potassium bromide and pressed as wafers. Scans were performed between 4000 and $400\,cm^{-1}$; 20 scans for the samples and 30 scans for background recording.

^{27}Al NMR spectra were obtained in a Bruker DRX300 spectrometer operated at a field of 7.05 T (78.9 MHz), using a CPMAS Bruker probe, 4 mm zirconia rotors with sample spinning rate of 7 kHz. Details of the analyses are given elsewhere [20].

The X-ray absorption spectra at the Ni K-edge were obtained at the XAFS1 line at the Laboratório Nacional de Luz Síncrotron–LNLS, Campinas, Brazil. The samples were mounted as a thin layer on filter paper and all spectra were obtained in transmission mode. The Athena program), from the IFEFFIT software package [21] was used to extract the EXAFS oscillations in k space. Further details are given elsewhere [20].

The XANES spectra at the molybdenum L_2 and L_3-edges (2625 and 2520 eV respectively) were recorded at the SXS beamline of the Laboratório Nacional de Luz Sincrotron, in Campinas, Brazil. The spectra were obtained in total electron yield (TEY) mode using an electrometer connected to the sample holder to measure the