CoMo/Al$_2$O$_3$-SiO$_2$ catalysts prepared by co-equilibrium deposition filtration: Characterization and catalytic behavior for the hydrodesulphurization of thiophene

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A B S T R A C T

Four CoMo catalysts supported on Al$_2$O$_3$-SiO$_2$ mixed materials of varying SiO$_2$ content (1.5, 10, 20 and 30% SiO$_2$ w/w) were prepared following the co-EDF methodology. The catalysts were characterized using various techniques (BET, potentiometric mass titrations, XRD, DRS, XPS, LRS, TPR, TPD of ammonia and NO chemisorption). Two additional catalysts were prepared and characterized on two mixed supports, which contain 1.5 and 20% SiO$_2$ w/w, following the conventional impregnation procedure. The hydrodesulphurization (HDS) activities of the catalysts studied were determined using thiophene as a probe molecule.

The co-EDF catalysts were proved to be more active than the corresponding ones prepared following the conventional impregnation procedure. This was attributed to the relatively high dispersion of the Mo supported phase achieved by applying co-EDF. The following activity trend was obtained over the co-EDF catalysts, 20Si > 30Si > 1.5Si > 10Si, which indicates that the activity is maximized over the catalyst prepared on a mixed support containing 20% SiO$_2$ w/w. This zigzag trend was explained in terms of two parameters, the ratio "tetrahedral (monomer) /octahedral (polymer) Mo species" and the amount of cobalt aluminate formed, both regulated by changing the composition of the mixed support.

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1. Introduction

Hydrodesulphurization (HDS) is a key reaction for producing clean fuels. The environmental regulations relevant to sulphur specifications for transportation fuels become more and more strict. A critical issue is that a significant part of the reserves of some oil-producing countries consists of heavier fractions with a high content of contaminants. Among these contaminants sulphur is significant. The demand for lower sulphur content in fuels requires the development of more active HDS catalysts. These catalysts usually consist of supported MoS$_2$ on an alumina carrier promoted by cobalt or nickel [1]. The use of some additives (e.g. P, F, B) in the catalyst formulations [1–9] or the addition of some chelating compounds in the impregnation solution [10–17] are proved to be important tools for improving the HDS activity of the catalysts.

The modification of the preparation procedure is another approach. The impregnation step, the most important in the preparation sequence, is usually carried out following the conventional incipient wetness or wet impregnation techniques. In the last years we have developed an alternative impregnation methodology, *the equilibrium deposition filtration technique* (EDF) [18–20]. The application of EDF for depositing the Mo(VI) species, or both the Mo(VI) and Co(II) species, on the γ-alumina surface (co-EDF), has resulted in more active catalysts than those prepared by the conventional impregnation techniques [21–23]. More precisely, CoMo/γ-Al$_2$O$_3$ catalysts prepared by EDF were proved to be about 30–43% more active in HDS than the corresponding catalysts prepared following the conventional impregnation techniques. Moreover, these catalysts exhibited relatively low hydrogenation activity. Thus, EDF or co-EDF could be used for the preparation of very active CoMo/γ-Al$_2$O$_3$ catalysts for deep hydrodesulphurization of oil with relative low hydrogen consumption.

A third approach for improving HDS activity is by using new supports. Many studies have shown that one of the major factors affecting this activity is the interaction between the active components and the support. A large number of new materials have been developed and tested [24–31]. Among these materials the mixed Al$_2$O$_3$-SiO$_2$ supports are quite promising. La Parola et al. [26] studied the HDS activity and the structural properties of CoMo catalysts supported on mixed Al$_2$O$_3$-SiO$_2$ supports of varying alumina content (0–100%). It was found that the HDS activity depends on the Al/Si atomic ratio. The maximum activity was obtained using

a mixed Al_2O_3-SiO_2 support (66% Al_2O_3 and 34% SiO_2). The activity profile was related to the dispersion and the reducibility of the active species determined by the acidity of the support. On the mixed oxide with the aforementioned composition a good compromise was obtained between dispersion and reduction during sulphidation. Dalama and Stanislaus [27] studied the HDS activity of a series of CoMo catalysts supported on γ-alumina and a mixed Al_2O_3-SiO_2 support containing 30% SiO_2. The impregnation solution used was free or contained a chelating agent. The HDS activities of all catalysts were tested in a micro reactor using straight run gas oil as feed. The catalysts prepared using SiO_2–Al_2O_3 as support were remarkably more active than those prepared using γ-Al_2O_3. A deep hydrodesulphurization of diesel to ultra low sulphur levels (<15 ppm) was obtained over a catalyst with high Mo and Co loading developed on the Al_2O_3-SiO_2 support. CoMo HDS catalysts were recently developed using Al modified mesoporous silicas [28–31]. A good synergy between Al and Si has been found in all cases. It is important to stress that in all cases the CoMo catalysts supported on mixed Al_2O_3-SiO_2 supports or Al modified mesoporous silicas have been prepared using the conventional incipient or co-incipient wetness impregnation.

In the present work we combine the EDF methodology and the use of mixed silica-alumina supports for improving further the catalytic HDS activity of the CoMo catalysts. More precisely, we prepared a series of CoMo catalysts supported on Al_2O_3-SiO_2 mixed materials of varying SiO_2 content (1.5, 10, 20 and 30% SiO_2 w/w) *following the co-EDF methodology*. The catalysts were characterized using various techniques. The hydrodesulphurization (HDS) activities over the catalysts studied were determined using thiophene as a model molecule. For comparison, two additional catalysts were prepared and characterized on two mixed supports (1.5 and 20% SiO_2 w/w) following the conventional impregnation technique. These catalysts have been also tested using the same probe reaction.

2. Experimental

2.1. Equilibrium deposition experiments

Isotherms were obtained at 25 °C and various pHs for studying the deposition of Mo(VI) oxo-species and Co(II) aqua complexes on pure γ-alumina (Condea) and silica (Alfa Aesar). Ammonium heptamolybdate (Merck, analytical grade) and cobalt nitrate hexahydrate (Merck, analytical grade) were used for preparing the Mo(VI) and Co(II) solutions, respectively. The initial concentrations of Mo(VI) varied in the range 0–5×10^{-2} M (γ-alumina) and 0–2×10^{-2} (silica). The initial concentrations of Co(II) varied in the range 0–4×10^{-2} M for both γ-alumina and silica. The photometric determination of the Mo concentration in the impregnation solution was performed at 490 nm, before and after adsorption of the Mo(VI) oxo-species, following the catechol method described by Snell [32]. The deposited amount of Mo was calculated from the difference in the two concentration values. The Co^{2+} deposition was also determined photometrically at 560 nm by measuring the Co^{2+} concentration in the impregnating solution before and after deposition. The determination was based on the Nitroso R-salz procedure [33]. A spectrophotometer (Cary 3 Varian) was used in all cases. Details concerning the equilibrium deposition experiments have been reported elsewhere [34].

2.2. Preparation of the specimens

Four CoMo/Al_2O_3-SiO_2 co-EDF samples (denoted by 1.5Si, 10Si, 20Si and 30Si) were prepared using four Al_2O_3-SiO_2 mixed supports of varying silica content (1.5, 10, 20 and 30% SiO_2 w/w). These powdered supports were obtained from Condea. Following the co-EDF technique [22], the molybdenum(VI) oxo-species and

the cobalt(II) aqua complexes were deposited onto the surface of the supports at 25 °C from a mixed Co–Mo solution (2.5×10^{-2} M Mo and 2×10^{-2} M Co). Ammonium heptamolybdate (Merck, analytical grade) and cobalt nitrate hexahydrate (Merck, analytical grade) were used for preparing the mixed solutions. The amount of the deposited Mo and Co was determined spectrophotometrically [32,33]. Following the co-EDF technique the deposition takes places during the equilibration of the suspension. The pH was kept constant at 4.9 upon equilibration. The samples were dried in air at 110 °C for 2.5 h and then air-calcined at 500 °C for 5 h. In order to compare the influence of the preparation method on the catalytic activity we prepared two additional samples, corresponding to the samples 1.5Si and 20Si, following the conventional procedure. In these samples Mo was deposited first by wet impregnation following by drying and calcination. The cobalt was then deposited by incipient wetness impregnation followed by drying and calcination. The drying and calcination conditions were those mentioned before. These conventionally prepared samples are denoted by 1.5Si$_{conv}$ and 20Si$_{conv}$. The samples 1.5Si$_{conv}$ and 20Si$_{conv}$ contain the same amount of the supported cobalt and molybdenum to the samples 1.5Si and 20Si, respectively.

2.3. Characterization of the specimens and determination of their catalytic activity

2.3.1. Specific surface area (SSA)

Specific surface area measurements have been carried out by the three-point dynamic BET method using a laboratory-constructed apparatus. Pure nitrogen and helium (Air Liquide) were used as adsorption and carrier gas, respectively. A thermal conductivity detector (VICI, Valco Instruments Co. Inc.) was used for the detection of the adsorbed amount of nitrogen at a given partial pressure.

2.3.2. Diffuse reflectance spectroscopy (DRS)

The diffuse reflectance spectra of the samples studied were recorded in the range 200–800 nm at room temperature using a UV–vis spectrophotometer (Varian Cary 3) equipped with an integration sphere. The carrier was used as a reference in all cases. The powder samples were mounted in a quartz cell which provided a sample thickness greater than 3 mm and thus guaranteed "infinite" sample thickness.

2.3.3. X-ray photoelectron spectroscopy (XPS)

The XPS analysis of the oxidic specimens was performed at room temperature in an UHV chamber (base pressure 8×10^{-10} mbar) which consists of a fast specimen entry assembly, a preparation and an analysis chamber. The residual pressure in the analysis chamber was below 10^{-8} mbar. The latter was equipped with a hemispherical electron energy analyzer (SPECS, LH10) and a twin-anode X-ray gun for XPS. The unmonochromatized Mg KR line at 1253.6 eV and a constant pass energy mode for the analyzer were used in the experiments. Pass energies of 36 and 97 eV resulted at a full width at half-maximum (fwhm) of 0.9 and 1.6 eV, respectively, for the Ag 3d$_{5/2}$ peak of a reference foil. The binding energies were calculated with respect to the C1s peak (C–C, C–H) set at 285.5 eV. The normalized intensities I_{Mo3d}, I_{Co2p}, I_{Al2p}, I_{Si2p} and I_{O1s} of the corresponding XPS peaks, corrected using the sensitivity factors published by Wagner et al, [35–36] were used to determine the atomic surface composition of the catalysts studied.

2.3.4. Temperature-programmed reduction (TPR)

The TPR experiments were performed in laboratory-constructed equipment, in which the ideas of the Rogers–Amenomiya–Robertson arrangement [37] have been followed. An amount of sample, 0.1 g, was placed in a quartz reactor and the reducing gas mixture (H_2/Ar:5/95 v/v) was passed